Improvement of sludge dewaterability and disintegration efficiency using electrolytic zero-valent iron activated peroxymonosulfate

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ABSTRACT

Electrolysis zero-valent iron activated peroxymonosulfate (EZVI-PMS) was applied to enhance sludge dewaterability and disintegration performance. Sludge dewaterability was characterized by capillary suction time (CST), specific resistance to filtration (SRF), and disintegration performance was explored by measuring sludge DNA content, ammonia nitrogen, chemical oxygen demand (COD), extracellular polymeric substances (EPS) and dissolved organic carbon (DOC). EPS including soluble EPS (SB-EPS), loosely bound EPS (LB-EPS), tightly bound EPS (TB-EPS) were analyzed by three dimensional fluorescence excitation-emission spectrum (3D-EEM) to confirm the proteins transformation tendency. DOC, protein and polysaccharide in EPSs were quantified to investigate the conditioning mechanism. The results showed that sludge CST and SRF were reduced significantly when the current was 0.2 A and PMS dosage was 130 mg/gDS with the reductions of 43.8% and 74.1%, respectively, and DNA was released from sludge cells to liquid phase. Mechanically, sludge TB-EPS converted to SB-EPS with DOC in TB-EPS decreasing from 367.0 mg/L to 210 mg/L, while DOC in SB-EPS increased from 44 mg/L to 167.4 mg/L. Besides, the changes of proteins and polysaccharides contents in SB-EPS and TB-EPS were similar to DOC, and protein in TB-EPS transformed to other protein-like or organic substances obviously.

Key words: electrolysis zero-valent iron, extracellular polymeric substance (EPS), peroxymonosulfate (PMS), sludge disintegration, sludge filterability

HIGHLIGHTS

- Electrachemically activated peroxymonosulfate (PMS) was useful for conditioning.
- A electric current of 0.2 A was enough to produce Fe(II) to activate PMS using iron bar as the cathodes.
- Electrachemically activated PMS could oxidized extracellular polymeric substances in sludge to enhance sludge dewaterability.

1. INTRODUCTION

With the increase of sewage treatment amount, the waste activated sludge produced by waste water treatment plant (WWTP) is huge in China (Wang et al. 2018; Gao et al. 2021), and the moisture content of which reaches to more than 99% (Liang et al. 2020), and still about 96% even after thickening process. In order to reduce the moisture content of waste activated sludge, sludge conditioning combined with mechanical dewatering is widely applied at present. However, sludge moisture content in most WWTP can only be reduced to about 75% after most mechanical dewatering process (Lin et al. 2020; Bian et al. 2021), which will produce huge costs on sludge transportation and final disposal undoubtedly (Ye et al. 2012).

Extracellular polymeric substances (EPS), as the main component of sludge flocs, accounts for 80% of sludge solids (Yang et al. 2017), and mainly are microbial metabolites, such as proteins, polysaccharides and humic substances (More et al. 2014). These substances are highly hydrophilic (Yuan et al. 2017), making EPS able to wrap up a large amount of water and impede the separation of sludge particle and water. In actually, mechanical dewatering pressure is limited, but the EPS and bound water (including interstitial water, capillary water and intracellular water) are difficult to be removed from the sludge even under high pressure (Wei et al. 2018). Therefore, it is necessary to destroying sludge EPS structure during sludge conditioning through chemical, physical and biological methods to improve the efficiency of sludge filtration, disintegration, and mechanical dewatering. However, simply destroying EPS structure does not necessarily to improve the dewatering performance, if the
properties of proteins and other substances in EPS do not change, water will still be wrapped in them. Therefore, EPS should be oxidized and its inherent properties should be changed in order to improve sludge dewatering performance effectively. At present, many researches committed to divide EPS into different layers, mainly soluble EPS(S-EPS), loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS), and investigate the influence of each component on sludge dewaterability. Some researchers found that LB-EPS content was positively correlated with the dewaterability (Zhen et al. 2018), while others suggested that the TB-EPS content was negatively correlated with sludge dewaterability (Fan et al. 2020). As for the influence of protein, humic substances and polysaccharide, the main components in EPS, some researchers found that high protein amount in sludge was not benefit for sludge dewaterability (You et al. 2017), while others believed that the substances played different roles in affecting sludge dewatering performance (Wu et al. 2016; Ge et al. 2019).

Advanced oxidation process as a promising approach of sludge condition, has received extensive concern, because the oxidizers can disintegrate sludge structure, organic matters and sludge cell (Feng et al. 2014), such as ozone (Zhang et al. 2016), peroxide (Kim et al. 2009), chlorine (Wang 2014), persulfate (PS) (Xiao et al. 2017; Maqbool et al. 2019), and fenton reagent (Xiao et al. 2018; Cai et al. 2019) etc, which are usually used to degrade macromolecular organic matters and reduce sludge volume and some of them could also improve sludge dewatering performance. The oxidants listed above are almost all based on the production of highly active reaction free radicals, such as superoxide radicals, hydroxyl radicals and sulfate radicals. Due to producing sulfate radicals, the advanced oxidation process based on activated persulfate has been paid more and more attention in sludge conditioning due to the significant advantages in treatment effect and relatively loose using conditions, such as high REDOX potential, long continuous oxidation time and wide applicable pH range (Zhen et al. 2012a, 2012b). For example, some researchers found that activated persulfate could degrade the digested sludge and enhance sludge dewatering effect (Waclawek et al. 2016). Meanwhile, activated persulfate coupled with other sludge conditioning methods had also achieving excellent synergic effects, such as microwave and persulfate/Fe(II) could reduce 94.6% CST (Zhen et al. 2019), and persulfate/Fe(II) with polymerized material could reduce 94.9% specific resistance to filtration (SRF) reduction (Wang et al. 2017).

However, as a kind of strong oxidant, persulfate produces sulfate radical only under certain activation conditions (such as transition metal, ultrasound and heat) (Li et al. 2018; Wang et al. 2018; Bian et al. 2021). At present, there are many researches on ferrous ion (Fe(II)) and thermally activated persulfate to improve the sludge filtration performance (Kim et al. 2016; Guo et al. 2019; Ge et al. 2020). Due to the easily operate condition and simple equipment, Fe(II) was the most widely used reagent to activate persulfate in sludge conditioning. It should be noted that Fe(II) readily convert to ferric iron, while the conversion rate of ferric iron (Fe(III)) converting to Fe(II) is very slow, which makes it necessary to add large amounts of ferrous salts to activate persulfate. When zero-valent iron (ZVI) is used as electrode, sequential conversion between ZVI, Fe(II) and Fe(III) could be achieved easily, and the activation efficiency of persulfate could be improved by certain electrolytic conditions (Lin et al. 2014).

Therefore, the object of this study is to: investigate the improvement of sludge dewatering and disintegration performance using peroxymonosulfate (PMS) activated by electrolysis zero-valent iron (EZVI-PMS); evaluate the effects of the oxidizing condition on sludge dewaterability; examine the effects of EZVI-PMS oxidation on solubilization and physico-chemical properties of organic substances; and get more comprehensive insights into the mechanism of EZVI-PMS in conditioning sludge.

2. METHODS AND MATERIALS
2.1. Raw sludge

The raw sludge was took from the reflux pipe from secondary sedimentation tank to biochemical pool in a WWTP using improved oxidation ditch process in Wuhan city. The daily treatment capacity of the sewage plant was 50,000 t/d. The collected sludge was filtered using a 30 mesh sifter to get rid of large particulate matter then condensed to a moisture content of about 97.8%. The sludge was stored at 4 °C in a plastic bucket before using, and all the relevant indicators of sludge samples was measured integrally within 3 days. Raw sludge has a pH of about 7.4, suspended solid (SS) concentration of about 21.7 g/L, and volatile suspended solid (VSS) content of about 12.3 g/L.
2.2. Experimental method

The device for conditioning sludge with EZVI-PMS is shown in Figure 1. The anode and cathode both use iron rods, of which the diameter is 12 mm. The center distance between the two electrodes is 50 mm, and the depth of immersion in the sludge is 60 mm. During the experiment process, 600 g sludge was poured into a 1 L beaker, and PMS was dosed when the power supply was switched on. PMS dosage was controlled at 130 mg/gDS which was determined by previous laboratory tests. The current levels were controlled at 0.2 A and 0.4 A, respectively. The experimental group with PMS was defined as the electric oxidation group, while the group without PMS was defined as the electric flocculation group. CST and other indicators were sampled at 15, 30 and 60 min in each group.

2.3. EPS extraction and detection

EPS was extracted using thermal extraction method (Guo et al. 2019). In brief, 25 mL of sludge was centrifuged at 4,000 r/min. After the centrifugal liquid was filtered through a 0.45 μm membrane, the organic substance in the filtrate was defined as SB-EPS. The residue solid after centrifugation was diluted to the original volume with deionized water and centrifuged at 10,000 r/min. The organic matter in the filtrate was defined as LB-EPS after the centrifugal liquid filtered through a 0.45 μm membrane. The residue solid was diluted to the original volume with deionized water once again. Then put the sample into a water bath at 80 °C for 10 min, followed by centrifuging at 4,000 r/min and collecting the centrifugate. The organic matter in the filtrate of centrifugate filtering through a 0.45 μm membrane was defined as TB-EPS. The concentrations of dissolved organic carbon (DOC), polysaccharide (PS) and protein (PN) in SB-EPS, LB-EPS and TB-EPS were detected. The contribution of each EPS layer to sludge dewaterability was assessed determined by a three dimensional fluorescence excitation – emission (3D-EEM) spectrometer (F7000, Hitachi, Japan). The polysaccharide and protein content was detected by anthrone – concentrated sulfuric acid method and fast Lowry method, respectively. All indexes were tested three times and the average was taken.

2.4. Other detection methods

All the reagents used in the experiment were analytical pure, among which persulfate (PMS) was Aladdin’s reagent. CST was monitored by a CST instrument (Triton, Modle 304M, Essex, UK). Specific resistance to filtration (SRF) was measured using buchner funnel method. According to the requirements of PowerSoil® DNA Isolation Kit, DNA was extracted from 0.25 g of sludge for quantitative detection by UV-VIS spectrophotometer (NanoDrop ND-2000, Thermo Fisher Scientific, US). Sludge particle size could reflect the sludge accumulation or diffuse state which was analyzed by a laser particle analyzer (Mastersizer 2000, Pennsylvania-based firm, UK). SS, VSS and moisture contents were conducted by gravimetric method. DOC was analyzed by organic carbon analyzer (multi N/C 2100, Jena, Germany). Bound water was detected by expansion method using dilatometer.
with xylene as indicator (Huo et al. 2014). Chemical oxygen demand (COD) and ammonia nitrogen (NH\textsubscript{4}+\text{-N}) were measured using international standard methods. All indexes were tested three times and the average was taken.

3. RESULTS AND DISCUSSIONS

3.1. Effect of electro-oxidation on sludge dewaterability

The effects of EZVI-PMS on sludge dewaterability in terms of CST and SRF under different current intensities are shown in Figure 1(a) and 1(b). When PMS dosage fixed at 130 mg/gDS and currents fixed at 0.2 and 0.4 A, respectively, sludge CST and SRF decreased rapidly and then tended to stabilize as the conditioning time increased from 15 to 60 min. The maximum reductions of CST and SRF were 49.6% and 76.9%, respectively. The results indicated that EZVI-PMS have a remarkable influence on sludge dewaterability. When sludge was conditioned by electro-flocculation only, i.e., no PMS was added, CST and SRF changed slightly, no matter the current was 0.2 or 0.4 A. It suggested that the flocculation effect of Fe (II) and Fe (III) generated by electro-lysis on sludge was negligible, so the sludge filtration performance could not be improved significantly. CST was signally reduced when both electrification and PMS were added to condition sludge. Sludge CST and SRF decreased from 195.5 s to 109.9 s and 1.47 × 10\textsuperscript{9} s\textsuperscript{2}/g to 0.38 × 10\textsuperscript{9} s\textsuperscript{2}/g with the reductions of 43.8% and 74.1%, respectively, as the current was 0.2 A and treating for 15 min. However, the CST just declined to 104.4 s and 100.5 s, while the treatment time increasing to 30 and 60 min, respectively, which indicated that the reduction of CST was not obvious when the treatment time was extended a certain value. When the current was increased to 0.4 A, sludge CST decreased to only 105.3 s after 15 min conditioning. The changing regulation of SRF was similar to CST. According to the above analysis, when the current higher than 0.2 A or the conditioning time exceeding 15 min, the improvement effect of sludge dewaterability tended to be stable. Therefore, in the subsequent experiment, the current intensity and treatment time was fixed at 0.2 A and 15 min, respectively.

3.2. The disintegration effect of electro-oxidation sludge

Sludge disintegration mainly analysis from following characterization parameter, namely sludge DNA, ammonia nitrogen and COD contents in supernatant. As shown in Figure 3(a), the DNA content extracted from raw sludge and sludge conditioned by electro-flocculation was 29.0 mg/L and 27.3 mg/L respectively. Nevertheless, the DNA content in the electro-oxidized sludge was only 2.7 mg/L. The results showed that the cell structure of electro-oxidation treated sludge was broken and lysed, and resulted in DNA releasing into liquid phase. For the sludge treated by electro-flocculation, there was no obvious release of DNA, indicating that the disintegration effect of electro-flocculation on sludge cells was negligible.

The change of ammonia nitrogen content in sludge supernate could show the degree of sludge disintegration on another aspect. The ratio of ammonia nitrogen in conditioned sludge supernate to that in raw sludge supernate is
shown in Figure 3(b) under different treatment conditions, which were 1.02 and 1.93 respectively for electro-flocculation and electro-oxidation treated sludge, respectively. The results suggested that nitrogenous organic matters such as protein-like substance were partially hydrolyzed under the oxidation of EZVI-PMS, and ammonia nitrogen was produced and released into liquid phase. However, electro-flocculation alone had no promoting effect on the release of ammonia nitrogen, and organic substances could not be oxidized in the sludge, so ammonia nitrogen content was basically unchanged.

The COD contents in supernate of raw sludge, electro-flocculation and electro-oxidation treated sludge are showed in Figure 3(c). COD contents in electro-oxidized sludge was the highest with about 5 times higher than that of the other two. The result showed that electro-oxidation could make sludge releasing COD into liquid phase. Which was highly consistent with the change of ammonia nitrogen in supernate and contrary to DNA content in sludge. It is main attribution to the sludge disintegration promoted by EZVI-PMS. Which destroyed the structure of sludge flocs and the organic matter inside and outside sludge cells.

3.3. Effects of electro-oxidation on sludge EPS

The DOC, protein and polysaccharide contents of S-EPS, LB-EPS and TB-EPS in each sludge sample are showed in Figure 4. The DOC content of S-EPS (as shown in Figure 4(a)) in electro-oxidation treatment sludge is the highest, at a value of 167.4 mg/L, while that of raw sludge and electro-flocculation treated sludge was relatively close, at about 45 mg/L. On the contrary, the DOC concentration in TB-EPS of electro-oxidized sludge was the lowest, at 210.4 mg/L, and the difference between the other two sludge samples was roughly equal with DOC content of about 375.0 mg/L. The difference of DOC content in LB-EPS extracted from the three sludge samples was relatively small. It can be seen from the above results that high DOC in TB-EPS would hamper sludge dewatering, and electro-oxidation can transform DOC in sludge TB-EPS into DOC in SB-EPS which was benefit for sludge dewatering. It might be owing to that the S-EPS can be easily removed along with free water. Hence, it
has an unobvious influence on limiting sludge dewatering (Bian et al. 2021). However, the compact structure of TB-EPS can prevent the separation of sludge and water.

The main substances in sludge EPS are proteins and polysaccharides. As shown in Figure 4(b), the protein in S-EPS of electro-oxidation treated sludge was the highest, followed by that of raw sludge and electro-flocculation treated sludge was the lowest. Nevertheless, the difference among the three samples was unobvious. The protein content in LB-EPS of raw sludge and electro-oxidation treatment sludge were close to each other, while that of the electro-flocculation treated sludge was the lowest, with a value of 181.9 mg/L. It should be noted that the protein content in TB-EPS was significantly different, with values of 532.9 mg/L and 272.9 mg/L corresponding to raw sludge and electro-oxidized sludge, which decreased by nearly 48.8% compared with raw sludge. The above results showed that under the oxidation of EZVI-PMS, the proteins in sludge TB-EPS were not only transformed into soluble proteins, but also converted into non-protein substances.

In presence of the polysaccharide in S-, LB- and TB- EPS of different sludge samples (as shown in Figure 4(c)), it presented a similar changing tendency to protein, but there is a big difference in the value of concentrations. The highest polysaccharide content in S-EPS appeared in electro-oxidation conditioned sludge with a value of 130.3 mg/L, which was more than 2.0 times of raw sludge and electro-flocculation sludge. The polysaccharides contents in LB-EPS were pretty close, and valued of 53.2 mg/L and 57.8 mg/L corresponding to raw sludge, electro-flocculation sludge and electro-oxidation sludge. The polysaccharides in TB-EPS of raw sludge reached to 138.3 mg/L which was the maximum and very close to that of the electro-flocculation conditioned sludge, and much higher than 95.1 mg/L for the electro-oxidation treatment sludge. The results showed that electro-oxidation could transform the adhesive polysaccharides into soluble polysaccharides.

The results indicated that protein-like substances might be mineralized by EZVI-PMS, while polysaccharides were not, when comprehensively analyzing proteins and polysaccharides. Besides, polysaccharides and proteins...
in S-EPS did not affect sludge dewatering performance. It can be speculated that protein substances in TB-EPS are the dominant substances limiting sludge dewatering efficiency.

3.4. Analysis of EPS by 3D-EEM

Figure 5 shows the 3D-EEM spectra of SB-EPS, LB-EPS and TB-EPS extracted from raw sludge, electro-flocculation and electro-oxidized sludge. According to the fluorescence spectra of the three kinds of EPS and the fluorescence substances at different Ex/Em regions (as shown in Table 1), the main fluorescence peaks were A (Ex/Em: 230/306), B (Ex/Em: 275/306), C (Ex/Em: 280/346), and D (Ex/Em: 325–350/438), representing aromatic family proteins (Zhu et al. 2015), soluble microbial byproducts (Bourven et al. 2012), tryptophan protein substances (Pang et al. 2014), and humic acids (Wang et al. 2009), respectively. In the 3D-EEM diagram of the raw sludge S-EPS, C peak was not obvious, and the sludge treated with electro-flocculation did not show a peak at this position, while peak B in the EEM diagram of the sludge SB-EPS treated with electro-oxidation was more significant than that of the raw sludge. For LB-EPS and TB-EPS, the peak C of raw sludge and electro-flocculation treatment sludge was significant, while the peak C of electro-oxidation treatment sludge became relatively insignificant. For SB-EPS and TB-EPS, the peak D changed negligibly. It can be inferred from the above results that protein substances in sludge TB-EPS was oxidized by EZVI-PMS and transferred to SB-EPS, while humic acid sludge was decomposed negligibly. Moreover, it was found through 3D-EEM spectra that the variation trend of protein contents in SB-EPS, LB-EPS and TB-EPS was consistent with the variation trend of directly detected

Figure 5 | 3D-EEM spectra of SB-EPS, LB-EPS and TB-EPS of sludge treated under 0.2 A current and 15 min condition time with 130 mg/gDS PMS.
protein contents. It could be confirmed again that there was a significant correlation between proteins in TB-EPS and sludge dewatering performance.

When comprehensively analysis the contents of TOC, polysaccharide and protein in EPSs, electro-oxidation can disintegrate the proteins and polysaccharides in TB-EPS into dissolved homogeneous substances, or transform them into other kinds of organic substances, especially the proteins into non-protein substances under the oxidation of electro-oxidation. By analyzing the changing tendency of EPS content and substance types in sludge, it was found that higher TB-EPS was corresponding to higher CST value, which was similar to other research results. With the cracking of TB-EPS, part of the bound water was released, and the separation effect of sludge and water was improved. The decrease of tryptophan – protein content in sludge TB-EPS was also positively correlated with the decrease of CST. In addition, the increase of ammonia nitrogen in the electro-oxidized sludge supernatant may mainly be derived from the fracture of some protein substances in TB-EPS. Moreover, the protein content was much higher than polysaccharide content in the three sludge EPS samples, which indicated that protein content had more significant influence on sludge dewatering performance to a certain extent. In a nutshell, TB-EPS in sludge was the main factor that restricted sludge dewatering.

### 3.5. The mechanism of electro-oxidation on sludge

The sludge particle size distribution is shown in Figure 6(a). It can be found that the average particle size increased slightly for electro-flocculation and electro-oxidation sludge, which were bigger than that of raw sludge with a value of 56 μm. The average particle size of conditioned sludge samples both were about 64 μm, however, it should be note that the sludge conditioned by EZVI-PMS accounted for a larger proportion at the position of average size, while the electro-flocculation sludge had a larger particle size range. The particle size distribution of electro-oxidation treated sludge were consistent with the change trend of sludge treated using activated persulfate by other researchers (Xiao et al. 2017). For the sludge treated by electro-flocculation, the particle size increased because ferrous ions and iron ions generated in electrolysis process could produce flocculation effect. However, for the sludge conditioned by electro-oxidation, although the sludge was disintegrated and the

![Table 1](https://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.229/899329/wst2021229.pdf)

| Region | Ex/Em               | fluorescence substances                                      |
|--------|---------------------|-------------------------------------------------------------|
| I      | 200–250/300–330     | Aromatic protein I (Tyronsine)                               |
| II     | 200–250/330–380     | Aromatic protein II (Tryptophan)                             |
| III    | 200–250/380–500     | Fulvic acid-like                                             |
| IV     | 250–400/300–380     | Soluble microbial by-product-like (Protein-like containing Tryptophan, Tryptophan & protein-like related to biological) |
| V      | 250–400/380–500     | Humic acid-like                                              |

![Figure 6](https://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.229/899329/wst2021229.pdf)

**Figure 6** | Particle size distribution (a) and changes of sludge bound water (b).
cells were destroyed, the electronegativity of sludge surface is reduced due to the reduction of TB-EPS, so the
sludge can be more easily aggregated, which leads to the increase of sludge particle size (Mikkelsen & Keiding
2002).

The enhancement of sludge dewaterability may be attributed to an oxidation step by SO4
through degrading
the EPS and sludge cell, and converting the bound water to free water and a subsequent re-coagulation step by the
generation Fe(III). As shown in Figure 6(b), the bound water content of raw sludge, electro-flocculation sludge
and electro-oxidation sludge were 5.4 g/gDS, 5.0 g/gDS and 3.6 g/gDS, respectively. The results showed that
the bound water of electro-oxidation conditioned sludge decreased significantly, which was mainly due to the
cracking of EPS and cell rupture, which played a promoting role in improving sludge dewaterability.

Comprehensive analysis indicated that the improvement of sludge filtration performance and disintegration
effect of sludge was mainly due to the oxidation of EZVI-PMS to destroy extracellular polymers and sludge
cells, so that the sludge was disintegrated and released bound water simultaneously. In the process of improving
sludge filtration performance, Fe(III) ions in the electrolysis process can also produce flocculation effect (Gao
et al. 2021), which made sludge re-aggregate into sludge flocs with larger particle size after being destroyed. Meanwhile, the change of protein types in sludge EPS improved the sludge-water separation effect to a certain extent.

3.6. Economic analyses of EZVI-PMS

The total cost of EZVI-PMS was 213.6 USD/t DS including the consumption of PMS, ZVI and Electricity (as
shown in Table 2). Though EZVI-PMS exhibits a lower sludge dewatering efficiency than Fe(II)-PMS (Liu
et al. 2016), the cost is much lower than using Fe(II)-PMS to condition sludge. So ZEVI-PMS still has a great
potential to be the effective alternates for sludge dewatering.

4. CONCLUSION

The effects and mechanism of electrolytic zero-valent iron activated peroxymonosulfate on enhancing sludge dis-
integrating and dewatering performance were investigate in this study. Sludge dewaterability was significantly
improved in term of CST and SRF with significant reductions. Besides, COD in supernate increased substantially,
while DNA content declined observably which were highly correlated with sludge disintegration. Simultaneously,
electrolytic zero-valent iron activated peroxymonosulfate could break down the tightly bound extracellular poly-
mers into dissolved extracellular polymers in sludge, change the protein substances types in sludge significantly,
and convert quite a few proteins into non-protein substances.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

Table 2 | Cost analyses of EZVI-PMS

| Methods   | CST raw sludge(s) | Reduction rate (%) | SRF raw sludge (\(\cdot 10^9\)s/g) | Reduction rate (%) | Oxidant dosage/consumption | Cost (USD/tDS) |
|-----------|-------------------|--------------------|----------------------------------|--------------------|---------------------------|-----------------|
| Fe(II)-PMS | 201.8             | 90.1               | 9.52                            | 97                 | Fe(II) 0.81 mmol/gVSS     | 336.2           |
|           |                   |                    | HSO₅⁻ 0.9 mmol/gVSS              |                    |                           |                 |
| EZVI-PMS  | 195.5             | 43.8               | 1.47                            | 74.1               | KHSO₅ 0.0611 g/gDS        | 213.6           |
|           |                   |                    | ZVI 0.004 g/gDS                 |                    | Electricity 0.045 W·h/gDS |                 |
REFERENCES

Bian, C., Ge, D., Wang, G., Dong, Y., Li, W., Zhu, N. & Yuan, H. 2021 Enhancement of waste activated sludge dewaterability by ultrasound-activated persulfate oxidation: operation condition, sludge properties, and mechanisms. *Chemosphere* **262**, 128385.

Bourven, I., Costa, G. & Guibaud, G. 2012 Qualitative characterization of the protein fraction of exopolymeric substances (EPS) extracted with EDTA from sludge. *Bioresource Technology* **104**, 486–496.

Cai, M., Wang, Q., Wells, G., Dionysiou, D. D., Song, Z., Jin, M., Hu, J., Ho, S.-H., Xiao, R. & Wei, Z. 2019 Improving dewaterability and filterability of waste activated sludge by electrochemical Fenton pretreatment. *Chemical Engineering Journal* **362**, 525–536.

Fan, X., Wang, Y., Zhang, D., Guo, Y., Gao, S., Li, E. & Zheng, H. 2020 Effects of acid, acid-ZVI/PMS, Fe(II)/PMS and ZVI/PMS conditioning on the wastewater activated sludge (WAS) dewaterability and extracellular polymeric substances (EPS). *Journal of Environmental Sciences* **91**, 73–84.

Feng, G., Tan, W., Zhong, N. & Liu, L. 2014 Effects of thermal treatment on physical and expression dewatering characteristics of municipal sludge. *Chemical Engineering Journal* **247**, 223–230.

Gao, S., Wang, Y., Zhang, D., Fan, X., Guo, Y., Li, E. & Zheng, H. 2021 Insight to peroxone-Fe(III) joint conditioning-horizontal electro-dewatering process on water reduction in activated sludge: performance and mechanisms. *Journal of Hazardous Materials* **402**, 123441.

Ge, D. D., Zhang, W. R., Yuan, H. P. & Zhu, N. W. 2019 Enhanced waste activated sludge dewaterability by tannic acid conditioning: efficacy, process parameters, role and mechanism studies. *Journal of Cleaner Production* **241**, 8.

Ge, D., Dong, Y., Zhang, W., Yuan, H. & Zhu, N. 2020 A novel Fe2+ /persulfate/tannic acid process with strengthened efficacy on enhancing waste activated sludge dewaterability and mechanism insight. *Science of The Total Environment* **733**, 139146.

Guo, S., Liang, H., Bai, L., Qu, F., Ding, A., Ji, B., Wang, X. & Li, G. 2019 Synergistic effects of wheat straw powder and persulfate/Fe(II) on enhancing sludge dewaterability. *Chemosphere* **215**, 333–341.

Huo, M. B., Zheng, G. Y. & Zhou, L. X. 2014 Enhancement of the dewaterability of sludge during bioleaching mainly controlled by microbial quantity change and the decrease of slime extracellular polymeric substances content. *Bioresource Technology* **168**, 190–197.

Kim, T.-H., Lee, S.-R., Nam, Y.-K., Yang, J., Park, C. & Lee, M. 2009 Disintegration of excess activated sludge by hydrogen peroxide oxidation. *Desalination* **246**(1), 273–284.

Kim, M. S., Lee, K.-M., Kim, H.-E., Lee, H.-J., Lee, C. & Lee, C. 2016 Disintegration of waste activated sludge by thermally-activated persulfates for enhanced dewaterability. *Environmental Science & Technology* **50**(13), 7106–7115.

Li, H., Song, L., Han, B. & Song, H. 2018 Improved sludge dewaterability using persulfate activated by humic acid supported nanoscale zero-valent iron: effect on sludge characteristics and reaction mechanisms. *Environmental Science Water Research & Technology* **4**(10), 1480–1488.

Liang, J., Zhang, L., Ye, M., Guan, Z., Huang, J., Liu, J., Li, L., Huang, S. & Sun, S. 2020 Evaluation of the dewaterability, heavy metal toxicity and phytotoxicity of sewage sludge in different advanced oxidation processes. *Journal of Cleaner Production* **265**, 121859.

Lin, H., Zhang, H. & Hou, L. 2014 Degradation of C. I. Acid Orange 7 in aqueous solution by a novel electro/Fe3O4/PDS process. *Journal of Hazardous Materials* **276**, 182–191.

Lin, N., Zhu, W., Fan, X., Wang, C., Chen, C., Zhang, H., Chen, L., Wu, S. & Cui, Y. 2020 Key factor on improving secondary advanced dewatering performance of municipal dewatered sludge: selective oxidative decomposition of polysaccharides. *Chemosphere* **249**, 126108.

Liu, J., Yang, Q., Wang, D., Li, X., Zhong, Y., Li, X., Deng, Y., Wang, L., Yi, K. & Zeng, G. 2016 Enhanced dewaterability of waste activated sludge by Fe(II)-activated peroxymonosulfate oxidation. *Bioresource Technology* **206**, 134–140.

Maqbool, T., Cho, J. & Hur, J. 2019 Improved dewaterability of anaerobically digested sludge and compositional changes in extracellular polymeric substances by indigenous persulfate activation. *Science of The Total Environment* **674**, 96–104.

Mikkelsen, L. H. & Keiding, K. 2002 Physico-chemical characteristics of full scale sewage sludges with implications to dewatering. *Water Research* **36**(10), 2451–2462.

More, T. T., Yadav, J. S. S., Yan, S., Tyagi, R. D. & Surampalli, R. Y. 2014 Extracellular polymeric substances of bacteria and their potential environmental applications. *Journal of Environmental Management* **144**, 1–25.

Pang, L., Ni, J. & Tang, X. 2014 Fast characterization of soluble organic intermediates and integrity of microbial cells in the process of alkaline anaerobic fermentation of waste activated sludge. *Biochemical Engineering Journal* **86**, 49–56.

Waclawek, S., Grubel, K., Dennis, P., Vinod, V. T. P. & Cernik, M. 2016 A novel approach for simultaneous improvement of dewaterability, post-digestion liquor properties and toluene removal from anaerobically digested sludge. *Chemical Engineering Journal* **291**, 192–198.

Wang, S.-b. s. 2014 Effect of different sludge reduction methods on sludge reduction rates, performance of activated sludge process and urban planning. *Desalination and Water Treatment* **52**(34–36), 6363–6368.

Wang, Z., Wu, Z. & Tang, S. 2009 Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor. *Water Research* **43**(9), 2504–2512.

Wang, H., Liu, C., Wu, Z., Yang, W. & Chen, C. 2017 Improved dewaterability of sewage sludge by Fe(II)-activated persulfate oxidation combined with polymers. *Water and Environmental Science* **51**(4), 603–608.
Wang, Q., Zhang, W., Yang, Z., Xu, Q., Yang, P. & Wang, D. 2018 Enhancement of anaerobic digestion sludge dewatering performance using in-situ crystallization in combination with cationic organic polymers flocculation. *Water Research* **146**, 19–29.

Weihua, H., Gao, B., Ren, J., Li, A. & Yang, H. 2018 Coagulation/flocculation in dewatering of sludge: a review. *Water Research* **143**, 608–631.

Wu, B., Chai, X. & Zhao, Y. 2016 Enhanced dewatering of waste-activated sludge by composite hydrolysis enzymes. *Bioprocess and Biosystems Engineering* **39**(4), 627–639.

Xiao, K., Seow, W. Y., Chen, Y., Lu, D., Jiang, X. & Zhou, Y. 2017 Effects of thermal-Fe (II) activated ozone treatment on sludge dewaterability. *Chemical Engineering Journal* **322**, 463–471.

Xiao, K., Pei, K., Wang, H., Yu, W., Liang, S., Hu, J., Hou, H., Liu, B. & Yang, J. 2018 Citric acid assisted Fenton-like process for enhanced dewaterability of waste activated sludge with in-situ generation of hydrogen peroxide. *Water Research* **140**, 232–242.

Yang, Q., Sun, J., Wang, D., Wang, S., Chen, F., Yao, F., An, H., Zhong, Y., Xie, T., Wang, Y., Li, X. & Zeng, G. 2017 Effect of nickel on the flocculability, settleability, and dewaterability of activated sludge. *Bioresearch Technology* **224**, 188–196.

Ye, F., Ji, H. & Ye, Y. 2012 Effect of potassium ferrate on disintegration of waste activated sludge (WAS). *Journal of Hazardous Materials* **219–220**, 164–168.

You, G., Wang, P., Hou, J., Wang, C., Xu, Y., Miao, L., Lv, B., Yang, Y., Liu, Z. & Zhang, F. 2017 Insights into the short-term effects of CeO2 nanoparticles on sludge dewatering and related mechanism. *Water Research* **118**, 93–103.

Yuan, D., Wang, Y. & Qian, X. 2017 Variations of internal structure and moisture distribution in activated sludge with stratified extracellular polymeric substances extraction. *International Biodeterioration & Biodegradation* **116**, 1–9.

Zhang, J., Zhang, J., Tian, Y., Li, N., Kong, L., Sun, L., Yu, M. & Zuo, W. 2016 Changes of physicochemical properties of sewage sludge during ozonation treatment: correlation to sludge dewaterability. *Chemical Engineering Journal* **301**, 238–248.

Zhen, G., Lu, X., Zhao, Y., Chai, X. & Niu, D. 2012a Enhanced dewaterability of sewage sludge in the presence of Fe(II)-activated persulfate oxidation. *Bioresearch Technology* **116**, 259–265.

Zhen, G. Y., Lu, X. Q., Li, Y. Y., Zhao, Y. C., Wang, B. Y., Song, Y., Chai, X. L., Niu, D. J. & Cao, X. Y. 2012b Novel insights into enhanced dewaterability of waste activated sludge by Fe(II)-activated persulfate oxidation. *Bioresearch Technology* **119**, 7–14.

Zhen, G., Lu, X., Su, L., Kobayashi, T., Kumar, G., Zhou, T., Xu, K., Li, Y.-Y., Zhu, X. & Zhao, Y. 2018 Unraveling the catalyzing behaviors of different iron species (Fe2+ vs. Fe0) in activating persulfate-based oxidation process with implications to waste activated sludge dewaterability. *Water Research* **134**, 101–114.

Zhen, G., Wang, J., Lu, X., Su, L., Zhu, X., Zhou, T. & Zhao, Y. 2019 Effective gel-like floc matrix destruction and water seepage for enhancing waste activated sludge dewaterability under hybrid microwave-initiated Fe(II)-persulfate oxidation process. *Chemosphere* **221**, 141–153.

Zhu, L., Zhou, J., Lv, M., Yu, H., Zhao, H. & Xu, X. 2015 Specific component comparison of extracellular polymeric substances (EPS) in flocs and granular sludge using EEM and SDS-PAGE. *Chemosphere* **121**, 26–32.

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