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# Key factor on improving secondary advanced dewatering performance of municipal dewatered sludge: selective oxidative decomposition of polysaccharides

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## ABSTRACT

Advanced dewatering technologies with moisture content from nearly 80% to below 60% have attracted widespread attention in the field of municipal dewatered sludge disposal. The usage of the correct types of oxidants and the degradation of key component on the effect of secondary advanced dewatering performance is a rising focus. In this study, three types of typical oxidants (Fenton's reagent, $H_2O_2$, and $KMnO_4$) were used to pre-treat dewatered sludge directly, then advanced dewatering performance, conversion rate of bio-bound water and decomposition trend of various organic biomass were analysed. Results showed that final moisture content of Fenton's reagent group reduced to below 50% with exposure to the compression of 1,000 kPa for 30 min. Different oxidants that were characterized by selective oxidizability and, compared with other oxidants, mainly decomposed proteins, lipids and humic substances, the key component of polysaccharides, which may combine with the most water were primarily decomposed by Fenton's reagent. This promoted the conversion from bio-bound water to free water and advanced dewatering performance significantly. From a morphological perspective, the ratio of dissolved polysaccharides from three layers showed Pellets: tightly bound EPS (T-EPS): loosely bound EPS (L-EPS) = 52.28%~66.56% : 8.37%~12.75% : 23.15%~39.08%, and due to the cell-breaking capacity, Fenton's reagent could mainly promote the release of intracellular polysaccharides-bound water.


*Keywords***:** advanced dewatering; selective oxidative decomposition; bio-bound water;

polysaccharides

## 1. Introduction

With the growing quantity and processing capacity of wastewater treatment plants (WWTPs), there remains an increase in dewatered sludge emissions which will pose a huge threat to environment and public health. In the next several years, the production of dewatered sludge will increase at a rate of 16% and, by 2020, will reach 60 million tons annually in frequent media reports. Most WWTPs in China, which generally produce dewatered sludge with a moisture content of nearly 80% are facing a great challenge of large amount of sludge need to be disposed urgently. Additionally, there are certain number of sludge pits, which contains huge amount of dewatered sludge in many cities. At the same time, in order to ensure the final disposal of dewatered sludge properly, government has established several relevant standards and moisture content is restricted to be 50%–65% for the disposals of individual incineration, mixed landfilling, agricultural and forest land improvement. In addition, there is a non-negligible volume reduction if the moisture content falls below 60% (Zhu et al., 2003). However, advanced dewatering is an expensive and difficult process due to the strong water binding capacity (Mustranta and Viikari, 1993), mechanical dewatering is often selected due to its relatively lower energy and charge (Mahmoud et al., 2010). Therefore, the ability to perform mechanical secondary advanced dewatering with a moisture content from nearly 80% to below 60% is now a focus in the field of dewatered sludge disposal.

The whole dewatering process (from approximately 98% to below 60%) could

be divided into two completely different sub-process: filtration stage (nearly 98% to nearly 80%) and compression stage (nearly 80% to below 60%). So far, filtration stage has been studied widely and It is well known that filter dewatering performance can be evaluated by two parameters: Specific Filtration Resistance (SRF) or Capillary Suction Time (CST), and the correspondence between the parameters and actual filter dewatering performance is very exact (Neyens et al., 2003). First, from the perspective of microstructure which influence SRF, Barber and Veenstra (1986) found SRF depended little on the amount of bound water, whereas significantly affected by particle distribution (i.e., smaller particles pose tinier channels to dewatering) and the smaller the floc size, the harder it was to dewater through comparing 28 different sources of excess sludge (raw moisture content ranging from 97.8% to 99.8%); Karr and Keinath (1978) classified anaerobic sludge, activated sludge, and excess sludge into four floc sizes with a sieving method, then mixed flocs of different sizes to study the effect of floc size on dewatering performance, and found that even if the types of sludge were different, the SRF with similar floc size distribution were almost similar. When the number of fine particles (< 100 μm) increased, the sludge cake became clogged during filtration, which, in turn, increased the SRF value; Xiao (2018) also found the increased amounts of small size particles caused by EPS degradation and sludge disintegration may clog the porous structure during filtration; Second, in terms of key component which influence SRF, You (2017) found that the increased proteins would corrected significantly with SRF. Higgins and Novak (1997) used divalent cations (e.g., $Ca^{2+}$ and $Mg^{2+}$) to culture activated sludge and found that the SRF value

decreased after increasing the bound proteins in the flocs, but did not significantly changed with the bound saccharides. Therefore, the key factor and component affecting the filtration dewatering performance is mainly microstructure and proteins respectively.

To obtain the final moisture content of approximately 60%, board-frame-pressure filter processing technology after the pre-treatment with flocculants and abundant lime is used commonly in practice. Besides, similar studies have analysed numerous other lime-like conditioning materials, such as cement kiln dust, fly ash, coal powder, lignite, gypsum, magnesia powder, magnesite powder, red mud, cement coke, bagasse, and waste incineration slag (Benitez et al., 1994; Thapa et al., 2009; Chen et al., 2010; Liu et al., 2012; Liu et al., 2013; Zhang et al., 2013). However, the decreasing final moisture content is mainly promoted by the addition of dry matters which would increase final volume of cake, rather than the discharge of bound water, so it could only be considered as a type of “quasi-advanced dewatering.”

To reach the “true-advanced dewatering”, methods of removing bound water by chemical oxidation is gradually becoming the research direction. Due to EPS represent up to 80% of the mass of activated sludge (Tony et al., 2008) and a considerable amount of water trapped either inside these sludge microorganisms or within the flocs (Erdincler and Vesilind, 2000), most of the water in dewatered sludge is bio-bound water. Recently, many studies have started to attempt to convert bio-bound water to free water in activated or excess sludge (moisture content of approximately 98%). Kato (1971) found that when protein was hydrolyse by protease,

SRF increased 10.7-fold and dewatering performance significantly decreased for producing smaller floc particles; Chen (2016) found that protein oxidation via $CaO_2$ peroxidation associated with chemical re-flocculation improved filtration dewatering performance but a high dosage resulted in the dissolution of a large quantity of protein-like substances, which was detrimental to filtration.

Overall, pre-treatment by flocculants and lime could not promote the removal of bound water while chemical oxidation of organic biomass would cause blockage at filtration stage (Liu et al., 2013), So, secondary advanced dewatering technology with chemical oxidation pre-treatment on the basis of dewatered sludge will overcome both the two shortcomings at the same time. With respect to the plate-frame-pressure filter operation principle, if bio-bound water could be converted to free water by oxidation, sludge fluidity will significantly increase and, after plunger pump feeding, the final moisture content may realize a reduction from 80% to below 60% through the pressure process directly. There are significant distinctions between filtration process (approximately 98% to nearly 80%) and compression process (nearly 80% to below 60%), which the separation process has entered the water extrusion process inside solid-like flocs instead of mud. O'Kelly (2005) classified the compression process as a soft soil consolidation process, which can only be evaluated with the theory of consolidation in 'Soil Mechanics' rather than the SRF or CST value. Besides, from the perspective of material composition, the complex and diverse organic biomass in dewatered sludge are still comprised of proteins, polysaccharides, humic substances, lipids and nucleic acid (Mowla et al., 2013); From the perspective of micro space,

EPS in sludge flocs are proposed to exhibit a dynamic double-layer-like structure, composed of loosely bound EPS (L-EPS) and tightly bound EPS (T-EPS) (Yu et al., 2007). Therefore, there are several uncertainties need to be confirmed further: (1) How to evaluate the advanced dewatering performance of dewatered sludge properly? (2) Could chemical oxidation promote the advanced dewatering performance through the conversion of bio-bound water to free water? (3) which is the key component control the advanced dewatering performance and what is the morphological properties? To answer to these questions, three types of conventional oxidants were selected to pre-oxidize the dewatered sludge directly for the first time and advanced dewatering performance was evaluated via consolidation dewatering experiments. Then, the key component was found through different kinds of analysis of components in free water. Finally, the mechanism of key component on advanced dewatering was discussed through the relationships in the changes of organic biomass, water form, and advanced dewatering performance.

## 2. Materials and methods

### 2.1. Raw dewatered sludge and reagents

Raw dewatered sludge was obtained from dewatering workshop of the Jiangning Development Zone WWTP in Nanjing city. The treatment technologies of sewage and excess sludge are “double-channel oxidation ditch” and belt filter press after polyacrylamide flocculation respectively. The sample was stored at 4ºC after obtaining and fibres, plastics, leaves, and hairs were removed. Table 1 lists the basic

characteristics of the raw dewatered sludge.

Table 1. Basic characteristics of the raw dewatered sludge (%).

| Moisture content | Free water | Bound water | Organic content | Status/colour |
|---|---|---|---|---|
| 80.30 | 46.34 | 33.96 | 41.59 | Solid-like/dark brown |

"Determination method for municipal sludge in wastewater treatment plant (CJ/T221-2005, in Chinese)" was used to determine the moisture content and organic content of the dewatered sludge. All reagents were analytical grade (AR), including Fenton's reagent (OH·, $n_{H_2O_2}/n_{7H_2O\cdot FeSO_4}$=2/1, according to the conclusion of our previous experiments, this ratio is the most suitable formula), $H_2O_2$ (30%), and $KMnO_4$. Table 2 lists the basic characteristics of the three oxidants.

Table 2. Basic characteristics of the three oxidants.

| Oxidant | Fenton's reagent | $H_2O_2$ | $KMnO_4$ |
|---|---|---|---|
| **Oxidation Reduction Potential (ORP)/V** | 2.85 | 1.78 | 1.68 |
| **Status** | Solution + powder | solution | powder |

2.2. Pre-oxidation experiment of dewatered sludge

Dewatered sludge (100 g) was well mixed with the identical amount of Fenton's reagent, $H_2O_2$, and $KMnO_4$, then reacted for 30 min with being kneaded continuously (According to the results of previous research, the oxidation reaction will finish in 30

166 min) at a reaction temperature of 25±1ºC, with the same dosages of 1.07, 2.15, 3.25,
167 4.30, and 5.37 mmol/gDs (gram dry substance) and the clear reagent ratio of Fenton's
168 reagent was listed in Table 3.

169 Table 3. Reagent ratio of Fenton's reagent.

| **Fenton's reagent (mmol/gDs)** | 1.07 | 2.15 | 3.25 | 4.30 | 5.37 |
|---|---|---|---|---|---|
| **$FeSO_4 \cdot 7H_2O$ (g/gDs)** | 0.15 | 0.30 | 0.45 | 0.60 | 0.75 |
| **$H_2O_2$(30%) (mL/gDs)** | 0.11 | 0.22 | 0.33 | 0.44 | 0.55 |

170

171 The oxidants were added stepwise described by Xu (2016) and raw dewatered
172 sludge without pre-oxidation was used as reference.

173

174 2.3. Evaluation of advanced dewatering performance

175 A self-made advanced dewatering test device (Fig. 1), based on the consolidation
176 tester introduced in "Soil Mechanics" (O'Kelly, 2008), was used to determine the
177 changes of moisture content range from nearly 80% to below 60%. This device has an
178 area of 30 $cm^2$ and a height of 3 cm. There is a filter paper and a permeable stone that
179 allowed for drainage at the bottom and the increasing of pressure in the upper parts
180 via a pressurizing piston. Samples were compacted after they were placed into the
181 chamber and a graded pressurization program was set as 0, 12.5, 25, 50, 100, 200, 400,
182 800, and 1,000 kPa. The cumulative time of increasing pressure was 10 min, then the
183 maximum pressure of 1,000 kPa was maintained for 30 min. After the experiment,
184 final moisture content of cake and amount of dewatering were measured. Advanced

dewatering performance was evaluated by both final moisture content and dewatering rate (η) through equation (1):

$$\eta = (m_F - m_L) / m \quad (1)$$

where $m_F$ is the amount of filtrate;

$m_L$ is the amount of the liquid reagent added ($H_2O_2$, the addition of $H_2O_2$ could hardly affect the final dry mass and it is assumed that $H_2O_2$ was added as foreign water, but not belongs to the raw sludge);

and $m$ is the quality of water in raw dewatered sludge (80.30g).

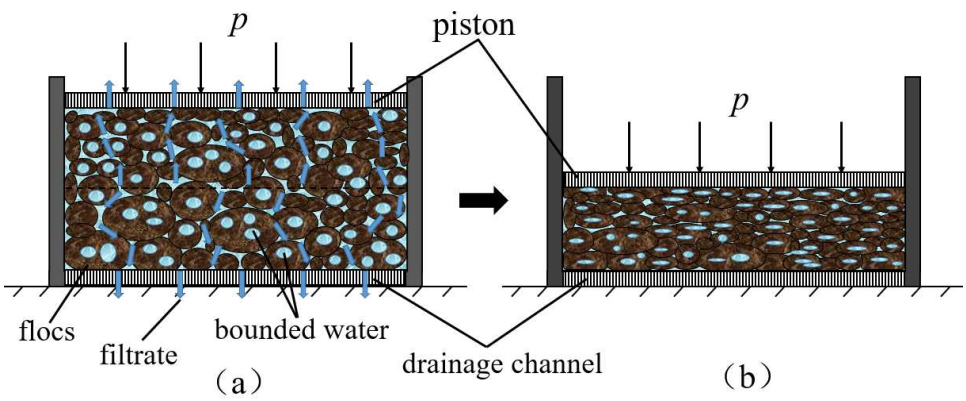



Fig. 1. Advanced dewatering test device: (a) Raw dewatered sludge and (b) Final advanced dewatered sludge cake.

## 2.4. Determination of moisture form

On the compression stage, moisture form may be the key factors affecting the advanced dewatering performance. According to Foth's study (1978), bound potential (pF value) could represent the combination strength between dry matters and water, and high-speed moisture centrifugation method was used to determine the moisture form of dewatered sludge for its better reflection to the mechanical dehydration

203 performance. Lebedev (1936) suggested that when the pF value less than 3.8, the
204 water is free water, whereas larger than 3.8, the water is bound water. In this study,
205 conversion of moisture form in dewatered sludge was measured by a CR2GIII
206 high-speed refrigerated centrifuge (Hitachi), and the experimental temperature was set
207 to 25ºC. Then the centrifuged water was simultaneously collected and filtered through
208 a 0.04 μm glass fibre filter as a free water sample for subsequent analysis.
209
210 2.5. Determination of decomposition degree of organic biomass
211 Dewatered sludge is divided into cake and free water by the high-speed
212 centrifugation method. Changes between the amount of Total Organic Carbon (TOC)
213 in cake (dry matters after freeze-drying treatment) and Dissolved Organic Carbon
214 (DOC) in free water could reflect the decomposition degree of organic biomass after
215 pre-oxidization (Zhang et al., 2005; Torrades et al., 2003). TOC was measured by
216 TOC-$V_{CPN}$ (Shimadzu) with Solid Sample Module and DOC with OTC-1 Module.
217
218 2.6. Determination of organic biomass type in free water
219 2.6.1. Molecular weight (MW) of the organic biomass in free water was
220 measured via high-performance size exclusion chromatography after purification by
221 dialysis (membrane with a cutoff-molecular weight of 500 Da) to remove the the
222 influence of Fe and Mn. The gel chromatograph (LC-20A, Shimadzu) consisted of an
223 SPD-20AV differential detector and a Shim-pack VP-ODS (150 × 4.6 mm; i.d. 5 μm)
224 column. The mobile phase was buffered with 5 mM phosphate and 0.01 M NaCl was

filtered through a 0.22-μm filter. Approximately 20 μL of liquid was injected at a flow rate of 1.0 mL/min and polyethylene glycol standards were used to obtain the apparent molecular weight.

2.6.2. Functional groups of the organic biomass in free water was measured by FTIR (BRUKER-ALPHA) spectrometer after freeze-drying treatment under vacuum at -60℃ for 72h. All the spectra were in a scanning range from 1000 to 4000 $cm^{-1}$.

2.6.3. Dissolved fluorescent organic biomass were measured by Three-dimensional excitation-emission fluorescent-parallel factor analysis method. A Hitachi F-7000 FL fluorescence spectrometer, with an excitation range of 200–500 nm and an emission range of 250–550 nm, was used to determine the types of organic biomass. Spectra were recorded at a scan rate of 2,400 nm/min while using excitation and emission slit bandwidths of 5.0 and 2.5 nm, respectively. After high-speed moisture centrifugation (see section 2.4), free water samples were diluted 10-fold before analysis. In addition, Due to the interference and overlap between the spectra of organic biomass, the identification of fluorescence peaks is often biased. So, parallel factor analysis (Xu et al., 2013) was used to decompose complex fluorescent peaks and distinguish the independent fluorescent substances.

2.6.4. The contents of aliphatic acid and polysaccharides in free water were measured via NaOH titration method after distillation provided by “Determination method for municipal sludge in wastewater treatment plant (CJ/T221-2005, in Chinese)” and Sulfate-anthrone method (Raunkjær et al., 1994) separately. Each

246 treatment sample was analysed in triplicate and the relative deviations for all analyses
247 were always less than 5%.
248
249 2.7. EPS extraction and analysis after the optimal pre-oxidation
250 SEPS, L-EPS, T-EPS, and Pellet in dewatered sludge were extracted based on the
251 extraction methods reported by Niu (2013): 5 g dewatered sludge after pre-oxidation
252 was resuspended in a 50 mL tube with distilled water, centrifuged at 3,000 g for 10
253 min, and the supernatant was then collected as SEPS; After SEPS removal, the
254 dewatered sludge in the tube was then resuspended into 15 mL of NaCl (0.05%),
255 sonicated for 2 min at 20 kHz, shaken horizontally for 10 min at a speed of 150
256 rpm/min, sonicated for another 2 min and diluted to 50mL. The liquor was
257 centrifuged at 8,000 g for 10 min, and the supernatant was then collected as L-EPS.
258 The residual sludge left in the centrifuge tube was resuspended in the NaCl solution,
259 sonicated for 3 min, heated for 30 min at 60ºC, diluted to 50mL, and then centrifuged
260 for at 12,000 g for 20 min, and the supernatant was T-EPS. Finally, sediments were
261 diluted with a NaCl solution to the original volume and mixed, which was defined as
262 the Pellet.
263

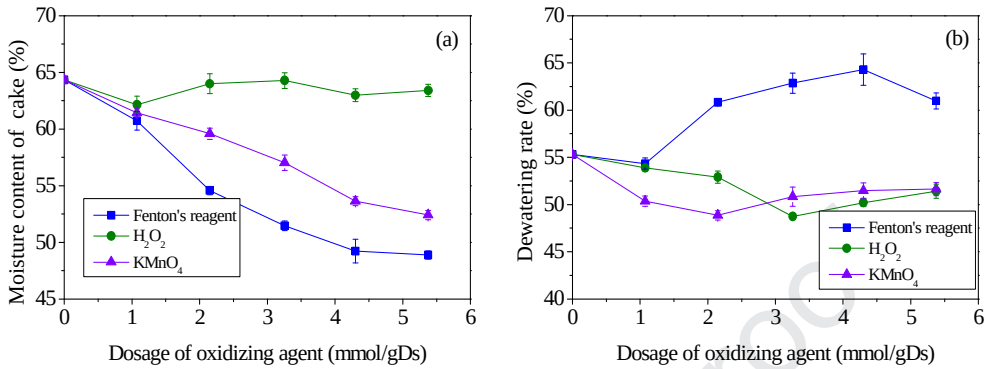
264 ## 3. Results and discussion

265 3.1. Advanced dewatering performance
266 Final moisture content was measured after pre-oxidization, following advanced
267 dewatering experiment (1,000 kPa, 30 min), as shown in Fig. 2(a). The final moisture

content of raw dewatered sludge was only reduced to 64.33% when exposed to a pressure of 1,000 kPa for 30 min. Obviously, when the dosage of Fenton's reagent was 4.30 mmol/gDs, the final moisture content was reduced to less than 50%. However, final moisture content is extremely susceptible to the effects of additional solid substances, and could not reflect the actual amount of dewatering completely. Combined with the dewatering rate (η) in Fig. 2(b), the significant emission of water in Fenton's reagent groups could be seen. When the dosage of Fenton's reagent was more than 4.30 mmol/gDs, the final moisture content ceased to decrease with a continued decline of dewatering rate (η) ,so the decrease of moisture content is caused by the addition of dry matters (The changes of final dry mass could be seen from Fig S1); There was nearly no significant change of the final moisture content and dewatering rate (η) after pre-oxidization with $H_2O_2$, which could not promote advanced dewatering performance, even prevented the discharge of water slightly at some point; Although the final moisture content of $KMnO_4$ groups was reduced to a minimum of 53%, no more water was removed based on the dewatering rate (η). Therefore, moisture content reduction caused by $KMnO_4$ is mainly due to the addition of dry matter to adjust the final moisture content, and could not be considered as "true-advanced dewatering". Overall, the decrease of final moisture content in Fenton groups depended on both the dry matters addition and the emission of more water in raw dewatered sludge. Final moisture content and dewatering rate of $H_2O_2$ groups did not change significantly, so $H_2O_2$ could be considered as free water-like liquid

289 approximately. The decrease of final moisture content in $KMnO_4$ groups which did
290 not drain more water depended on the dry solid addition only.

291




292

293 Fig. 2. Advanced dewatering performance: (a) Final moisture content and (b) Advanced
294 dewatering rate (η).

295

296 3.2. Moisture form conversion

297 The amount of bound water converted to free water is measured through the
298 changes of bound water between the dewatered sludge without pre-oxidant and after
299 pre-oxidant. The ratio of the amount of bound water converted to free water to the
300 amount of original bound water is defined as bound water conversion rate (i.e., this
301 value is positive when conversion occurs from bound to free water and negative when
302 conversion is from free to bound water; Fig. 3). The decomposition of organic
303 biomass would result in the conversion of moisture form necessarily. The bound
304 water converted to free water significantly after pre-oxidization with Fenton's reagent,
305 which was able to obtain a maximum conversion rate of 28%. How, when the dosage
306 was greater than 4.30 mmol/gDs, the generation of organic debris with larger specific

surface area could combine with free water to form bound water and the conversion would be impeded; Besides, there was no clear effect on the changes of moisture form in $H_2O_2$ groups; On the contrary, the amount of bound water increased 6.68% through the conversion from free water to bound water in $KMnO_4$ groups.

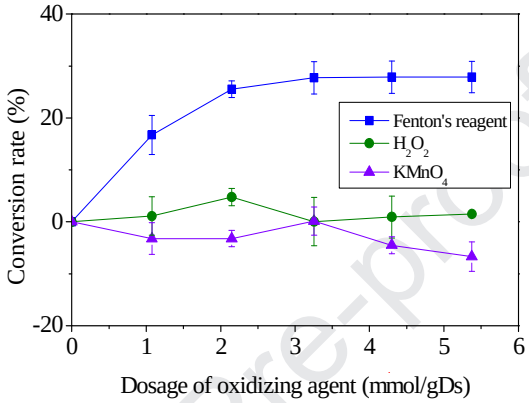



Fig. 3. Effects of three oxidants on the conversion of bound water.

Good correlation between conversion of bound water and discharge of water was found through the material balance calculation of Fenton's reagent groups (Fig. 4). It could be seen that, the water measured by dehydration rate is mainly free water instead of bound water which lack of fluidity and could not be discharged yet under the high compression. With the increasing amount of free water, more water accounting 83.90-95.81% of it would be discharged gradually. Compared with the conference sample and two other groups, Fenton's reagent has the unique and significant effect on advanced dewatering and this effect mainly depends on its capacity to promote the conversion of bound water (mainly combined with organic biomass) to free water, which is more easily discharged during the compression. This

is the direct reason of the promotion of advanced dewatering performance significantly by Fenton's reagent, and it is an efficient method to practical application. Since Fe would remain in the cake, the amount of dry matters increased with the addition of $FeSO_4 \cdot 7H_2O$. When the dosage was 3.25 mmol/gDs, the amount of dry matters increased 29.95%.

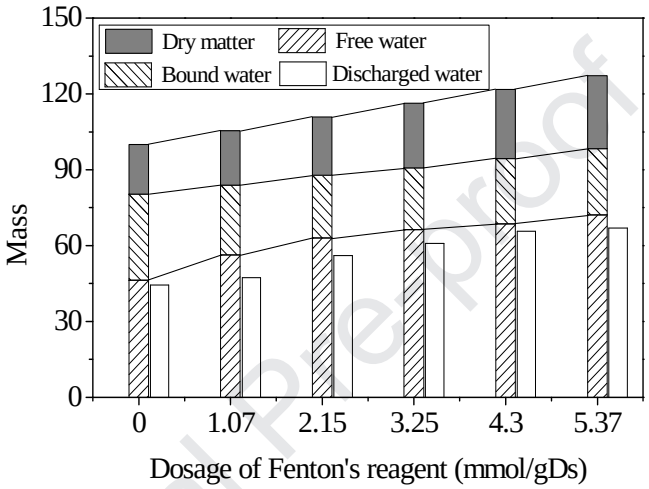



Fig. 4. Material balance of Fenton's reagent groups.

### 3.3. Decomposition degree of organic biomass

The content of residual organic biomass in the cake, from which the free water has been removed, is expressed by the TOC, and the results are shown in Fig. 5(a). Total organic biomass did not significantly decrease after pre-oxidization with $H_2O_2$, whereas there was a maximum reduction of 30.92% (TOC from 17.66% to 12.20%) after pre-oxidization with $KMnO_4$. The organic biomass content in free water is expressed by the DOC, and the results are shown in Fig. 5(b). The DOC of $KMnO_4$ groups was $10^4$ mg/L while the Fenton's reagent only contained approximately 1/10 of this amount and the DOC after treatment with $H_2O_2$, was approximately one order of magnitude smaller again, Neyens and Baeyens (2003) also found the insufficient oxidation capacity of $H_2O_2$ in excess sludge and Decomposition degree of organic

biomass showed $KMnO_4$＞Fenton's reagent＞$H_2O_2$. As the insoluble organic biomass in the dry matters were gradually decomposed and produced soluble organics which would flow into free water, DOC increased with the adding of oxidants. Besides, since the oxidation ability of Fenton's reagent which would generate kinds of free radical such as •OH and $HO_2$• is much stronger than $H_2O_2$, (Zhang et al., 2005; Torrades et al., 2003), the DOC of Fenton's reagent groups is much higher than $H_2O_2$.

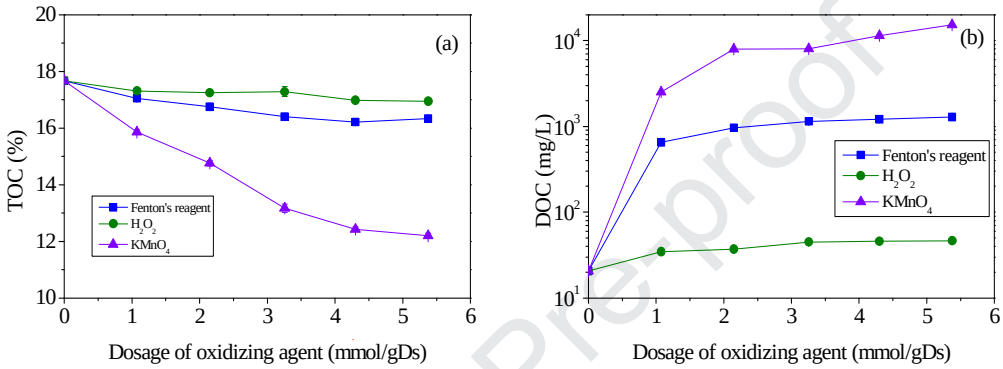



Fig. 5. Effects of the three oxidants on total organics: (a) TOC and (b) DOC.

From the comparison of the three groups, the most total organic biomass was removed (TOC→DOC) in $KMnO_4$ groups, but there was not the most conversion of bound water; $H_2O_2$ groups removed the least total organic biomass, which had nearly no effects on the conversion of bound water; Although not the most of total organic biomass were removed in Fenton's reagent groups, it did convert the most bound water to free water. It could be concluded that Pre-oxidative decomposition of the total organic biomass does not inevitably lead to the conversion of bound water to free water. This is possibly related to the combination between bound water and one type of key component rather than total organic biomass.

Ling (1965) suggested that bound water mainly existed in a hydration hard shell or multi-layer polarization form, and with the presence of hydrogen bonds that had a strong bond potential. Therefore, the bio-bound water is difficult to discharge even at high dewatering pressure and, only would be released through its degradation. Besides, he reported that organic biomass in dewatered sludge were mainly consisted of proteins, polysaccharides, humic substances and lipids, where 70%–80% is both proteins and polysaccharides, 20% is humic substances, so the key component in four above which combined with the majority of bound water may exist and needed to be confirmed further in this study.

### 3.4. MW distribution of organic biomass decomposed into free water

To confirm the compositions after pre-oxidation, the MW of organic biomass in free water was determined via high-performance gel permeation chromatography (the molecular weight chromatogram is in Figure S2). It could be seen from Fig.6 that Fenton's reagent groups mostly concentrated at 1650 Da peak, $H_2O_2$ groups only had a weak peak at 1650 Da, and $KMnO_4$ groups showed four distinct peaks at 640, 950, 1650 and 2030 Da respectively. Kiss (2003) suggested that, peaks at 640, 950, 1650 and 2030 Da referred to different substances. To this step, it was certain that different components in dewatered sludge were oxidized by the three oxidants and only the component produced 1650 Da was the key product during the pre-oxidation in Fenton's reagent group. The more Fenton's reagent added, the more substances of 1650 Da produced, but bound water would not convert to free water when the dosage

larger than 4.30 mmol/gDs. Besides, for the substance of 2030 Da containing more organic carbon element than 1650 Da, the DOC value of KMnO4 groups was large than Fenton's reagent groups.

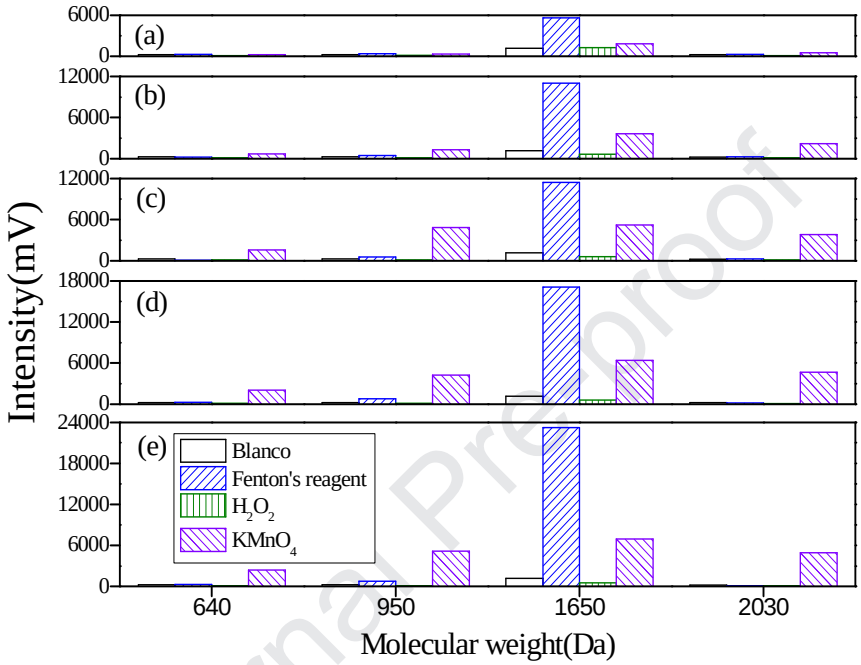



Fig. 6. Molecular weight (MW) distribution of organic biomass in free water: (a) 1.07, (b) 2.15, (c) 3.25, (d) 4.30, and (e) 5.37 mmol/gDs.

## 3.5. FTIR analysis

To further ensure the component in free water, three groups of samples with the same dosage of 3.25 mmol/gDs were analysed via FTIR, and the results are shown in Fig. 7. There was no significant difference of the three peaks in the range 3310-3315 $cm^{-1}$, which mainly included the O-H stretching vibration absorption peak in organic biomass (Sheng et al., 2006; Chai et al., 2007; Pere et al., 1993). peaks at 1050 and 1600 $cm^{-1}$ in both Fenton's reagent and $H_2O_2$ samples were distinct and clear, which

mainly included absorption of polysaccharides and polysaccharides-like substance (Wang et al. 2018); However, $KMnO_4$ sample showed multi-peak characteristics, where the distinct absorption peaks of amino □ (1630 $cm^{-1}$)， amino Ⅱ (1550 $cm^{-1}$), amino Ⅲ (1380 $cm^{-1}$)， amino Ⅵ (537~606 $cm^{-1}$, out-of-plane C=O bending) (Kong et al., 2007) and humic substance (2930 $cm^{-1}$). In connection with the MW distributions, polysaccharides, proteins and humic substance exist in $KMnO_4$ sample together while most concentrated polysaccharides existed in Fenton's reagent sample probably.

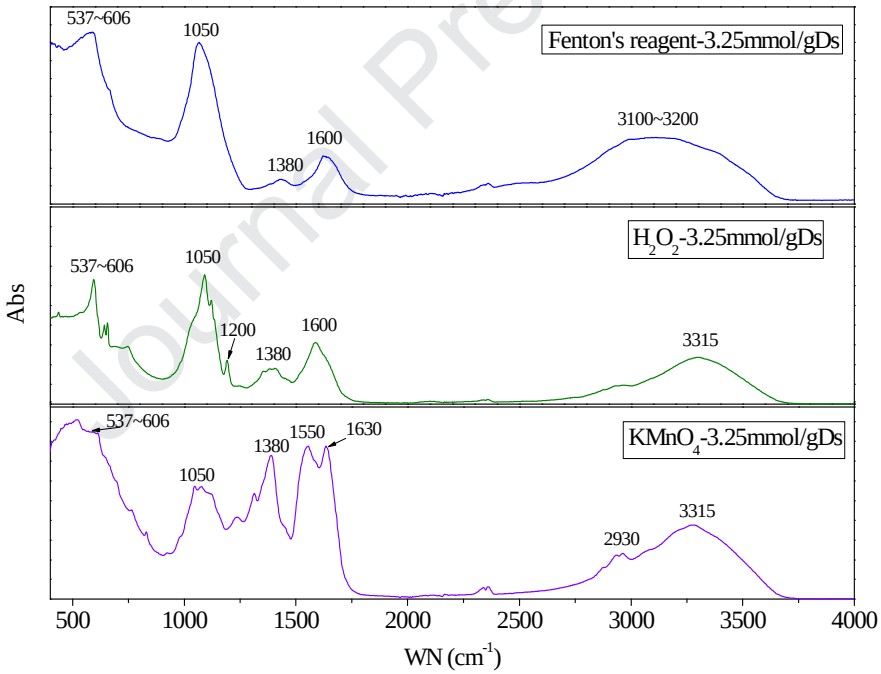


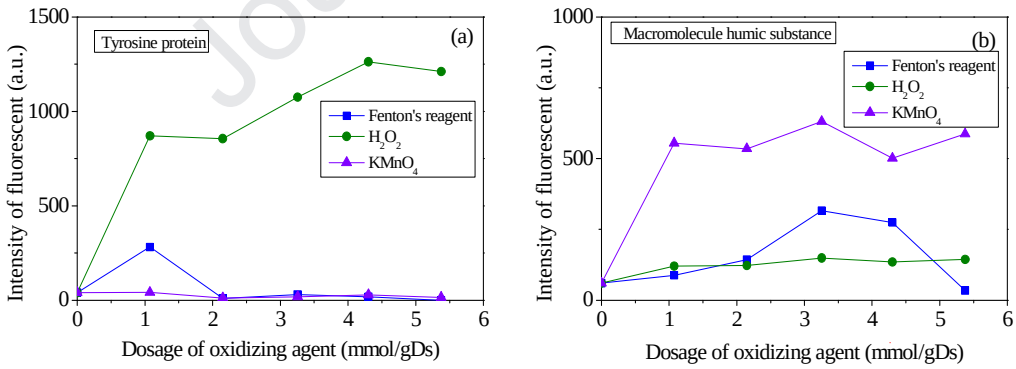

Fig. 7. Infrared spectrum of organic matter in free water.

## 3.6. Three-dimensional excitation-emission fluorescent-parallel factor analysis

The original fluorescence diagram of the response could be seen in Figure S3 and parallel factor method was used to separate the mixed samples into 3, 4 or 5

components. It could be seen that the error of between 4 and 3 components are larger while 5 components are more consistent with 4 components, so 4 components was chosen to obtain the standard components (in Fig S4 and S5), which included component 1 (a, two peaks, 225/325nm for the low excitation and 275/325nm for the high excitation region of tyrosine), component 2 (b, 325/400nm of macromolecular humic substances), component 3 (c, 370/450nm of humin acid) and component 4 (d, 240/440nm of fulvic acid). (Sheng and Yu, 2006; Dai et al., 2018).

According to the results (Fig.8) of semi-quantitative analysis between these components, there were very few tyrosine and other humic substances, except fulvic acid, in the Fenton's reagent groups; More humic substances appeared in the $KMnO_4$ groups while increased amounts of tyrosine and fulvic acid appeared in the $H_2O_2$ groups. So, the substance of 1650 Da couldn't be the decomposition product of proteins and humic substances in dewatered sludge.



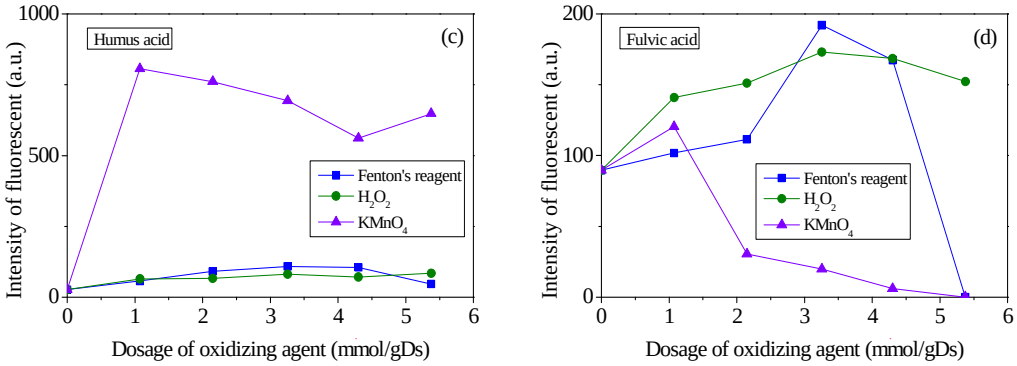



Fig. 8. Fluorescent substances in free water. (a) Tyrosine, (b) Macromolecular humic substance (c) Humic acid, and (d) Fulvic acid.

### 3.7. Lipids and polysaccharide analysis

The analysis results for the lipids and polysaccharides in three groups are shown in Fig. 9, wherein (a) is aliphatic acid and (b) is saccharide. It could be observed that Fenton's reagent groups contained the most polysaccharides and several aliphatic acids in free water, $H_2O_2$ groups contained a minimum amount of both substances while the $KMnO_4$ groups contained the most aliphatic and an increased concentration of saccharides but not the most.

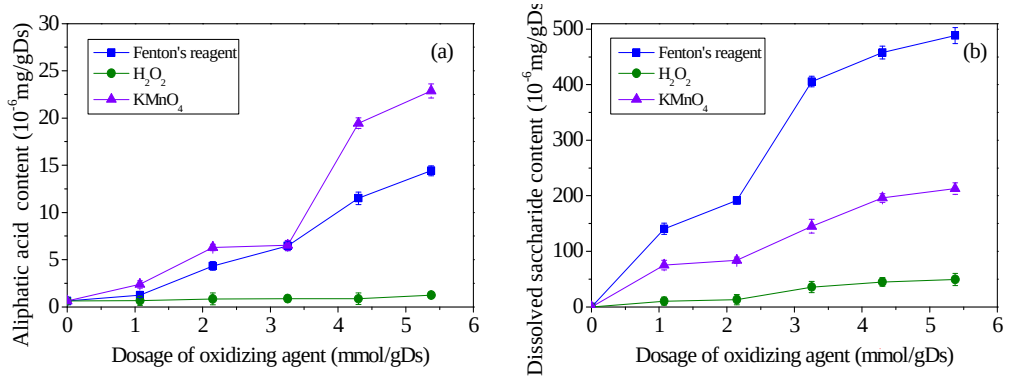


Fig. 9. Concentrations of aliphatic acids and polysaccharides in free water. (a) Aliphatic acids and (b) polysaccharides.

### 3.8. Mechanism of advanced dewatering

To summarize, all the oxidants showed, to a certain extent, a decomposition capacity on the proteins, polysaccharides, humic substances, and lipids in the dewatered sludge, but without the same trend. Based on the MW analysis of the organic biomass decomposition products in free water, there were several types of components in $KMnO_4$ groups, with less in $H_2O_2$ groups, whereas a specific type of component in Fenton's reagent groups. For increasing proportion of amino radicals in free water of $KMnO_4$ groups based on the FTIR analysis, Proteins could be excluded preliminarily. Both the proteins and humic substances were essentially excluded when using the three-dimensional excitation-emission fluorescent-parallel factor analysis method. The substances of 1650 Da were identified as saccharides through the measurement of aliphatic acids and saccharides at last.

Previous studies (Wang et al., 2011) have suggested that typical oxidative decomposition products of proteins were soluble amino acids, lipids were soluble aliphatic acids, humic substances were small amounts of soluble humins and fulvic acids, and polysaccharides produced low molecular saccharides. It could be concluded that the component in free water of Fenton's reagent groups was mainly soluble low molecular saccharides and polysaccharides were the key component. The mechanism of the conversion from bound water to free water via oxidative decomposition of

polysaccharides could be seen from Fig. 10 that, it does not require a large amount of dissolution of polysaccharides to promote the conversion. As long as this structure of polysaccharides is destroyed, the conversion will be promoted effectively, and this destruction of structure will cause a small amount of low molecular polysaccharides to dissolve into free water only. From the perspective of polarity, since the charge distribution inside the water molecule is asymmetric and the centres of positive and negative charges cannot overlap, water, which is bounded by covalent bonds, easily combines with polar organic molecules. Saccharide polarity is greater that the bond potential between water and polysaccharide mole is stronger than that of other components such as proteins, humic substances, and lipids; From the perspective of organic groups, polysaccharide molecules with a large quantity of hydrophilic groups, including the hydroxyl and aldehyde groups, are hydrophilic molecules themselves. Proteins with hydrophilic groups, such as amino groups, contain a large quantity of hydrophobic groups yet, such as hydrocarbon groups. Furthermore, lipids contain aliphatic hydrocarbon groups while humic substances, which are highly hydrophobic, have an aromatic nucleus with a large number of aromatic and alicyclic rings (Neyens et al., 2004). Therefore, the decomposition of polysaccharides which may combine the most water could promote the conversion of bio-bound water to free water effectively and favourable for actual advanced dewatering. Due to the larger specific surface areas and stronger bounded ability of smaller organic biomass molecules, the composition of proteins, humic substance and lipids may produce more bound water conversely from free water. The possible transformation approach of polysaccharides

which mainly existed as the form of insoluble polymers in raw dewatered sludge were decomposing to the fractional saccharides, even up to monosaccharide by oxidants and releasing into free water with the conversion of bound water to free water simultaneously.

In addition, different oxidants should have a certain selectivity for the decomposition of organic biomass in dewatered sludge. Based on the three oxidants used in this study, $KMnO_4$ had the ability of decomposing the largest quantity of total organic biomass matter and several oxidative decomposition effects on various organic biomass. The $H_2O_2$ had the poorest ability to decompose total organic biomass matter and focuses on proteins and humic substances. Fenton's reagent selectively decomposed the most polysaccharides in the dewatered sludge. Comparing the ORP of three oxidants, polysaccharides could only be decomposed heavily when the value reach 2.85 V. When the oxidizing ability was insufficient, the decomposition of polysaccharides could not occur fully while most other components would be decomposed simultaneously.

Since polysaccharides were characterized by the maximum water-bound capacity, their decomposition would effectively enhance the conversion of bound water and actual advanced dewatering performance. In the whole dewatering cycle (moisture content from nearly 98% to below 60%), the key substance of controlling the dewatering performance may transfer from proteins to polysaccharides and conditioning method from keeping the effective permeability of cake to promoting conversion of bound water.

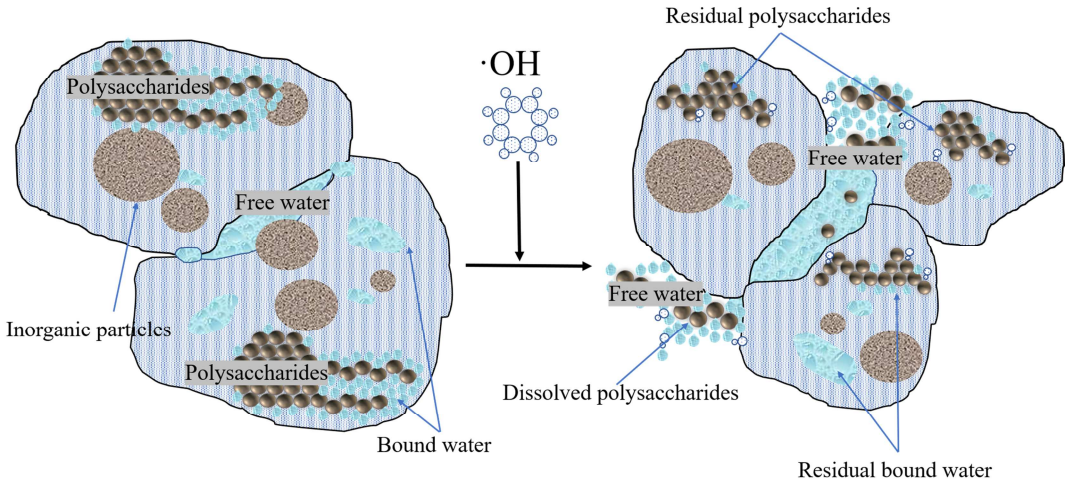



Fig. 10. Mechanism of the conversion from bound water to free water via oxidative decomposition of polysaccharides.

### 3.9. Morphological properties of polysaccharides after Fenton's reagent pre-oxidation

Dissolved polysaccharides mainly derived from the three-layer structure of the pellet, T-EPS, and L-EPS (Fig. 11). As shown in Fig. 11, With the increasing of Fenton's reagent, the quantity of polysaccharides in the three-layers structure decreased and released into free water together, and the decrement of polysaccharides in dewatered sludge was 0.71~3.24 mg/gDs in Pellet, 0.15~0.50 mg/gDs in T-EPS and 0.34~1.13 mg/gDs respectively. Assuming that the pathways from insoluble polysaccharides in three-layers to dissolved polysaccharides in free water are parallel, it could be seen that pellets contributed 52.28~66.56%, T-EPS contributed 8.37~12.75%, and L-EPS contributed 23.15~39.08% of the total dissolved polysaccharides through calculating the reduction of polysaccharides in three layers.

From the morphological perspective, more than half the dissolved saccharides of Fenton's reagent groups most likely came from Pellets, followed by L-EPS and T-EPS. We could speculate that the portion of free water converted from bio-bound water may primarily originate from microbial cells. Therefore, the effect on promoting the release of intracellular water could mainly attribute to the cell-breaking capacity of Fenton's reagent.

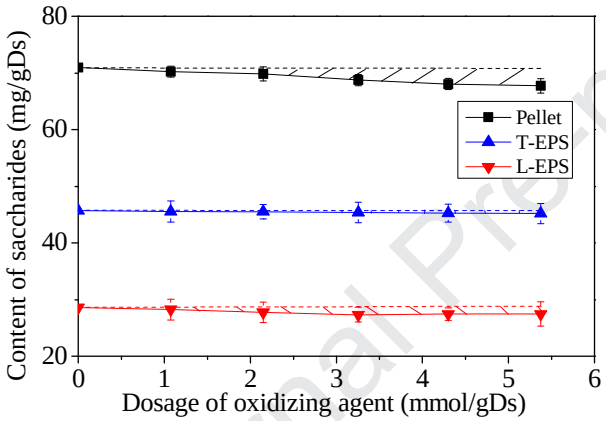



Fig. 11. Morphological properties of polysaccharides after Fenton's reagent pre-oxidation.

## 4. Conclusions

This study attempted to investigate the effects of three oxidants on advanced dewatering and to explore the key mechanisms that occur during this process. The following summarizes the conclusions of this study:

(1) Conversion from bio-bound water to free water in dewatered sludge could improve actual performance of subsequent advanced dewatering, and final moisture content of which would fall below 50%.

(2) Polysaccharides may be the key component influences conversion from bio-bound water to free water, which would be oxidized selectively by Fenton's reagent

(3) Dissolved polysaccharides primarily came from Pellets and the release of intracellular water could attribute to cell-breaking capacity of Fenton's reagent.

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**Highlights**

- Effect of oxidants on secondary advanced dewatering for dewatered sludge directly explored.
- TOC reduction could not enhance conversion of bound water predicatively.
- Key component enhances advanced dewatering confirmed
- Release of intracellular polysaccharide-bound water promoted by Cell-breaking capacity of Fenton's reagent.
- Polysaccharides would be oxidized selectively by Fenton's reagent.

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**Le Chen:** Resources

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**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: