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A highly efficient conditioning process to improve sludge dewaterability by combining calcium hypochlorite oxidation, ferric coagulant re-flocculation, and walnut shell skeleton construction



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HIGHLIGHTS

- Ca(ClO)₂, ferric salt, and walnut shell were used to deeply dewater sludge.
- A three-step mechanism was proposed for the combined conditioning process.
- Walnut shell was used to enhance sludge compressibility for the first time.
- Low dose Ca(ClO)₂ removed the EPS and bound water, forming a loose structure.
- A novel pressure filtration was used to decrease sludge cake moisture below 50 wt%.

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G R A P H I C A L A B S T R A C T



ABSTRACT

High levels of extracellular polymeric substances (EPS) and bound water in sludge negatively impact sludge dewaterability. This study applied a novel sludge conditioning process involving calcium hypochlorite (Ca (ClO)₂) oxidation, ferric coagulant re-flocculation, and walnut shell (WS) skeleton construction to remove EPS and bound water and improve sludge dewaterability. The study also described the underlying mechanisms for this activity, by investigating the changes in EPS distribution, morphological structure, flocs morphology,

Abbreviations: NH_4^+ , ammonia nitrogen; AOPs, advanced oxidation processes; $Ca(ClO)_2$, calcium hypochlorite; COD, chemical oxygen demand; DS, dry solids; DSC, differential scanning calorimetry; D_{50} , median value of particle size; DOC, dissolved organic carbon; EEM, excitation-emission matrix; FRI, fluorescence regional integration; EPS, extracellular polymeric substances; FeCl₃, ferric chloride; FESEM, field emission scanning electronic microscopy; FA, fulvic acid; G, gravitational acceleration; *k*, consistency index; LB-EPS, loosely bound extracellular polymeric substances; MCSC, moisture content of sludge cake; *n*, flow behavior index; $\dot{\gamma}$, shear rate; PDS, peroxydisulfate; PMS, peroxymonosulfate; PAM, polyacrylamide; PFS, polymeric ferric sulfate; PAHA, polyaromatic-type humic acid; PCHA, poly-carboxylate-type humic acid; PS, polysaccharide; PN, protein; Rpm, revolutions per minute; NaOH, sodium hydroxide; SB-EPS, soluble extracellular polymeric substances; SRF, specific resistance of filtration; *SWR*(*t*), net percentage sludge water removal at time; H₂SO₄, sulfuric acid; τ , shear stress; τ_y , yield stress; TB-EPS, tightly bound extracellular polymeric carbon; TP, total phosphorus; TSS, total suspended solids; TTAC, tyrosine/tryptophan amino acid; TTPN, tyrosine/tryptophan protein; VSS, volatile suspended solids; WS, walnut shell; WWTPs, wastewater treatment plants; Y_N , net sludge solids yield

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rheological behavior, and bound water. Using single factor experiments, the optimal dosages of the composite conditioner included 10 mg/g dry solid (DS) of Ca(ClO)₂, 60 mg/g DS of ferric chloride (FeCl₃) or 100 mg/g DS of polymeric ferric sulfate (PFS), and 600 mg/g DS of WS. Using a novel pressure filtration system, the moisture content of the dewatered sludge cake conditioned with Ca(ClO)₂/ferric coagulant/WS was reduced to below 50 wt%. The study described a three-step mechanism for the composite conditioning of sludge. First, protein-like substances and polysaccharide-like materials in the EPS and bound water were degraded by Ca(ClO)₂ oxidation. Second, the porous structure and compact flocs were re-flocculated using high charge neutralization and the bridging ability of ferric coagulant. The flowability increased and the viscosity decreased compared with raw sludge. Third, a rigid networked structure was formed by adding the WS skeleton. The combined Ca(ClO)₂/ferric coagulant/WS treatment has a lower impact on the environment. The combined treatment is an appropriate was to treat sludge prior to landfilling and incineration. Furthermore, the economic analysis showed that using the Ca (ClO)₂/FeCl₃/WS treatment had economic advantages over other treatments.

1. Introduction

In 2016, there were approximately 5300 municipal wastewater treatment plants (WWTPs) in China, generating an annual volume of approximately 30 million tons of 80 wt% moisture content sludge [1,2]. Large sludge production has created significant environmental problems in China [3]. As such, it is vital to develop new measures for treating sludge [4]. Sludge dewatering is an essential part of sludge treatment and disposal [5]. Therefore, China needs to develop high-performance dewatering processes.

Extracellular polymeric substances (EPS) are the main constituents of sludge flocs [6,7]. Proteins and polysaccharides account for 60–80% (w/w) of the organic matter in EPS [8]. When EPS has a high affinity, it forms a stable hydrated membrane, leading to difficulties in achieving an effective dewatering effect [9]. Determining the exact role of EPS in sludge dewaterability remains a significant challenge [10,11]. The intrinsic mechanisms involved in the EPS-mediation of sludge dewaterability also remain a subject of debate [12]. Therefore, EPS variations in the conditioning process still needs to be explored.

Over the past few decades, many studies have reported that advanced oxidation processes (AOPs) effectively dewatered sludge by solubilizing EPS compositions; examples include Fenton's reagents [13–15], Fe (II)/peroxydisulfate (PDS) [16,17], thermal/Fe (II)/peroxymonosulfate (PMS) [18], Fe0/PDS [19], and permanganate/bisulfite conditioning-horizontal electro-dewatering [20]. These methods break the sludge flocs and disintegrate the organic matter in EPS, leading to the release of the bound water. However, most AOPs have some disadvantages, including high energy demand, the need for high doses, and long reaction times [8]. Therefore, it is imperative to develop a feasible and economical AOPs to enhance sludge dewaterability.

Today, the alternative approach of chlorination is a low cost, highly efficient, and extensively used oxidizing process. This reagent has been widely used in the tertiary treatment of polluted water and swimming pools. It is also as an agent with high bleaching capacity [21]. In the chlorine process, OCl- is expected to be generated through a HClO reaction (Eq. (1)) [22]. Chlorination has been used to efficiently decompose organic pollutants, due to its oxidation and coagulation capabilities [23]. According to Wu et al. [24], a UV/chlorine process effectively degraded trimethoprim much faster compared to UV/H2O2. In addition, Zhu et al. [25] demonstrated that Fe(II) combined with calcium hypochlorite (Ca(ClO)₂) treatment effectively dissolved EPS and destroyed microbial cells, promoting sludge dewaterability. Chlorination has been shown to have great potential for organic pollutant removal from water and sludge. However, it is rarely used in sludge conditioning to improve dewatering. In addition, chlorine doses and initial pH significantly influence the efficiency of the process [26]. Chlorination could provide a novel way to enhance sludge dewaterability.

A single sludge disintegration approach reduces the sludge particle size and forms a stable dispersed sludge system. This restricts the degree of sludge dewatering [27]. This is the primary disadvantage of AOPs. In practice, when processing cost and efficiency are considered, coagulation/flocculation is a relatively mature sludge dewatering technology [28]. The coagulation/flocculation agglomerates the sludge flocs into larger particles through charge neutralization and bridging, and the water is separated from the sludge flocs [29]. This further improves sludge dewaterability. Therefore, studies have investigated combined oxidation and coagulation/flocculation re-flocculation treatments to enhance sludge dewaterability. For example, one study applied calcium peroxide pre-oxidation and chemical re-flocculation to improve sludge dewaterability [12]. Chen et al. [30] investigated the feasibility of the combined process of enzymatic lysis and inorganic coagulants re-flocculation to treat sludge. These outcomes demonstrate that combining technologies can improve sludge dewatering performance. In addition, ferric salts have been widely used as a chemical coagulant to improve sludge conditioning and dewatering [27,28]. The production of Fe (III) has been used as a coagulant and binding agent with EPS [31]. Ferric salts were better able to strongly neutralize the electric charge and form compact flocs, enhancing sludge dewaterability [29]. This highlights





(1)

Table 1

| The | distribution | of | fluorophore | regions. |
|-----|--------------|----|-------------|----------|
| | | | | |

| Region | Organic compounds | Ex/Em Wavelength (nm) |
|--------|--|-----------------------|
| I | Tyrosine/tryptophan amino acid region | 220-240/280-360 |
| II | Tyrosine/tryptophan protein region | 220-290/280-360 |
| III | Polysaccharide region | 300-330/360-390 |
| IV | Fulvic acid region | 220-240/410-450 |
| V | Polyaromatic-type humic acid region | 260-290/420-460 |
| VI | Polycarboxylate-type humic acid region | 330-370/420-460 |

the importance of exploring ferric salts combined with chlorination oxidation to reduce sludge volume.

At high pressures, AOPs and coagulation/flocculation do not enhance sludge compressibility, nor does it strengthen the hardness of sludge cake. This makes it more difficult to further release the remaining water [27]. Physical conditioners including lime [15], rice husk [32], flyash [33], and red mud [14] are commonly used to enhance sludge compressibility. These physical conditioners form a permeable and rigid sludge cake structure and drain free water under high pressure. In China, walnut shell (WS) is an agricultural waste, with more than 100,000 tons produced each year [34]. WS disposal has become a serious environmental problem, as it wastes resources and pollutes the environment. As public awareness about sustainable development has increased, the use of renewable biomass has rapidly grown [35]. WS is a type of biomass that has sparked significant research attention in recent years [35,36]. Song et al. [35] investigated the use of modified WS biochar as a green adsorbent to simultaneous catalyze and hydrolyze CS₂ and COS. Banerjee et al. [36] investigated the use of WS as a green adsorbent to remove Cr(VI) in a continuous fixed bed adsorption column. WS is a low-cost porous material and has the potential to serve as an economically viable skeleton builder for sludge dewatering.

Wu et al. [27] demonstrated that a combined treatment consisting

of potassium permanganate, ferric chloride (FeCl₃), and biochar effectively enhanced sludge dewaterability. Similarly, combining Ca(ClO)₂, ferric salt, and WS may be an effective way to improve dewatering performance. No previous studies have specifically combined Ca(ClO)₂ oxidation, ferric salt re-flocculation, and WS skeleton construction as a new technology to improve sludge dewaterability. There is little information about the synergistic mechanism of these materials. In this study, we propose a novel sludge conditioning process involving Ca (ClO)₂ oxidation, ferric coagulant re-flocculation, and WS skeleton construction to simultaneously remove EPS and bound water and improve sludge dewaterability. Given this background, this study: (1) investigated the effect of the combined Ca(ClO)₂/ferric coagulant/WS treatment on sludge dewaterability and EPS properties, with the goal of optimizing the operating conditions for the combination treatment; (2) clarified the mechanism of the combined treatment by analyzing the morphological structure, flocs morphology, rheological behavior, and bound water; (3) verified the industrial feasibility of the combined treatment by applying a controllable pressure filtration; and (4) assessed the economic cost of the combined treatment and validated the potential sludge disposal methods.

2. Materials and methods

2.1. Raw sludge and reagents

The sludge for this study was collected from the secondary sedimentation tank of a WWTP in Guangzhou, China. Samples were stored at 4 °C and analyzed within 3 days. The main characteristics of the concentrated sludge were as follows: the pH was 6.68 \pm 0.30; the moisture content was 96.80 \pm 0.05 wt%; the total suspended solids (TSS) was 46.52 \pm 0.36 g/L; the volatile suspended solid (VSS) was 20.93 \pm 0.29 g/L; and the specific resistance of filtration (SRF) was 5.29 \pm 0.02 \times 10¹² m/kg.



Fig. 2. Effects of Ca(ClO)₂ dosage on sludge properties: (a) SRF and MCSC; (b) DOC concentration; (c) PN concentration; (d) PS concentration.

Та

| able | 2 | | |
|------|---|--|--|
| | | | |

| Influ | uence of | $Ca(ClO)_2$ | dosage o | n EEM area | volumes of | organics i | n thre | e EPS | fractions | (Units: | 104 RI | J). |
|-------|----------|-------------|----------|------------|------------|------------|--------|-------|-----------|---------|--------|-----|
|-------|----------|-------------|----------|------------|------------|------------|--------|-------|-----------|---------|--------|-----|

| EPS fractions | Ca(ClO) ₂ dosage (mg/g DS) | Tyrosine/ tryptophan amino acid | Tyrosine/ tryptophan protein | Polysaccharide | Fulvic acid | Polyaromatic-type humic acid | Polycarboxylate-type humic acid |
|------------------|--|--|------------------------------------|----------------|----------------|---------------------------------|------------------------------------|
| | 0 | 3.10 | 4.02 | 1.87 | 8.08 | 2.47 | 1.81 |
| | 5 | 5.96 | 5.61 | 2.24 | 5.74 | 3.14 | 2.01 |
| | 10 | 6.19 | 6.94 | 2.54 | 4.86 | 5.98 | 3.47 |
| C EDC | 20 | 7.90 | 9.66 | 3.20 | 5.51 | 10.88 | 7.84 |
| S-EPS | 40 | 4.96 | 7.32 | 3.92 | 4.57 | 11.58 | 13.07 |
| | 60 | 2.62 | 4.77 | 3.89 | 3.64 | 10.91 | 14.54 |
| | 80 | 1.19 | 2.02 | 4.15 | 3.47 | 10.88 | 15.88 |
| | 100 | 0.25 | 0.94 | 4.86 | 1.47 | 7.53 | 14.62 |
| | 0 | 13.09 | 11.10 | 2.40 | 4.72 | 4.03 | 2.37 |
| | 5 | 13.01 | 11.17 | 2.10 | 5.08 | 4.45 | 2.87 |
| | 10 | 13.21 | 11.42 | 2.18 | 5.27 | 5.81 | 3.68 |
| ID EDC | 20 | 12.31 | 10.29 | 1.98 | 4.95 | 6.75 | 4.27 |
| LD-EPS | 40 | 8.37 | 8.24 | 2.35 | 3.92 | 7.35 | 5.99 |
| | 60 | 6.42 | 6.79 | 2.38 | 4.10 | 7.73 | 6.05 |
| | 80 | 4.77 | 5.01 | 2.62 | 4.72 | 7.83 | 6.78 |
| | 100 | 2.14 | 3.64 | 3.37 | 5.30 | 7.28 | 7.11 |
| | 0 | 8.79 | 13.22 | 31.13 | 2.09 | 4.65 | 5.42 |
| | 5 | 6.65 | 10.82 | 26.75 | 1.51 | 4.00 | 5.87 |
| | 10 | 6.25 | 10.30 | 29.53 | 1.45 | 4.02 | 6.44 |
| TD EDC | 20 | 4.95 | 7.94 | 6.80 | 1.07 | 3.61 | 6.86 |
| IB-EPS | 40 | 3.34 | 5.37 | 3.46 | 0.74 | 3.03 | 7.45 |
| | 60 | 3.26 | 4.73 | 3.27 | 1.11 | 3.38 | 6.50 |
| | 80 | 3.17 | 4.54 | 3.61 | 2.05 | 4.85 | 7.06 |
| | 100 | 1.70 | 2.88 | 4.41 | 3.45 | 5.75 | 7.83 |

Note: Red color denoted the extreme high values (> 10.0×10^4 RU).

The Ca(ClO)₂, with a purity exceeding 60.0%, was technical grade, and was purchased from the Aladdin Chemical Reagent Factory in China. FeCl₃ and polymeric ferric sulfate (PFS), at a purity exceeding 99.0%, were chemical grade from the Xiya Chemical Reagent Factory in China. Stock solutions of FeCl₃ (20.0 wt%) and PFS (20.0 wt%) were prepared before the experiments. WS was procured from a local market. A ball mill was used to prepare the WS powder; the powder was then crushed to a size that would pass through an 80 mesh sieve (180 ± 7.6 µm). All other chemical reagents were of analytical grade.

2.2. Experimental procedure

2.2.1. Sludge treatment with $Ca(ClO)_2$ oxidation

Individual 300 mL sludge samples were transferred to separate 500 mL beakers with different doses (0, 5, 10, 20, 40, 60, 80, and 100 mg/g dry solid (DS)) of $Ca(ClO)_2$. The beakers were then placed into a coagulation agitator at the speed of 200 revolutions per minute (rpm) for 30 min. The samples were analyzed for SRF, moisture content of sludge cake (MCSC), and EPS.

To further understand the effects of pH on sludge treatment with Ca $(ClO)_2$, sulfuric acid $(H_2SO_4, 10 \text{ wt}\%)$ and sodium hydroxide (NaOH, 10 wt%) were added to seven different sludge suspensions to establish different pH levels (2.0, 3.0, 4.0, 5.0, 6.0, 6.6, 8.0 and 9.0). Then, the sludge samples were conditioned with the Ca(ClO)₂ treatment. Each experiment was conducted in triplicate.

2.2.2. Ferric coagulant re-flocculation of sludge treated with $Ca(ClO)_2$

After the $Ca(ClO)_2$ treatment, seven different amounts of ferric coagulant (FeCl₃ and PFS) were added to individual sludge samples, with respective ferric coagulant concentrations of 0, 40, 60, 80, 100,

120, and 160 mg/g DS. The sludge system was slowly stirred at 100 rpm for 10 min. After this mixing, the conditioned sludge settled for 10 min. SRF, MCSC, and EPS were measured for each conditioned sludge sample. Each experiment was conducted in triplicate.

2.2.3. WS skeleton construction of sludge treated with $Ca(ClO)_2$ oxidation and ferric coagulant re-flocculation

Different doses of WS (0, 50, 100, 200, 400, and 600 mg/g DS) were added into each beaker; each sample had already been conditioned with $Ca(ClO)_2$ and ferric coagulant. Sludge samples were mixed using a coagulation agitator at the speed of 100 rpm for 10 min. The conditioned sludge samples were used to measure sludge SRF, MCSC, the net sludge solids yield (Y_N), and EPS. All experiments were repeated in triplicate.

2.2.4. Mechanical dewatering device with controllable pressure

Fig. 1 shows the mechanical dewatering device, which was constructed based on a novel controllable pressure filtration system developed by Dai et al. [10]. The device includes a sample container, a pressure controller system, a vacuum pump, a hydraulic system, and an electronic scale. The pressure was adjusted from 2 to 6 MPa. A 400 mL sample volume was used for each test. Detailed descriptions of the operation process are provided in Supplementary data, Text S1. All reagents for these tests were industrial standards.

Sludge dewatering performance was assessed by measuring the amount of water removed and the moisture content of the dewatered cake [37]. The net percentage of sludge water removed at time t, $SWR_{(t)}$, was determined using Eq. (2).



Fig. 3. Effects of initial pH on sludge properties with Ca(ClO)₂ treatment: (a) SRF and MCSC; (b) DOC concentration; (c) PN concentration; (d) PS concentration (Experimental condition: Ca(ClO)₂ dosage of 10 mg/g DS).

$$SWR_{(t)}(\%) = \left(\frac{m_{F(t)} - m_{W}}{m_{s} - m_{ss}}\right) \times 100\%$$
(2)

In this expression, $m_{F(t)}$ (kg) is the mass of the filtrate at time t; m_w (kg) is the total mass of extra water added, including chemical agents; m_s (kg) is the total mass of the sludge at the start; and m_{ss} (kg) is the mass of sludge solids.

To evaluate the environmental impact of the filtrate characteristics, we measured the chemical oxygen demand (COD), ammonia nitrogen (NH_4^+) , and total phosphorus (TP) [38]. These were assessed using American Public Health Association (APHA) methods [39].

2.3. Analytical methods

2.3.1. Sludge dewaterability

Sludge dewaterability was determined using the following variables: SRF, the MCSC, and the Y_N . The SRF and the Y_N were measured using standard methods [40]. The MCSC was measured using a gravimetric method [39].

2.3.2. EPS extraction and analysis

2.3.2.1. EPS extraction. EPS was extracted from sludge samples using a modified heat extraction method [19,41]. EPS can be characterized as soluble EPS (S-EPS), loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS). Detailed descriptions of the extraction process are included in Supplementary data, Text S2.

2.3.2.2. EPS chemical analysis. EPS samples were analyzed for dissolved organic carbon (DOC), protein (PN), and polysaccharide (PS). DOC concentrations were determined using a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan) [29]. PN concentrations were measured using the Coomassie Brilliant Blue G-

250 method, with bovine serum albumin as the standard [42]. PS concentrations were determined using the Anthrone method, with glucose as the standard [43]. All experiments were repeated in triplicate.

2.3.2.3. Three-dimensional excitation-emission matrix of EPS. The threedimensional excitation-emission matrix (3D-EEM) fluorescence spectra were measured using a Hitachi F-4500 fluorescence spectrophotometer. EEM spectra with subsequent scanning emission spectra were collected from 280 to 500 nm at 5 nm increments, by varying the excitation wavelength from 200 to 400 nm at 5 nm increments. The spectra were recorded at a scan rate of 1200 nm/min, using excitation and emission slit bandwidths of 5 nm. The EEM spectrum was delineated into six regions based on research by Kunacheva and Stuckey. [44]. Table 1 shows the regional distributions. A fluorescence region integration (FRI) technique was developed to quantitatively analyze the fluorescence composition of EPS [45].

2.3.3. Flocs morphology and morphological structure

The zeta potential was determined using a zeta potential instrument (Zeta PALS, Brookhaven, USA). A laser diffraction instrument (Mastersizer 3000, Malvern, UK) was used to measure the size and structure of the dynamic flocs. The morphology of the sludge samples was observed using an Olympus microscope (SZX10, Olympus, Japan). The freeze-dried sludge samples were observed using a field emission scanning electronic microscope (FESEM) (SU8220, Hitachi, Japan).

2.3.4. Rheological test

The rheological behavior of sludge was determined using a rotational rheometer (Physica MCR 301, Anton Paar, Austria), with PP 50 parallel plate geometry. The temperature was controlled at 35 ± 0.1 °C with a water bath. A continuous ramp-up in the shear rate was applied

Table 3

EEM area volumes of organics in three EPS fractions after Ca(ClO)₂ under different pH conditions (Units: 10⁴ RU).

| EPS fractions | Initial pH | Tyrosine/ tryptophan amino acid | Tyrosine/ tryptophan protein | Polysaccharide | Fulvic acid | Polyaromatic-type humic acid | Polycarboxylate-type humic acid |
|------------------|---------------|--|------------------------------------|----------------|----------------|---------------------------------|------------------------------------|
| | 2 | 0.39 | 0.60 | 2.77 | 0.85 | 1.53 | 7.66 |
| | 3 | 0.86 | 3.66 | 2.91 | 1.59 | 13.99 | 9.53 |
| | 4 | 1.10 | 4.61 | 2.64 | 1.47 | 14.19 | 7.21 |
| C EDC | 5 | 2.59 | 4.94 | 2.41 | 3.51 | 10.91 | 5.27 |
| S-EPS | 6 | 6.61 | 6.53 | 2.80 | 6.72 | 6.29 | 3.57 |
| | 6.6 | 6.19 | 6.94 | 2.54 | 4.86 | 5.98 | 3.47 |
| | 8 | 11.71 | 13.21 | 4.05 | 4.79 | 6.19 | 4.81 |
| | 9 | 6.35 | 9.87 | 4.18 | 2.33 | 4.33 | 5.69 |
| | 2 | 2.18 | 1.82 | 1.35 | 4.07 | 5.51 | 2.56 |
| | 3 | 4.48 | 4.36 | 1.58 | 4.92 | 10.21 | 4.50 |
| | 4 | 6.01 | 5.59 | 1.76 | 4.74 | 8.71 | 4.04 |
| | 5 | 8.90 | 7.85 | 1.91 | 4.97 | 6.61 | 3.11 |
| LB-EP5 | 6 | 11.83 | 9.39 | 1.69 | 4.06 | 3.68 | 1.84 |
| | 6.6 | 13.21 | 11.42 | 2.18 | 5.27 | 5.81 | 3.68 |
| | 8 | 14.76 | 13.50 | 2.56 | 4.52 | 4.62 | 3.79 |
| | 9 | 15.52 | 13.55 | 2.54 | 4.25 | 4.61 | 3.04 |
| | 2 | 5.83 | 4.80 | 1.33 | 4.84 | 7.13 | 3.31 |
| | 3 | 5.36 | 8.48 | 1.75 | 4.47 | 8.77 | 4.47 |
| | 4 | 5.68 | 9.15 | 4.53 | 3.56 | 8.72 | 6.58 |
| TD EDC | 5 | 5.77 | 9.70 | 12.50 | 2.18 | 6.12 | 7.45 |
| IB-EPS | 6 | 6.14 | 10.01 | 25.44 | 1.42 | 4.19 | 6.69 |
| | 6.6 | 6.25 | 10.30 | 29.53 | 1.45 | 4.02 | 6.44 |
| | 8 | 7.30 | 10.64 | 18.32 | 1.47 | 3.68 | 5.51 |
| | 9 | 7.91 | 11.06 | 18.01 | 1.62 | 3.62 | 5.20 |

Note: Red color denoted the extreme high values (> 10.0×10^4 RU).

Table 4

Coefficients of Pearson's correlation between sludge SRF and EPS composition of sludge with Ca(ClO)₂ conditioning.

| | | S-EPS | LB-EPS | TB-EPS |
|---------------------------------|------------|-----------------|---|----------------|
| DOC Protein | SRF SRF | 0.407 -0.315 | 0.541 [*] 0.657 ^{**} | 0.380 0.378 |
| Polysaccharide | SRF | 0.373 | 0.961** | 0.195 |
| Tyrosine/tryptophan amino acid | SRF | 0.274 | 0.312 | 0.023 |
| Tyrosine/tryptophan protein | SRF | 0.276 | 0.414 | 0.013 |
| Polysaccharide | SRF | 0.594 | 0.851 | 0.166 |
| Fulvic acid | SRF | 0.184 | -0.090 | -0.406 |
| Polyaromatic-type humic acid | SRF | -0.313 | -0.356 | -0.563* |
| Polycarboxylate-type humic acid | SRF | 0.169 | 0.287 | 0.184 |

Note:

* Correlation is significant at the level of 0.05 level (two tailed).

** Correlation is significant at the level of 0.01 level (two tailed).

to achieve an increase from 0.1 to 1000 s^{-1} ; the reverse pattern was then assessed. Each shear rate was held for 30 s to ensure than an equilibrium point in a stationary state was reached [46,47].

The Herschel-Bulkley model (Eq. (3)) was used to analyze the rheological data. The model efficiently describes the sludge's rheological behavior under rest and flow conditions [46].

$$\tau = \tau_y + k \dot{\gamma}^n \tag{3}$$

In this expression, τ is the shear stress (Pa); $\dot{\gamma}$ is the shear rate (s⁻¹); τ_{γ} is the yield stress (Pa); k is the consistency index (Pa·s^{*n*}); and n is the flow behavior index (dimensionless).

Amplitude sweep oscillation tests were used to measure the viscoelastic characteristics. In the test, the angular frequency (1 Hz) and temperature (35 $^{\circ}$ C) were held constant, while the strain on the sludge samples was logarithmically adjusted from 0.01 to 100% to obtain the structural properties of the sludge and determine the linear viscoelastic region.

2.3.5. Bound water content

The bound water content was determined using the differential scanning calorimetry (DSC) method [48]. The sample mass was maintained at approximately 10 mg. The sample temperature was initially set at -20 °C; the temperature was then increased to 10 °C a rate of -2 °C/min. The free water content was determined by integrating the peak area under the endothermic curve. Then, the bound water content was calculated using Eq. (4):

$$W_{\rm B} = W_{\rm T} - \Delta H / \Delta H_0 \tag{4}$$

In this expression, W_B is the bound water content in the sludge samples (g/g DS); W_T is the total water in the sludge samples; ΔH is the DSC enthalpy of the sludge samples; and ΔH_0 is the standard melting heat of ice (334.7 mJ/mg) [20].

2.3.6. Other indicators

Other sludge parameters were assessed using APHA methods [39], including moisture content, TSS, VSS, and pH. The proximate analysis was conducted using the Chinese National Standards of Proximate Analysis of Coal (GB/T 212-2008). An organic element analyzer (EA 3000, Eurovector, Italy) was used to measure the C, H, N, and S content.

2.4. Statistical analysis

The Pearson's correlation between parameters pairs was determined using the software package Statistical Product and Service Solutions (SPSS) version 20.0 for Windows. The correlations were considered



Fig. 4. Effects of ferric coagulant dosage on sludge dewatering performance and LB-EPS distribution: (a) (b) FeCl₃; (c) (d) PFS (Experimental conditions: Ca(ClO)₂ dosage of 10 mg/g DS, initial pH of 3).

statistically significant at a 95% confidence interval (probability (p) < 0.05) [49].

Ca(ClO)₂ oxidation benefited sludge dewatering.

3. Results and discussion

3.1. Effects of individual Ca(ClO)₂ treatment on sludge properties

3.1.1. Effects of Ca(ClO)₂ dose on sludge properties

3.1.1.1. Sludge dewaterability. Fig. 2a shows the effects of the individual Ca(ClO)₂ treatments on the SRF and MCSC in the sludge. As the Ca(ClO)₂ dose increased, the SRF and MCSC first decreased and then increased. The lowest SRF and MCSC were seen at a Ca(ClO)₂ dose of 10 mg/g DS. At the optimal Ca(ClO)₂ dose, the sludge SRF decreased from 5.29×10^{12} to 2.95×10^{12} m/kg and the MCSC dropped from 90.81 to 86.27 wt%, compared with the raw sludge. However, at a high Ca(ClO)₂ dose of 100 mg/g DS, sludge dewaterability was even worse than with the raw sludge. This may be because, based on Eq. (5), excessive HClO and Ca(OH)₂ were released, significantly damaging the organic matter in the sludge [21]. A strong alkaline environment and excess EPS dissolution may disrupt the sludge's ability to flocculate and inhibited further dewatering [15].

$$Ca(CIO)_2 + 2H_2O = Ca(OH)_2 + 2HCIO$$
(5)

Fig. S1 shows that the filtrate TOC values increased as the $Ca(ClO)_2$ concentration increased. At a dose of 100 mg/g DS $Ca(ClO)_2$, the filtrate TOC value reached 12.98 mg/g DS, a level 12 times larger than seen with the raw sludge. Higher filtrate TOC concentrations occurred at higher pH values, which worsened dewatering. These results are consistent with Liang et al. [15]. Thus, the sludge micro-disintegration by

3.1.1.2. Sludge EPS characterization. EPS are high molecular weight biopolymers that affect sludge dewaterability [50]. Fig. 2b shows that at a low Ca(ClO)₂ dose, the minimum total DOC concentration was 96.73 mg/g DS. This result suggests that adding a low dose of $Ca(ClO)_2$ effectively released organic matter. The flocs were dissolved and oxidized into smaller molecules, likely enhancing sludge dewaterability. However, with the continuous increase of Ca(ClO)₂, the DOC concentration in the TB-EPS layers decreased from 58.86 to 37.44 mg/g DS. The DOC concentrations in the S-EPS layer increased from 12.65 to 40.16 mg/g DS; the DOC concentrations in the LB-EPS layer increased from and 26.37 to 54.93 mg/g DS. Past research found that excessively high molecular weight substances in S-EPS and LB-EPS were consistently associated with poor sludge-water separation performance and sludge flocculation [12,49,51]. These results confirmed that when the DOC concentrations in S-EPS and LB-EPS reached a certain threshold, it deteriorated sludge dewaterability. Thus, high doses of Ca(ClO)₂ oxidation caused the sludge flocs to disintegrate, possibly blocking the sludge dewatering channel.

Fig. 2c and d shows the variations in PN and PS concentrations in three EPS fractions before and after conditioning with different Ca $(ClO)_2$ concentrations. As $Ca(ClO)_2$ concentration increased from 0 to 10 mg/g DS, PN concentrations in LB-EPS decreased from 7.74 to 6.54 mg/g DS, and decreased in TB-EPS from 51.04 to 27.12 mg/g DS, respectively. PS concentrations showed a similar trend. However, the total PS concentrations increased when the $Ca(ClO)_2$ dose exceeded 10 mg/g DS. Many studies have demonstrated that high PS concentrations lead to the high absorption of water molecules from the flocs,

Table 5

Effects of combined $Ca(ClO)_2$ and ferric coagulant conditioning on LB-EPS fluorescent intensities (Units: 10^4 RU).

| The types of | Ferric coagulant dosage | Tyrosine/ | Tyrosine/ | |
|-------------------|-------------------------|------------|------------|----------------|
| treatment | (mg/g DS) | tryptophan | tryptophan | Polysaccharide |
| licutificiti | (119,9,200) | amino acid | protein | |
| | 0 | 13.09 | 11.10 | 2.40 |
| | 40 | 2.00 | 4.20 | 1.96 |
| Control | 60 | 2.12 | 4.18 | 2.10 |
| | 80 | 2.03 | 3.23 | 1.70 |
| $+ \text{FeCl}_3$ | 100 | 1.80 | 3.58 | 1.39 |
| | 120 | 1.33 | 1.81 | 0.75 |
| | 160 | 1.57 | 2.13 | 0.89 |
| | 0 | 4.48 | 4.36 | 1.58 |
| | 40 | 2.67 | 2.14 | 1.12 |
| Ca(C(0)) | 60 | 2.44 | 2.32 | 1.41 |
| Cu(CIO)2 | 80 | 2.18 | 1.72 | 0.98 |
| $+ \text{FeCl}_3$ | 100 | 1.90 | 1.68 | 1.02 |
| | 120 | 1.68 | 1.61 | 1.04 |
| | 160 | 1.12 | 1.48 | 0.99 |
| | 0 | 13.09 | 11.10 | 2.40 |
| | 40 | 2.57 | 4.01 | 1.21 |
| Control | 60 | 2.19 | 3.36 | 1.16 |
| control | 80 | 2.35 | 2.94 | 1.08 |
| + PFS | 100 | 2.00 | 1.84 | 0.99 |
| | 120 | 1.85 | 1.33 | 0.98 |
| | 160 | 1.21 | 0.86 | 0.74 |
| | 40 | 4.48 | 2.25 | 1.58 |
| | 60 | 2.26 | 1.89 | 1.55 |
| $Ca(ClO)_2$ | 80 | 1.34 | 1.99 | 1.69 |
| + PFS | 100 | 1.34 | 1.67 | 1.36 |
| | 120 | 0.88 | 1.62 | 0.95 |
| | 160 | 0.77 | 1.12 | 0.75 |

Note: Red color denoted the extreme high values (> 10.0×10^4 RU).

leading to poor dewaterability [18,41]. In addition, a mass of fine colloidal particles is released to the S-EPS at higher $Ca(ClO)_2$ doses. These fine colloidal particles may block the filter medium and the cake layer, limiting filtration efficiency.

The 3D-EEM fluorescence spectroscopy approach has been widely used to measure dissolved organic matter in water and EPS fractions [52]. Table 2 shows the FRI results for the three EPS fractions before and after conditioning with Ca(ClO)₂. The main EPS components included tyrosine/tryptophan amino acid (TTAC), tyrosine/tryptophan protein (TTPN), and PS. As the Ca(ClO)₂ dose increased, the intensities of TTAC and TTPN organic compounds weakened significantly in LB-EPS and TB-EPS, and were enhanced in S-EPS. The intensities of PS organic compounds in the TB-EPS experienced a downward trend, but trended upward in the S-EPS and LB-EPS. These results suggest that Ca (ClO)₂ oxidation treatment led to the disintegration of protein-like substances and polysaccharide-like materials in the LB-EPS and TB-EPS. Many studies have reported that decreases in protein-like substances and polysaccharide-like materials in LB-EPS and TB-EPS may positively impact sludge flocculation and flocs structure, causing better sludge filterability [49]. The results were consistent with the DOC, PN and PS analyses in Fig. 2. In addition, the intensities of fulvic acid (FA), polyaromatic-type humic acid (PAHA), and polycarboxylate-type humic acid (PCHA) in three EPS layers increased during Ca(ClO)₂ treatment.

3.1.2. Effects of initial pH on sludge properties with $Ca(ClO)_2$ treatment 3.1.2.1. Sludge dewaterability. A previous study found that pH significantly affects $Ca(ClO)_2$ oxidation [53]. The initial pH values used in this study ranged from 2.0 to 9.0, and were tested with the

optimal Ca(ClO)₂ dose (10 mg/g DS). Fig. 3a shows that pH significantly impacted the SRF and MCSC values of the sludge. Initially, a decrease of pH benefited dewatering (pH from 9.0 to 3.0). However, as the pH was reduced below 3.0, the SRF and MCSC values did not change significantly (pH from 3.0 to 2.0). The Ca(ClO)₂ conditioning was most efficient when the reaction pH was approximately 3. At this level, the SRF and MCSC values were 1.51×10^{12} m/kg and 85.32 wt%, respectively. These results indicate that sludge dewatering performance was significantly enhanced by lowering the pH level of sludge [54]. The pH can affect EPS and sludge properties and change the chemical characters of Ca(ClO)₂ and Ca (OH)₂, significantly influencing sludge dewaterability. Based on this finding, the EPS properties were further characterized to reveal the mechanism of sludge dewaterability.

3.1.2.2. Sludge EPS characterization. Fig. 3b–d shows the influence of different pH values on EPS contents under $Ca(ClO)_2$ oxidation. When the pH decreased from 9.0 to 2.0, the DOC concentrations in LB-EPS decreased from 29.43 to 19.32 mg/g DS, and decreased in TB-EPS from 52.87 to 18.29 mg/g DS. However, DOC concentrations in the S-EPS fraction first increased and then decreased. The PN and PS concentrations in LB-EPS and TB-EPS decreased as the acidity increased. These results indicate that under acidic conditions, Ca $(ClO)_2$ treatment may trigger the collapse of the sludge matrix and polymeric structures. One past study [54] suggest that the breakdown of the polymeric structure also strengthens the sludge's relative hydrophobicity, positively impacting the release of the bound water and enhancing filtrate flow. This led to better sludge dewaterability.



Fig. 5. Effects of WS dosage on sludge dewaterability and LB-EPS distribution: (a) (c) $Ca(ClO)_2 + FeCl_3$; (b) (c) $Ca(ClO)_2 + PFS$ (Experimental conditions: Ca (ClO)_2 dosage of 10 mg/g DS, initial pH of 3, FeCl₃ dosage of 60 mg/g DS, PFS dosage of 100 mg/g DS).

This can be explained by the oxidation activity of $Ca(ClO)_2$ and the limited production of $Ca(OH)_2$. At a lower pH, more HOCl and less Ca (OH)₂ emerged [53], possibly dissolving the protein-like substances and polysaccharide-like materials.

Table 3 shows the influence of pH on FRI in three EPS fractions with the Ca(ClO)₂ conditioning. As the pH decreased, the intensities of TTAC, TTPN, and PS organic compounds in the three EPS layers weakened significantly. This result suggests that more organic materials (such as protein-like and polysaccharide-like substances) were removed under acidic conditions. This trend was consistent with the results of the EPS chemical analysis. This may be because when exposed to strong acid, PN and PS were unstable and readily damaged. For example, protein-like substances lost their natural shapes and polysaccharide-like materials were hydrolyzed [49]. However, the intensities of FA, PAHA,

Table 6

| Effects | of | combined | Ca(ClO) ₂ /ferric | coagulant/WS | conditioning | on | LB-EPS |
|---------|------|---------------|------------------------------|--------------|--------------|----|--------|
| fluores | cent | t intensities | (Units: 10 ⁴ RU) | | | | |

| The types of treatment | WS dosage (mg/g DS) | Tyrosine/ tryptophan amino acid | Tyrosine/ tryptophan protein | Polysaccharide |
|---------------------------|------------------------------|---------------------------------------|------------------------------------|----------------|
| $Ca(ClO)_2 + FeCl_3 + WS$ | 0 | 2.44 | 2.32 | 1.41 |
| | 50 | 3.95 | 3.49 | 1.62 |
| | 100 | 4.07 | 3.45 | 1.74 |
| | 200 | 4.36 | 4.18 | 2.61 |
| | 400 | 4.52 | 4.65 | 3.58 |
| | 600 | 4.58 | 4.16 | 4.27 |
| $Ca(ClO)_2 + PFS + WS$ | 0 | 1.34 | 2.94 | 1.36 |
| | 50 | 3.44 | 3.84 | 1.97 |
| | 100 | 2.91 | 2.77 | 1.63 |
| | 200 | 4.06 | 4.12 | 2.57 |
| | 400 | 3.87 | 4.29 | 3.36 |
| | 600 | 5.12 | 4.24 | 4.25 |

and PCHA in LB-EPS layers did not change with the increased acidity. This result implies that FA and HA substances resisted $Ca(ClO)_2$ treatment under acidic condition. Thus, the change in pH level more significantly impacted protein-like and polysaccharide-like substances. The destruction of protein-like substances and polysaccharide-like materials in EPS resulted in the release of trapped water.

3.1.3. Pearson correlation analysis of $Ca(ClO)_2$ treatment: Comparing sludge dewaterability and sludge EPS distribution, and composition

Table 4 shows the relationships between SRF and EPS distribution, and composition in the three sludge fractions when treated with Ca $(ClO)_2$. The result shows that the protein-like substances and poly-saccharide-like materials in LB-EPS were key to impacting sludge dewatering efficiency with the Ca $(ClO)_2$ treatment. Detailed descriptions of Pearson correlation analysis are provided in the Supplementary data, Text S3.

3.2. Effects of ferric coagulant re-flocculation on sludge properties

3.2.1. Sludge dewaterability

After $Ca(ClO)_2$ oxidation, sludge flocs were dispersed and part of the sludge EPS was solubilized, making it difficult to further compress. This makes it important to increase flocs strength and compression ability. Ferric coagulant can neutralize negatively charged colloids. As such, they tend to aggregate flocs and reduce the moisture content of sludge [29]. To further improve sludge dewatering efficiency, this study applied a combined treatment with Ca(ClO)₂ and ferric coagulant.

Figs. 4a and S2a show that when sludge is treated with a combination of 10 mg/g DS Ca(ClO)₂ and 60 mg/g DS FeCl₃, the SRF decreased by 85.66% and the MCSC decreased from 90.81 to 81.65 wt% compared with raw sludge. Figs. 4c and S2b show that combining 10 mg/g DS Ca(ClO)₂ with 100 mg/g DS PFS resulted in SRF being reduced to 0.72×10^{12} m/kg and MCSC being reduced to 80.55 wt%, respectively. In comparison, the SRF and MCSC of sludge conditioned with combined Ca(ClO)₂ and ferric coagulant were lower that the SRF and MCSC levels in the sludge conditioned in the control experiments. Combining the Ca(ClO)₂ oxidation and ferric coagulant re-flocculation appears to be a highly efficient method to enhance sludge dewatering performance (increase sludge filtration rate and decrease MCSC). This may be because the flocs were oxidized and the flexible EPS was broken down by using Ca(ClO)₂ oxidation. The led to the release of the cellular contents and bound water [15]. Adding ferric coagulant allowed the dispersed sludge flocs to be more easily re-aggregated, causing the formation of more compact flocs and a dewatering channel.



Fig. 6. FESEM images of the raw sludge and the conditioned sludges: (a) raw sludge; (b) 10 mg/g DS Ca(ClO)₂; (c) Ca(ClO)₂ + 60 mg/g DS FeCl₃; (d) Ca (ClO)₂ + 100 mg/g DS PFS; (e) Ca(ClO)₂ + FeCl₃ + 600 mg/g DS WS; (f) Ca(ClO)₂ + PFS + 600 mg/g DS WS (Magnified by 5,000 times).

3.2.2. Sludge LB-EPS characterization

As noted above, LB-EPS played a significant role in sludge dewatering; as such, studying variations in the LB-EPS fractions along with the ferric coagulant re-flocculation should provide significant insights. Fig. 4b and d show that DOC, PN, and PS concentrations in the LB-EPS layer decreased with the ferric coagulant treatment. The removal efficiency of DOC, PN, and PS concentrations in the LB-EPS layer conditioned with combined the Ca(ClO)₂ and ferric coagulant was higher than the removal efficiency seen with the sludge conditioned with ferric coagulant alone. This may be related to the Ca(ClO)₂ oxidation. After Ca(ClO)₂ oxidation, the high molecular weight biopolymers were degraded into low molecular weight substances. The ferric coagulant had a significant effect on the absorption and removal of low molecular weight organic compounds [8]. The DOC concentrations in LB-EPS decreased from 21.71 mg/g DS to 13.04 and 11.57 mg/g DS, when the sludge was conditioned with combined Ca(ClO)₂ and FeCl₃ and PFS, respectively. These results indicate that the combined Ca(ClO)₂ oxidation and ferric coagulant re-flocculation further removed organic compounds in the LB-EPS.

Table 5 shows that the intensities of TTAC, TTPN, and PS organic compounds in the LB-EPS layers weakened as the ferric coagulant dose increased. Furthermore, the combined Ca(ClO)₂ and ferric coagulant

treatment was more effective in removing TTAC, TTPN, and PS compared to the ferric coagulant treatment alone. This may be due to the higher affinity of the ferric ions to the protein-like substances and polysaccharide-like materials in the sludge samples [12]. As noted above, the protein-like substances and polysaccharide-like materials in LB-EPS were key to impacting sludge dewatering efficiency. The combined treatment with Ca(ClO)₂ and ferric coagulant was highly effective in removing protein-like substances and polysaccharide-like materials, and was responsible for the improved sludge dewatering.

3.3. Effects of WS skeleton construction on sludge properties

3.3.1. Sludge dewaterability

Researchers have found that skeleton builders enhance sludge compressibility and strengthen the hardness of sludge cake during the compression process [13–15]. In this study, we used WS as a skeleton builder to further enhance sludge compressibility. Based on the optimized values established above, WS was added at doses from 50 to 600 mg/g DS (pH = 3, Ca(ClO)₂ = 10 mg/g DS, FeCl₃ = 60 mg/g DS; PFS = 100 mg/g DS). Fig. 5a and b show that the SRF and MCSC gradually decreased as the WS dose increased; in contrast, the Y_N of treated sludge showed a reverse trend. The sludge dewaterability achieved the



Fig. 7. Zeta potential (a) and particle size distributions (b) of the raw sludge and the conditioned sludges.

best effect (the lowest SRF and MCSC, and the highest Y_N) at a WS dosage of 600 mg/g DS. Fig. 5a shows that a treatment of 600 mg/g DS WS, combined with the Ca(ClO)₂/FeCl₃, resulted in a decrease of 90.42% in sludge SRF compared with the raw sludge. The Y_N increased by 3.96 times and the MCSC decreased from 90.81 to 78.58 wt%. Fig. 5b shows that after 600 mg/g DS WS was combined with the Ca (ClO)₂/PFS treatment, the sludge SRF decreased by 90.84%, the Y_N increased by 4.26 times and the MCSC decreased by 77.66 wt%, compared with the raw sludge. These results suggest that the WS further improved sludge dewaterability. The combined Ca(ClO)₂/ferric coagulant/WS treatment achieved significantly better sludge dewaterability than the combined Ca(ClO)₂ and ferric coagulant treatment. These results may be due to the formation of a porous dewatering channel in the sludge cake and an increase in sludge cake compressibility. Many researchers have found similar results with respect to the effect of the skeleton builder in sludge conditioning [14,16]. Thus, the combined Ca(ClO)₂/ferric coagulant/WS treatment was a feasible and highly efficient way to improve sludge dewatering.

3.3.2. Sludge LB-EPS characterization

Fig. 5c shows the changes in the organic matter in the three EPS fractions after the Ca(ClO)₂/ferric coagulant/WS treatment. After conditioning, DOC, PN, and PS concentrations continued to slowly increase in the LB-EPS. These results indicated that DOC, PN, and PS in LB-EPS did not significantly change after the WS was added. The added WS did not significantly change the LB-EPS concentrations, because the main mechanism of WS conditioning was to act as a skeleton builder. This changed the sludge structure, increased flocs strength, and improved sludge compressibility [14].

Table 6 shows that the intensities of TTAC, TTPN, and PS organic compounds in the LB-EPS layers slowly increased as WS was added. This suggests that adding WS released more TTAC, TTPN and PS to the loose layer, possibly accounting for the flocs structure and compressibility. The WS was dispersed in the flocs, and could bind with protein-like substances and polysaccharide-like materials. This formed complexes with biopolymers through hydrophobic and electrostatic interactions. As the result, more organic matter was released to the loose layer.

Thus, adding WS established a skeleton structure in the sludge cake.



Fig. 8. Rheological properties of the raw sludge and the conditioned sludges: (a) flow curves; (b) dynamic strain sweep curve.



Fig. 9. Bound water content of the raw sludge and the conditioned sludges.

The free water was able to more easily pass through the incompressible and permeable sludge cake, further improving sludge dewatering.

3.4. Initial exploration of the dewatering mechanism

The experiments above revealed the optimal dewatering condition for sludge. To investigate the sludge dewatering mechanism, six types of samples were analyzed, including: raw sludge, Ca(ClO)₂, Ca(ClO)₂/FeCl₃, Ca(ClO)₂/PFS, Ca(ClO)₂/FeCl₃/WS, and Ca(ClO)₂/PFS/WS.

3.4.1. Morphological structure and flocs morphology

Fig. 6 shows the FESEM images of the raw sludge and the conditioned sludges. The raw sludge flocs were relatively compact and smooth, which is characteristic of poor dewaterability, bad permeability, and weak compressibility (Fig. 6a). The microstructure of the sludge conditioned by Ca(ClO)₂ appears loose and porous (Fig. 6b). The sludge flocs conditioned with ferric coagulant experienced more agglomeration and had a more abundant porous structure (Fig. 6c and d). These flocs exhibited good permeability, compressibility, and dewaterability. When WS was added, the skeleton structure was built into the sludge cake. Numerous stratified and rigid structure appeared in the sludge (Fig. 6e and f). This stable stratified and rigid structure was inserted into the external surfaces of the flocs, which helped remove the EPS and release the bound water. Microphotographs are intuitive evidence for the changes in the sludge flocs (Fig. S3). Detailed descriptions and explanations were summarized in Supplementary data, Text S4.

The zeta potential and flocs size of sludge were used to analyze the mechanism driving the flocs morphology, which plays an important role in sludge dewatering [32]. Fig. 7a shows that the zeta potential of raw sludge was -26.25 mV. Adding Ca(ClO)₂ caused a significant increase in the negative charge (-10.26 mV). This indicated that Ca (ClO)₂ oxidation weakened the ionization effects of the anionic functional groups. After ferric coagulant re-flocculation, the zeta potential increased. In addition, after the WS was added as a skeleton, the zeta potential was associated with a small decrease in the negative charge, which tends to 0 mV. The results indicated that the combined Ca(ClO)₂/ ferric coagulant/WS treatment neutralized the negative surface charge. The charge attraction caused sludge agglomeration, which favors sludge dewatering.

Fig. 7b shows the variations in mean flocs size (D50) under different conditions. The flocs size of the sludge conditioned with the Ca(ClO)₂ (58.7 μ m) was lower than the size of the flocs in the raw sludge (61.3 μ m). This may be because of the destruction of the EPS structure and the breakage of dense sludge flocs into smaller particles by oxidation [31]. The flocs size of sludge conditioned with the combined Ca (ClO)₂/ferric coagulant/WS treatment became larger. This suggests that the sludge flocs and small fragments (such as the dissociated EPS) regrouped; and a networked structure was formed when the sludge was treated with the combined Ca(ClO)₂/ferric coagulant/WS. This resulted in better sludge dewaterability. Moreover, the flocs size results were consistent with the morphological structure results (Figs. 6 and S3) and zeta potential results (Fig. 7a).

3.4.2. Rheological behavior

Rheology tests were conducted to assess the effects of the combined treatment on the rheological properties of the sludge. Fig. 8a shows the rheological properties across six types of sludge samples. The result shows that the shear-thinning behavior, the non-Newtonian characteristics, and the apparent viscosity of the treated sludge decreased more compared with the raw sludge and the other treatments.

The Herschel-Bulkley model was used to further understand the basic non-Newtonian behavior of these sludge samples [49]. Table S1 lists the fitting results of the Herschel-Bulkley model for different types of sludge samples. Higher n values indicate that sludge behavior gradually reflected Newtonian behavior [55]. Lower k values indicate sludge firmness and viscosity is low [56]. Table S1 shows that after



Fig. 10. The possible dewatering mechanism of sludge by combined Ca(ClO)₂/ferric coagulant/WS treatment.

conditioning, the k value decreased and the n value increased. This indicated that sludge flowability increased and viscosity decreased after the conditioning. Based on these results, it was determined that, across the five treatments, the k value was lowest for $Ca(ClO)_2/PFS/WS$. The k values increased for Ca(ClO)₂/FeCl₃/WS, followed by Ca(ClO)₂/PFS, followed by Ca(ClO)₂, and then by Ca(ClO)₂/FeCl₃. The n value showed the reverse rank as the k value. This is consistent with the gradual decrease in DOC, PN, and PS concentrations in the LB-EPS and TB-EPS. These results were consistent with Pham et al. [57], who found that the destruction of the internal structure increased flowability and decreased viscosity. The research found that the EPS distribution and composition in the sludge may be the major factor affecting rheological behavior, further influencing sludge dewaterability [58]. Moreover, sludge with a lower viscosity and higher flowability was easier to dewater. The combined Ca(ClO)₂/PFS/WS treatment significantly changed the rheological properties of the sludge. Due to these changes, the flowability increased and viscosity decreased. This improved sludge dewaterability. Fig. 8b shows the dynamic measurement results of different sludge samples. Detailed descriptions of the dynamic measurement results are provided in the Supplementary data, Text S5.

3.4.3. Bound water content

The bound water content is one of the most important factors in determining sludge dewatering properties [54]. The bound water content of sludge can be calculated from the DSC endothermic curve area, as shown in Fig. S4, and Eq. (4). Fig. 9 shows the calculated bound water content of the raw and conditioned sludges. The bound water content of the raw sludge was 2.51 g/g DS. The bound water content of conditioned sludge samples was lower than the values for the raw sludge. The result indicated that the bound water content was lowest for the Ca(ClO)₂/PFS/WS combination, followed by the Ca(ClO)₂/ FeCl₃/WS, Ca(ClO)₂/PFS, and Ca(ClO)₂/FeCl₃. The bound water content was highest with the Ca(ClO)₂ treatment. The bound water of sludge samples conditioned by the composite conditioner (Ca(ClO)₂/ ferric coagulant/WS) was lower than the samples conditioned with the other composite conditioners. These results were supported by the sludge dewatering performance, EPS concentrations, and rheological behavior. Moreover, the combined Ca(ClO)₂/ferric coagulant/WS treatment obtained a significantly higher removal rate of bound water (49.84%), when compared with Fenton's reagent/red mud [14], Fe (II)/ PDS/rice husk [32], and citric acid/Fe0/polydiallyldimethylammonium chloride [59].

Based on the results and analysis above, Fig. 10 shows the possible dewatering mechanism. The mechanism is divided into three major processes: (1) $Ca(ClO)_2$ oxidation; (2) ferric coagulant re-flocculation;

and (3) WS skeleton construction. The Ca(ClO)₂ oxidation process led to the oxidation of protein-like substances and polysaccharide-like materials in LB-EPS and TB-EPS (Figs. 2 and 3), dispersing the large flocs (Fig. 7). This significantly changed the rheological properties of sludge (Fig. 8) and released cellular materials and bound water (Fig. 9). Through the ferric coagulant re-flocculation process, the disrupted sludge flocs and small fragments re-flocculated due to the higher charge neutralization and bridging ability (Figs. 4 and 7). This led to the formation of abundant porous structure and dehydration channel (Fig. 6). The flowability became higher and viscosity became lower compared with the raw sludge (Fig. 8), further releasing the bound water (Fig. 9). The sludge flocs and small fragments were rearranged by the WS skeleton construction process (Figs. 5 and 7). The WS interleaved along the external surfaces of the flocs (Fig. 6), forming new channels to release the bound water (Fig. 9). This formed a rigid networked structure. This structure facilitated subsequent high-pressure filter treatment. Therefore, the sludge dewaterability improved significantly with the combined Ca(ClO)₂/ferric coagulant/WS treatment.

3.5. Feasibility assessment of controllable pressure filtration

To obtain more reliable results that better reflect industrial conditions, the experiments introduced a novel controllable pressure filtration to explore sludge filtration efficiency. In addition, experiments were conducted at optimal conditions based on the results above, to compare sludge filtration efficiency. Fig. 11a–f show the sludge water removal rates, with variations across different sludge samples at different pressure filtration times at three pressure levels (2 MPa, 4 MPa and 6 MPa). There was a sharp increase in the filtration efficiency at the initial stage, followed by a gradual increase at a later stage before reaching a plateau.

Table 7 shows that as the pressure increased, the MCSC decreased. Fig. 11a and b and Table 7 show that $Ca(ClO)_2$ oxidation treatment achieved a higher sludge dewatering efficiency than achieved with raw sludge. The results indicate that when the filtration pressure was 6 MPa, the MCSC decreased from 87.40 wt% (raw sludge) to 84.24 wt% (with $Ca(ClO)_2$ oxidation). This indicated that $Ca(ClO)_2$ oxidation treatment improved sludge compressibility and increased permeability. This may be explained by EPS dissolution and flocs separation during $Ca(ClO)_2$ oxidation. Fig. 11c and d and Table 7 show that the MCSC decreased by 54.85 wt% ($Ca(ClO)_2/FeCl_3$) and 52.39 wt% ($Ca(ClO)_2/PFS$), respectively, at a 6 Mpa filtrate pressure. This result demonstrates that the Ca ($ClO)_2$ oxidation and ferric coagulant re-flocculation was a highly efficient method to achieve sludge deep dewatering (MCSC less than 60 wt%). This could account for the re-flocculation effect and the



Fig. 11. Sludge water removal profiles at different treatment using a novel controllable pressure filtration system: (a) raw sludge; (b) $Ca(ClO)_2$; (c) $Ca(ClO)_2 + FeCl_3$; (d) $Ca(ClO)_2 + PFS$; (e) $Ca(ClO)_2 + FeCl_3 + WS$; (f) $Ca(ClO)_2 + PFS + WS$.

formation of the more compact structure. Fig. 11e and f and Table 7 show that the MCSC was lower than 50 wt% when the sludge was treated using the combined $Ca(ClO)_2$ /ferric coagulant/WS. This verifies that the WS induced the formation of a rigid skeleton, further strengthening sludge compressibility and forming new channels to release bound water. Fig. S5 shows photos of the dewatered sludge cake. These results were supported by the filter press results (Fig. 11 and Table 7).

In summary, results demonstrated that the combined $Ca(ClO)_2/$ ferric coagulant/WS treatment achieved quick dewatering efficiency, good permeability, and excellent compression. Deep dewatering of the sludge was realized through the combined oxidation, re-flocculation, and skeleton construction. Table S2 compares the improvements in sludge dewaterability with different conditioners. In terms of MCSC reduction, the combined Ca(ClO)₂/PFS/WS conditioning performed better than other conditioning treatments [27,31,59]. Thus, the Ca $(ClO)_2$ /ferric coagulant/WS conditioning, combined with the pressure filtration system, was a highly efficient strategy to realize deep dewatering of the sludge.

Table S3 shows the filter COD, NH_4^+ , and TP levels under different treatments. The results showed that filtrate COD values increased after the combined Ca(ClO)₂/ferric coagulant/WS treatment. This may be explained by the release of cellular materials. Filtrate TP values decreased from 28.28 mg/L to 3.12 mg/L after the combined treatment. This may be because the WS, with large pore volume and surface area, can absorb the TP of sludge [34]. However, the combined Ca(ClO)₂/ferric coagulant/WS process had no significant effect on NH_4^+ concentration, as it was relatively resistant to chemical oxidation [38]. Compared with traditional Fenton's reagent/lime treatment, the filter liquor of the combined Ca(ClO)₂/ferric coagulant/WS treatment had

Table 7

The results of moisture content of sludge cake with combined Ca(ClO)₂/ferric coagulant/WS treatment using a novel controllable pressure filtration system.

| Treatment conditions | Filtrate pressure (Mpa) | Moisture content of sludge cake (wt%) |
|-----------------------------------|----------------------------|--|
| Raw sludge | 2 4 6 | 91.03 ± 0.28 89.85 ± 0.53 87.40 ± 0.26 |
| Ca(ClO) ₂ ^a | 2 4 6 | 87.78 ± 0.34 85.51 ± 0.60 84.24 ± 0.14 |
| $Ca(ClO)_2 + FeCl_3^{b}$ | 2 4 6 | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ |
| $Ca(ClO)_2 + PFS^c$ | 2 4 6 | $59.67 \pm 0.58 \\ 55.84 \pm 0.22 \\ 52.39 \pm 0.12$ |
| $Ca(ClO)_2 + FeCl_3 + WS^d$ | 2 4 6 | $56.73 \pm 0.15 \\ 53.09 \pm 0.43 \\ 49.65 \pm 0.18$ |
| $Ca(ClO)_2 + PFS + WS$ | 2 4 6 | $\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$ |

Note:

 a The dosage of Ca(ClO)_2 was 10 kg/ton DS, The dosage of H_2SO_4 was 16.4 kg/ton DS;

^b The dosage of FeCl₃ was 60 kg/ton DS;

^c The dosage of PFS was 100 kg/ton DS;

^d The dosage of WS was 600 kg/ton DS.

less of an impact on the environment. In the Lijiao Municipal WWTP, the standard for influent wastewater is 250-300 mg/L COD, 25-40 mg/L L NH⁴₄, and 1-5 mg/L TP. The filtrate quality of the combination treatment meets the standard of influent wastewater, allowing it to be recycled in the WWTP. This suggests that the combined condition could solve the problem of excessive filtrate residue.

3.6. Economic analyses

Table 8 summarizes the preliminary cost estimate for the five composite conditioners. The optimal doses of the combined treatments were based on Section 3.1-3.3. The Fenton's reagent/lime doses were from Dai et al. [10]. Energy and transport costs were determined using information gathered from the local market. The chemical agent costs were collected from http://www.alibaba.com/. The WS cost was determined by the local market. The approximate total cost of the composite conditioners and the associated moisture content of the dewatered sludge cake were as follows: USD \$44.3/ton DS for 54.85 wt% (Ca (ClO)₂/FeCl₃); USD \$60.4/ton DS for 52.39 wt% (Ca(ClO)₂/PFS); USD \$66.9/ton DS for 49.65 wt% (Ca(ClO)₂/FeCl₃/WS); USD \$82.9/ton DS for 48.31 wt% (Ca(ClO)₂/PFS/WS); and USD \$80.2/ton DS for 48.87 wt % (Fenton's reagent/lime). The result indicated that Ca(ClO)₂/FeCl₃/ WS, Ca(ClO)₂/PFS/WS, and Fenton's reagent/lime experienced similar dewatering performance, with a MCSC of less than 50 wt%. The total cost of the composite conditioner using Ca(ClO)₂/FeCl₃/WS was 16.58% less than that total cost associated with the commonly used Fenton's reagent/lime.

The Lijiao Municipal WWTP treats $400,000 \text{ m}^3/\text{d}$, with a daily sludge production of 60 ton DS/d. The total annual sludge production is 21,900 ton DS/y. The annual costs of the composite conditioner using Ca(ClO)₂/FeCl₃/WS and using Fenton's reagent/lime are approximately USD \$1,465,110/y and USD \$1,756,380/y, respectively. The dewatered sludge disposal fee is USD \$62.5/t. The sludge disposal cost of the conditioned sludge cakes are USD \$2,718,470/y (Ca(ClO)₂/FeCl₃/WS) and USD \$2,676,999/y (Fenton's reagent/lime). Therefore, the total

Table 8

Economic analysis of the combined Ca(ClO)₂/ferric coagulant/WS treatment and Fenton's reagent/lime conditioning processes for the sludge dewaterability improvement.

| Treatment conditions | Chemical agents | Unit price ^g (USD\$/ton) | Agents cost (USD \$/ton DS) | Energy cost ^h (USD\$/ton DS) | Transport cost (USD \$/ton DS) | Total cost (USD \$/ton DS) | Moisture content of sludge cake (wt%) |
|--|---|--|--------------------------------|--|-----------------------------------|-------------------------------|--|
| $Ca(ClO)_2 + FeCl_3$ | $H_2SO_4^{a}$ Ca(ClO) ₂ ^b FeCl ₂ ^c | 78.0 755.1 261 7 | 24.5 | 11.8 | 8.0 | 44.3 | 54.85 ± 0.22 |
| $Ca(ClO)_2 + PFS$ | H_2SO_4 Ca(ClO) ₂ PFS ^d | 78.0 755.1 317.2 | 40.6 | 11.8 | 8.0 | 60.4 | 52.39 ± 0.12 |
| $Ca(ClO)_2 + FeCl_3 + WS$ | H_2SO_4 Ca(ClO) ₂ FeCl ₃ WS ^e | 78.0 755.1 261.7 31.7 | 43.6 | 15.3 | 8.0 | 66.9 | 49.65 ± 0.18 |
| $Ca(ClO)_2 + PFS + WS$ | H ₂ SO ₄ Ca(ClO) ₂ PFS WS | 78.0 755.1 317.2 31.7 | 59.6 | 15.3 | 8.0 | 82.9 | 48.31 ± 0.15 |
| Fenton's reagent and lime ^f | H ₂ SO ₄ FeSO ₄ ·7H ₂ O H ₂ O ₂ Lime | 78.0 64.7 161.4 80.7 | 56.9 | 15.3 | 8.0 | 80.2 | 48.87 ± 0.28 |

Note:

^a The dosage of H_2SO_4 was 16.4 kg/ton DS.

^b The dosage of Ca(ClO)₂ was 10 kg/ton DS.

^c The dosage of FeCl₃ was 60 kg/ton DS.

^d The dosage of PFS was 100 kg/ton DS.

^e The dosage of WS was 600 kg/ton DS.

 $^{\rm f}$ The dosage of H_2SO_4, FeSO_4'7H_2O, H_2O_2, and lime was 16.4, 366.2, 141.7, and 112.5 kg/ton DS, respectively [10].

^g Chemical agents was industrial grade, http://www.alibaba.com/; The WS cost was determined by the local market.

^h Energy cost was calculated based on energy consumption (kwh) multiplying USD\$ 0.23/kwh.

operational cost of sludge treatment and disposal are USD 4,183,581/ y (Ca(ClO)₂/FeCl₃/WS) and USD 4,433,380/y (Fenton's reagent/lime).

The cost of traditional polyacrylamides (PAM) can be as high as USD \$65.0/ton DS for WTTPs in China. The water content in the dewatered sludge conditioned with PAM is approximately 80 wt% [14]. Therefore, total sludge treatment and disposal costs are approximately USD \$8,700,870/y (PAM). Using Ca(ClO)₂/FeCl₃/WS as the composite conditioner saves approximately 51.92% per year compared with using the traditional treatment, and saves 5.63% per year compared to using Fenton's reagent/lime treatment. Thus, the Ca(ClO)₂/FeCl₃/WS, combined with the pressure filtration system, is a rapid and practical sludge treatment technique.

3.7. Environmental implication

After our deep dewatering process $(Ca(ClO)_2/FeCl_3/WS \text{ combined})$ with the pressure filtration system), the moisture content of dewatered sludge was below 50%, meeting landfill requirements in China (GB/T 23485-2009). In this study, a landfill is considered a potential disposal route for study products.

In many countries, incineration is an effective disposal approach, because of the reduction in the quantity and toxicity of sludge and the ability to recover energy [60]. Table S4 shows the ultimate analysis, proximate analysis, and heating values of the different sludge. It was noted that the contents of volatile matters and fixed carbon in the Ca (ClO)₂/FeCl₃/WS samples were higher than that in the Fenton's reagent and lime samples. The result shows that the lower heating value of raw sludge was 12.40 MJ/kg. The lower heating value of sludge treated by combined Ca(ClO)₂/FeCl₃/WS increased to 14.08 MJ/kg. This indicated that the treated sludge has good combustion characteristics. The addition of WS biomass may significantly promote the mixed fuel combustion characteristics. WS is a skeleton builder that forms the rigid skeleton and further increases the deep dewatering of the sludge. The lower heating value of sludge conditioned by the combined Ca(ClO)₂/ FeCl₃/WS treatment increased by 1.97 times, compared with the value achieved with Fenton's reagent/lime. This indicated that after the combined treatment, the dewatered cake may be more suitable for disposal through incineration, compared with that of Fenton's reagent/ lime.

In conclusion, the combined Ca(ClO)₂/FeCl₃/WS treatment provides a feasible and economic sludge treatment process, with high dewatering performance and low operational cost. It is an appropriate technique to facilitate sludge disposal through landfilling and incineration.

4. Conclusions

This study is the first attempt to apply combined Ca(ClO)₂/ferric coagulant/WS conditioning to deeply dewater sludge. Using a series of single-factor experiments, the study identified the optimal conditioning combinations. The results indicated that a combination treatment significantly improved sludge dewaterability (SRF decreased by approximately 90.84%). Using a novel controllable pressure filtration system, the combined treatment achieved deep sludge dewatering (MCSC < 50 wt%). An investigation of the mechanism driving the dewatering indicated that the efficiency of the sludge dewatering was mainly due to the synergistic effect of Ca(ClO)₂ oxidation/ferric coagulant re-flocculation/WS skeleton construction. Ca(ClO)₂ oxidation effectively broke the sludge flocs and EPS structure, resulting in the release of bound water. Ferric coagulant re-flocculated the sludge flocs and formed the porous structure through electrostatic neutralization. Adding the WS formed a rigid networked structure. This significantly improved sludge dewaterability, as demonstrated by the higher flowability and lower viscosity. Based on the economic analysis, the total operational cost of the combination treatment could save USD \$249,799 per year, compared with traditional Fenton's reagent/lime

treatment. Moreover, using the composite conditioner presents advantages in sludge dewatering and subsequent disposal. Finally, the Ca (ClO)₂/FeCl₃/WS, combined with a pressure filtration system, is an economical, promising, and environmentally friendly sludge treatment technique.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2018.10.143.

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