Persulfate and Zero Valent Iron Combined Conditioning as a Sustainable Technique for Enhancing Dewaterability of Aerobically Digested Sludge

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Abstract

Aerobic digestion followed by dewatering is a widely applied method for sludge stabilization and reduction in decentralized wastewater treatment plants. It is important to enhance the sludge dewaterability of the aerobically digested sludge due to its considerable impact on cost of sludge disposal and management. In this study, an innovative technique is developed for improving the dewaterability of aerobically digested sludge by combined conditioning with persulfate (PS) and zero valent iron (ZVI). The results demonstrated that the dewaterability of aerobically digested sludge could be significantly enhanced with the PS and ZVI dosage in the range of 0 to 0.5 g/gTS and 0 to 0.4 g/gTS, respectively. The highest improvement was achieved at 0.05 g ZVI/g TS with 0.1 g PS/g TS, and the capillary suction time was reduced by ~80%. The extracellular polymeric substances (EPS) characterization revealed that the combined PS-ZVI treatment could largely reduce proteins, polysaccharides and humic acids-like compounds in the tightly bounded EPS of the aerobically digested sludge, leading to bound water releasing from sludge flocs. The recovery of the ZVI particles could reach around 45% - 80% after the treatment, further proved the sustainability of the approach. The proposed PS-ZVI conditioning would not have significant impact on the final choice of sludge disposal and the mainstream wastewater treatment. However, plant-scale test are still required for better assessing the proposed technique.

Keywords: aerobically digested sludge; zero valent iron; persulfate; dewaterability;

extracellular polymeric substances

1. Introduction

Activated sludge processes are a widely used for the treatment of both domestic and industrial wastewater. However, this process could generate a huge volume of waste sludge, which has been considered as an important secondary pollutant to the environment (Luo et al., 2016; Wang, 2017). Therefore, effective sludge treatment and management has become an indispensable part in the wastewater treatment plant (WWTP) operation nowadays. It has been estimated that the expenditures for sludge treatment and disposal could accounted for up to 60% of the total operational cost for WWTPs (Foladori et al., 2010).

Aerobic digestion is a commonly used method for sludge treatment in decentralized WWTPs with small scales (Wang and Yuan, 2015; Zhang et al., 2016). During the aerobic digestion process, microbial cells and organic matter in the sludge are degraded into small molecular matter through endogenous respiration processes to achieve sludge stabilization and reduction (Liu et al., 2017; Wang et al., 2018). Compared with the anaerobic digestion, the aerobic digestion is more preferable for sludge treatment in decentralized WWTPs as it requires less constructional cost and provides more operational ease (Zhang et al., 2016). A following dewatering process was usually applied after the aerobic digestion, for further reducing the sludge volume, thereby

decreasing the cost for sludge disposal. However, several studies have been revealed that aerobic digestion could lead to poorer dewatering property due to changes in the sludge flocs (Murthy and Novak, 1999; Novak et al., 2003). Therefore, effectively improving the dewaterability of aerobically digested sludge was of vital importance before the sludge dewatering process.

So far, a variety of sludge conditioning techniques have been developed to improve the sludge dewaterability, such as microwave irradiation, flocculation, alkaline or acid treatment, freezing or heating and advanced oxidation (Kuutti et al., 2011; Ruiz-Hernando et al., 2014; Yu et al., 2009; Yu et al., 2016). Among these methods, Fenton peroxidation is one of the promising approaches as it strikingly improved the sludge dewaterability in an environmental friendly way (Buyukkamaci, 2004). The conventional Fenton reaction comprised a battery of reactions between hydrogen peroxide (H_2O_2) and ferrous (Fe^{2+}) under acidic conditions. A large number of hydroxyl radicals are generated and contact with the sludge, which rapid destruct the rigid structures of sludge flocs, facilitating the release of bound water. However, a major drawback of the traditional Fenton method is that both Fe^{2+} and H_2O_2 are unstable and the reaction requires extremely acidic conditions with pH in range of 2.0 to 3.0 (Zhang et al., 2015).

The advance oxidation process could also be achieved by zero valent iron (ZVI or Fe^0)

activated with persulfate (PS) (Liang and Guo, 2010; Zhao et al., 2016). Compared with the traditional Fenton reagents, PS and ZVI are much safer and easier for transportation and storage. Furthermore, the reaction could be occurred under pH neutral conditions (Zhen et al., 2012). Therefore, the adjustment of the pH of sludge to acidic conditions (commonly required for traditional Fenton reaction) is no longer needed. In the PS-ZVI system, Fe^0 was firstly oxidized to Fe^{2+} by the persulfate anion ($\text{S}_2\text{O}_8^{2-}$) (Equation (1)), and then the sulfate radical ($\bullet\text{SO}_4^-$) was produced through $\text{S}_2\text{O}_8^{2-}$ reduction by Fe^{2+} (Equation (2)):

The sulfate radicals had a high redox potential ($E^0(\bullet\text{SO}_4^-/\text{SO}_4^{2-})=2.60\text{V}$)(Liang et al., 2004), which enabled the easy reaction with organic substances in the sludge. Recently, the PS-ZVI system was explored for enhancing the WAS dewaterability (Song et al., 2016). It was observed that over 50% reduction in the capillary suction time (CST) was achieved at 2.0 g ZVI/g TS total solids (TS) with 0.5 g PS/g. However, characteristics of aerobically digested sludge could be distinctive from that of WAS. Especially, extracellular polymeric substances (EPS) fractions were altered during aerobic digestion, which were critical for sludge dewatering (Liu and Fang, 2003). Therefore, the effect of PS-ZVI conditioning technique on the dewaterability of aerobically digested sludge needs to be studied separately.

This study aims to evaluate the feasibility of improving dewatering performance of aerobically digested sludge by PS-ZVI treatment. The CST of the aerobically digested sludge was compared before and after PS-ZVI treatment, regarded as an indicator for the dewaterability of sludge. The effect of PS-ZVI treatment on the EPS and flocs characteristics of the aerobically digested sludge was also studied. The ZVI recovery after the treatment was evaluated and economic benefits of the PS combined ZVI conditioning was also discussed. To best of our knowledge, it is the first investigation on the dewaterability of aerobically digested sludge treated through PS-ZVI conditioning.

2. Material and methods

2.1 Aerobically digested sludge and chemicals

The aerobically digested sludge was obtained from a lab-scale aerobic digester treating WAS produced from a WWTP for domestic wastewater treatment (Shanghai, China) (Dong et al., 2019). The sludge retention time (SRT) of the aerobic digester was 15 days and the dissolved oxygen in the reactor was above 4 mg/L. The main properties of the aerobically digested sludge were as follows: pH 6.84; TS 26.1 ± 0.1 g/L; volatile solids (VS): 16.5 ± 0.1 g/L; water content 97.4%, total oxygen demand (TCOD) 23306.7 ± 358.4 mg/L; soluble oxygen demand (SCOD) 1127.3 ± 90.9 mg/L; dissolved iron 1407.6 ± 56.5 mg/L; CST 119.1 ± 4.0 s.

Analytical grade of potassium persulfate (>99.0%, Sinopharm Chemical Regent Co. Ltd) and ZVI powder (Alfa-Aesar Co.) with the size of 200 meshes were used for the sludge treatment tests.

2.2 Sludge conditioning experiments

Batch experiments (Test I and Test II) were conducted to study effects of ZVI and PS concentrations on the dewaterability of aerobically digested sludge, respectively. The experimental conditions of each set of tests were summarized in Table 1. Batch test I was designed to investigate the effect of ZVI concentrations (range: 0-0.5 g/g TS), with the PS concentration kept at 0.5 g/g TS. Batch test II evaluated the effect of PS concentrations (range: 0-0.4 mg/g TS), with the ZVI concentration being constant at 0.05 g/g TS (the minimum concentration achieving the highest CST reduction indicated by the result of Batch test I). All tests were carried out in triplicate in this work.

During each test, 100 ml of aerobically digested sludge was transferred into a glass flask of 200 ml. Then, different combinations of PS and ZVI were added to the flasks to achieve their concentrations as described in Table 1. Afterwards, all flasks were moved to an orbital shaker and mixed at the 100 rpm for 30 min. The pH was uncontrolled during the conditioning experiment, as the preliminary tests showed that the PS-ZVI treatment would not significantly affect the pH of the sludge. The CSTs of the sludge

were then measured with the method as described below (Section 2.4). Meanwhile, the residual undissolved ZVI were separated from the sludge by the force of the magnetic stirrer bar. A magnetic bar was placed in each flask and was consequently rotated by a magnetic stirrer at 200 rpm for 5 mins. The saturated magnetization was 400KA/m for ZVI recovery. The magnetic bar was then removed from the flask and the undissolved ZVI attached on the magnetic bar was washed off. This procedure was repeated for three times to ensure the maximum ZVI recovery. The iron concentrations of both untreated aerobic digested sludge and ZVI-recovered sludge were measured with the method as described below (Section 2.4).

The improvement of sludge dewaterability was reflected by CST reduction ratio r_{CST} (%), which is calculated according to Equation (3)

$$r_{CST} (\%) = \frac{CST_0 - CST_a}{CST_0} \times 100\% \quad (3)$$

Where CST_a is the CST of the PS-ZVI treated sludge (s) and CST_0 is the CST of the original aerobically digested sludge (s).

The iron concentration dissolved from ZVI (ZVI_{dis}) and the recovery of the ZVI (ZVI_r) were determined according to Equation (4) and Equation (5), respectively.

$$ZVI_{dis} = Iron_a - Iron_0 \quad (4)$$

$$ZVI_r (\%) = \frac{Iron_0 + ZVI_0 - Iron_a}{ZVI_0} \times 100\% \quad (5)$$

Where, $Iron_a$ is the iron concentration in ZVI-recovered sludge (mg/L); $Iron_0$ means the iron concentration in the untreated aerobic digested sludge (mg/L); ZVI_0 is the ZVI used for sludge treatment (mg/L).

2.3 EPS extraction and characterization

To investigate the effect of PS-ZVI conditioning on the EPS of the aerobically digested sludge, the EPS were extracted from PS-ZVI treated sludge (0.1 g PS/g TS and 0.05g ZVI/g TS) and untreated aerobically digested sludge for further composition analysis and characterization.

The EPS of the sludge were extracted using a heat extraction method (Dai et al., 2017; Li and Yang, 2007). 50 ml of the sludge sample was firstly centrifuged at 4000g and 4 °C for 15 min. The settled sludge was then re-suspended in 15 mL of the sodium chloride (NaCl) solution (0.05% w/w). The mixture was then diluted with the 0.05% NaCl solution of the same concentration to the volume of 50 mL. The NaCl solution used for dilution was pre-heated to 70 °C to make sure that the suspension of the sludge reached a temperature of 50 °C. The sludge suspension was then vortexed for 1 min without any delay, followed by centrifugation at 4000g for 15 min. The organics in the supernatant was collected, regarded as the loosely bounded EPS (LB-EPS) of the biomass. Afterwards, the sludge pellet was diluted and re-suspended in 0.05% NaCl

solution to a volume of 50 ml. The suspension was heated up to 60 °C for 30 min in a water bath, and was then centrifuged at 4000g for 15 min. The supernatant was collected, which was regarded as the tightly bounded EPS (TB-EPS). After filtrated through a 0.45 µm microfiber filter, the LB-EPS and TB-EPS extractions were analyzed for protein, carbohydrate and humic acids-like compounds (HAs) compositions and Excitation–emission matrix (EEM) fluorescence spectra according to the methods described in Section 2.4

2.4 Aerobically digested sludge flocs characterization

The change in the flocs properties of the aerobic digestion sludge is also important for the improvement of the dewaterability. Therefore, the effect of PS-ZVI treatment on sludge flocs was investigated by comparing the key sludge characteristics with and without PS-ZVI treated sludge (0.1 g PS/g TS and 0.05g ZVI/g TS). The TCOD and SCOD concentrations, bound water contents, zeta potentials and the particle size distributions of the untreated and treated sludge were measured and compared using the methods described below.

2.5 Analytical methods

The CST of the sludge was measured using a capillary suction time apparatus (Type 304B, Triton Electronics, UK). The sludge was added into a stainless-steel funnel above a filter paper. The time required for the free water in the tested sludge to permeate the

filter paper was determined as CST. The concentration of iron in the sludge was measured using Inductive Coupled Plasma coupled with Optical Emission Spectroscopy (ICP-OES) (Sun et al., 2015b). The sludge samples were firstly digested by a mixture of 70% nitric acid (HNO_3), 40% hydrofluoric acid (HF) and 70% perchloric acid (HClO_4) for 8h. The TCOD, SCOD, TS and VS concentrations of the sludge were measured with standard methods (Sun et al., 2015a; Wang et al., 2017).

The polysaccharide contents in the EPS were analyzed using the Anthrone method with glucose as a standard (Qian et al., 2016). Proteins and HAS were determined using the modified Lowry method with bovine serum albumin (BSA, Beijing Aoboxing Biotechnology Co., Ltd., China) and HAS (Sigma, USA) as standards, respectively (Frølund et al., 1995). The Excitation–emission matrix (EEM) fluorescence spectra of the extracted EPS were obtained using a Luminescence Spectrometry (F-4500 FL Spectrofluorimeter, Hitachi, Japan). All samples were filtered with a 0.45- μm membrane before the analysis and 10 mL sample volumes were used for the EEM spectra. EEM were constructed for each sample over excitation wavelengths between 240–550 nm in 5 nm intervals and emission wavelengths between 260–550 nm in 2 nm intervals, with 10 nm and 5 nm bandwidths on excitation and emission modes, respectively. The software Origin 8.0 (Origin Lab Inc., USA) was employed to handle the EEM data.

The bound water of the sludge was determined by the combination use of differential

scanning calorimetry (DSC, TAQ2000, TA Co., USA) and thermo gravimetric analyzer (TGA, TGA5500, TA Co., USA), according to the method described by He et al. (2015). The zeta potential of the sludge was measured using a zeta potential Nanosizer ZS instrument (Malvern Co.,UK) and the particle size distribution was determined with a laser diffraction particle size analyser (Mastersizer 3000 ,Malvern).

3 Results and Discussion

3.1 Effect of the ZVI concentration on aerobically digested sludge dewaterability

The effect of the ZVI concentration on the dewaterability of aerobically digested sludge was presented in Figure 1. The CST of the sludge decreased substantially from 113.8 ± 7.3 s to 22.8 ± 0.7 s with the increasing ZVI concentrations from 0 to 0.05 g/g TS and PS concentration maintained at 0.5 g/g TS, and the CST reduction increased from ~4% to 81%, correspondingly. This suggested that dewaterability of the aerobically digested sludge could be significantly improved with increasing ZVI concentrations when PS was present. This could be due to that a higher ZVI concentration could lead to a larger contact surface between PS and ZVI particle. As a result, more Fe^{2+} could be produced (Equation (1)) and the sulfate radicals generation (Equation (2)) could be promoted (See section 3.4). The generated sulfate radicals would then react with the sludge flocs to produce free water from bound water, and consequently, the dewaterability of the aerobically digested sludge was improved (Zhen et al., 2012). However, the dewaterability was not further improved when the concentration of ZVI

further increased from 0.05 to 0.5 g/g TS. This could probably be attributed to the competition of the reaction between Fe^0 and Fe^{2+} with PS. As the redox potential of $\text{Fe}^{2+}/\text{Fe}^0$ ($E^0 = -0.447$ V) was much lower than that of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^0 = 0.771$ V), the Fe^0 would be more easily to be oxidized by PS than Fe^{2+} (Schüring et al., 2000). Thus, the excessive ZVI addition generated more non-oxydic sulfate ions (SO_4^{2-}), and consequently, the generation of sulfate radicals ($\text{SO}_4^\bullet$) might be limited.

3.2 Effect of the persulfate concentration on aerobically digested sludge dewaterability

The effect of the PS concentrations on the dewaterability of aerobically digested sludge was investigated with the ZVI concentration kept at 0.05 g/g TS, which was the minimum ZVI dosage to achieve the highest improvement of aerobically digested sludge dewaterability as shown in Figure 1. Figure 2 presented that the CST of the aerobically digested sludge decreased significantly from 102.8 ± 2.3 s to 21.9 ± 1.4 s with the PS concentration increasing from 0 to 0.1 g/g TS. Correspondingly, CST reduction ratio increased from around 13% to 82%. This result demonstrated that a high PS concentration would be beneficial to the dewaterability of the aerobically digested sludge. However, it is worthwhile to note that PS concentration further increasing from 0.1 to 0.4 g/g TS would no longer enhance the sludge dewaterability. This might be attributed to slow release of Fe^{2+} due to the rapid surface inactivation as well as the slow surface corrosion of ZVI particles. It has also been found that the oxidation of organic G

was hampered by the Fe^{2+} releasing in PS-ZVI system (Xiong et al., 2014).

3.3 Change of EPS characteristics of aerobically digested sludge with persulfate-ZVI treatment

3.3.1 Effect of persulfate-ZVI treatment on EPS compositions

The EPS contents in the sludge were proven to have a strong correlation with the dewaterability of the sludge as it bounded a large volume of water within the sludge flocs and exert the determinate effect on the stability of microbial aggregation. (Zhang et al., 2016). Figure 3 compares the fractions of proteins, polysaccharides and HAs in the bounded EPS of the aerobically digested sludge with and without PS-ZVI treatment. The total contents of proteins and HAs in the bounded EPS both decreased significantly after the pretreatment, with the protein decreasing for 61% (from 13.7 mg/gVS to 5.3 mg/gVS) and the HAs decreasing for 53% (from 14.8 mg/gVS to 6.9 mg/gVS), respectively. The contents of polysaccharides declined less significantly for 32%, i.e., from 4.1 mg/gVS in the untreated sludge to 2.8 mg/gVS in the PS-ZVI pretreated sludge. The significant decrease in the EPS contents suggested the capability of sulfate radical in oxidation various polymers and destroying the major hydrophilic substances in the aerobically digested sludge, which consequently reduced the water-holding capability of flocs and facilitated the release of bound water. The PS-ZVI pretreatment was proven to be more effectively in damaging the extracellular proteins than polysaccharide and HAs. This is favorable for enhancing sludge dewaterability because

extracellular proteins was considered more important in holding bound water, as they comprise the major hydrophilic groups in the sludge (Wu et al., 2017).

The fractions of differently bonded EPS, i.e. LB-EPS and TB-EPS in PS-ZVI pretreated sludge and untreated sludge were also compared in Figure 3. It shows that, the proteins, polysaccharides and HAs in TB-EPS in the aerobically digested sludge substantially decreased after PS-ZVI treatment. The reduction of protein, polysaccharide and HAs were 11.3 mg/gVS, 2.9 mg/g VS and 11.2 mg/gVS respectively. In contrast, the PS-ZVI treatment resulted in increases in proteins, polysaccharides and HAs in the LB-EPS. The proteins increased from 0.4 mg/gVS to 1.7 mg/gVS, and the fraction of polysaccharides and HAs increased from 0.5 mg/gVS to 2.1 mg/gVS and from 0.9 mg/gVS to 4.2 mg/gVS, respectively. The different effect of PS-ZVI pretreatment on LB-EPS and TB-EPS probably due to the transfer from TB-EPS to LB-EPS caused by advanced oxidation processes (Ye et al., 2012). It is likely that the produced sulfate radicals in the PS-ZVI system damaged the adherence between the TB-EPS and the cell walls in the aerobically digested sludge flocs, and more LB-EPS were produced consequently.

The result of this study suggested that TB-EPS played an important role in increasing dewaterability of the aerobically digested sludge. The decrease of TB-EPS observed in this study in accordance with the that reported by Zhen et al (2012), who found that the TB-EPS in the WAS was also decreased with the increase of sludge dewaterability after

Fe(II)-activated PS oxidation. However, some other studies suggested that LB-EPS were more influential to water separation from the sludge than TB-EPS (Dai et al., 2018; Li and Yang, 2007). This could be partially due to different EPS extraction methods and sludge treatment methods were applied in these studies. In addition, the characteristics of the aerobically digested sludge investigated in this study were different from that of WAS in the studies mentioned above. The EPS compositions and floc structures could be significantly changed after aerobic digestion (Liu and Fang, 2003). As a result, the role of different EPS fractions on the sludge dewaterability could be different. The accumulation of LB-EPS in the aerobically digested sludge indicated that the PS-ZVI conditioning could not fully unbind or mineralize the organic compounds in the bounded EPS. However, the increase of protein, polysaccharide and HAs in the LB-EPS did not resulted in the deterioration of the dewaterability of the aerobically digested sludge. This is possibly because that the LB-EPS in the aerobically digested sludge only accounted for a low proportion and the increase was insignificant to bounded water release as more TB-EPS have been broken down (Figure 3).

3.3.2 EEM fluorescence spectra of EPS

EEM fluorescence spectroscopy was applied to characterize the fluorescence compounds in different factions of EPS and further reveal mechanisms responsible for the enhanced dewaterability. The EEM fluorescence spectra of LB-EPS and TB-EPS in PS-ZVI treated aerobically digested sludge and untreated sludge were compared in

Figure 4. As shown in Figure 4 (A) and (C), three main peaks could be identified in the spectra of LB-EPS and TB-EPS in untreated aerobically digested sludge. The first peak was located at the excitation/emission wavelengths (Ex/Em) of around 280/350–370 nm (Peak A), which referred to fluorescence of tryptophan and protein-like substances (Mayer et al., 1999; Sheng and Yu, 2006). The other two peaks were identified at Ex/Em of about 275/450–460 (Peak B) and 360/440–450 (Peak C) and they were regarded as fluorescence of fulvic acid and humic acid-like compounds (Chen et al., 2003).

After PS-ZVI pretreatment, the fluorescence intensity of fulvic acid and humic acid-like compounds (Peak B and Peak C) increased significantly in the LB-EPS of the aerobically digested sludge (Figure 4B). This is consistent with the observation that PS-ZVI pretreated aerobically digested sludge had more HAs in LB-EPS than the untreated sludge (Figure 3). Also, slight red shifts were found in the Peak B and Peak C after PS-ZVI pretreatment, which indicated an increase of hydroxyl, carbonyl, alkoxy, and amino groups in fluorophores (Chen et al., 2003; Liu et al., 2011). However, the intensity of fluorescence Peak A did not enhance after PS-ZVI pretreatment, although the proteins in LB-EPS were increased (Figure 3). This could probably due to that some other protein-like compounds were not included in the fluorescence spectra investigated in this study. For example, the aromatic proteins were excited by the wavelength of about 220 nm (Chen et al., 2003; Zhen et al., 2012), which was less than the minimum excitation wavelength (240 nm) applied in this study. In contrast, fluorescence intensity

of all peaks in TB-EPS reduced drastically after PS-ZVI pretreatment, which agreed with the reduction of protein and HAs in TB-EPS of the aerobically digested sludge after treated by PS-ZVI. The most significant fluorescence intensity reduction was observed in the peak of tryptophan and protein-like substances, indicating such compounds in TB-EPS were critical for the dewaterability of aerobically digested sludge.

3.4 Effect of persulfate-ZVI treatment on floc characteristics of aerobically digested sludge

The effect of PS-ZVI treatment on sludge floc characteristics, including COD concentration, bound water content, zeta potential and particle size distribution were presented in Figure 5. The result shows that the TCOD concentration was kept stable after the conditioning, while a slight increase was observed in SCOD concentration of the sludge. The result shows that the TCOD concentration was kept stable after the conditioning, while a slight increase was observed in SCOD concentration of the sludge. The increase of SCOD concentration could be a result of release of intercellular substances such as EPS, which is consistent with the decrease in EPS fractions of the sludge as discussed in Section 3.3.1. The increase of SCOD concentration was commonly occurred when using advanced oxidation methods for sludge conditioning (Ning et al., 2014; Zhen et al., 2018). However, in our study the increase in SCOD concentration only account for ~1% of the TCOD concentration, which would not

significantly affect the stability of the aerobically digested sludge. In fact, the released SCOD would be mainly remained in the water phase after the dewatering processes. As a result, with the enhanced dewatering performance, the organic matter in the sludge cake for final disposal would slightly decrease.

As shown in Figure 5A, the bound water content of the sludge decreased by ~20% after the treatment. This result further confirmed that PS-ZVI conditioning could effectively reduce the water-holding capability of aerobically digested sludge flocs, leading to the enhancement of sludge dewaterability. In addition, the zeta potential of the sludge significantly increased from - 4.80 mV to 0.15 mV after PS-ZVI treatment. The increase of zeta potential could be explained by the disintegration of EPS (Figure 3), which mainly contained negative charges. The zeta potential after PS-ZVI treatment detected in this study was close to zero, indicating that the negative charges in the sludge were just neutralized. This was believed being favorable for achieving good dewatering performance (Dai et al., 2018).

The particle sizes of the aerobically digested sludge slightly reduced after the PS-ZVI conditioning as presented in Figure 5B. The median particle size (dp50) and effective size (dp10) were decreased from 32.1 μm to 31.3 μm and from 10.9 μm to 10.2 μm , respectively. Also, the sludge flocs with particle sizes over 400 μm became negligible after PS-ZVI treatment. The result indicated that PS-ZVI treatment might broke up the

rigid gel-networks surrounding the sludge and destabilized the sludge floc structure. Similar results were also reported by other researchers, who applied advanced oxidation techniques for sludge conditioning (Kim et al., 2016; Ning et al., 2014). The destruction of the sludge structure, accompanied with the decrease in particle size, might create more passages for water removal and liberate the cells and water trapped within the sludge (Zhen et al., 2018). As a consequent, the dewaterability of the aerobically digested sludge could be enhanced.

3.5 Iron release and recovery of ZVI in the persulfate-ZVI conditioning system

The effect of ZVI and PS dosage on the iron release from ZVI particles and ZVI recovery were presented in Figure 6. The dissolved iron released from ZVI increased gradually from 0.006 g/gTS to 0.106 g/gTS with the ZVI dosage increasing from 0.01 g/gTS to 0.5 g/gTS and PS being maintained at 0.5g/g TS (Figure 6A). Accordingly, the recovery percentage of ZVI was remained about 45% when the ZVI dosage increased from 0.01 g/gTS to 0.1 g/gTS and it gradually climbed to 80% when ZVI dosage reached 0.5 g/gTS. This indicated that when ZVI dosage became higher, the iron release was limited by the PS concentration and the ZVI recovery increased accordingly. On the other hand, the increase of PS dosage from 0.01 g/gTS to 0.4 g/gTS with ZVI dosage kept at 0.05 g/gTS led to the increase of iron release (from 0.01 g/gTS to 0.025 g/gTS) but the decrease of ZVI recovery percentage (from 75% to 50%) (Figure 6B). This could be explained by that more ZVI was oxidized at a higher PS dosage and its

recovery consequently became lower. In this study, the ZVI recovery was in the range of about 45% - 80%, depending on the ratio of ZVI and PS dosage. This indicated that ZVI could be recycled when applying the PS-ZVI conditioning and the proposed technique could achieve substantial cost savings when enhancing dewaterability of aerobically digested sludge.

3.6. A potential persulfate-ZVI conditioning technique for enhancing dewaterability of aerobically digested sludge

This work demonstrated that PS-ZVI pretreatment could effectively improve dewaterability of aerobically digested sludge. The bounded EPS in the aerobically digested sludge, especially the proteins in the TB-EPS, were largely damaged by the PS-ZVI treatment, releasing the bound water from the sludge flocs.

Aerobic digestion was a commonly used method for sludge treatment in decentralized WWTPs with small scale to achieve sludge stabilization and reduction (Wang and Yuan, 2015). The PS-ZVI conditioning approach proposed in this study could facilitate the dewatering of the aerobically digested sludge. The enhanced sludge dewaterability would lead to a reduction in the volume of dewatered sludge cakes and consequently reduce the cost of sludge disposal. The proposed PS-ZVI conditioning combined with aerobic digestion for sludge stabilization and reduction in decentralized WWTP were shown in Figure 7. By adding a tiny conditioning reactor, the sludge after aerobic

digestion undergoes the PS-ZVI treatment and the treated sludge with improved dewaterability is further delivered for the dewatering process. The excess ZVI particles could be easily recovered using magnetic force. For example, Zanetti and Godio demonstrated that ZVI could be separated from the sludge by applying the electromagnets, which is utilized widely for iron recycling from the waste (Zanetti and Godio, 2006). The cost of PS-ZVI treatment and classical Fenton treatment for aerobically digested sludge conditioning were estimated and compared using a desktop scaling-up study in a WWTP with a population equivalent of 100,000 (Table S1, Supporting Information (SI)). The result suggested that the PS-ZVI conditioning could save up to 19 % of the cost compared with the classical Fenton conditioning. However, it should be noted that this is only a proof-of-concept study and the plant-scale tests are needed to better assess the proposed conditioning technique in future.

In practice, the approaches of sludge final disposal vary in many countries, which include incineration, agricultural use, composting and so on (Foladori et al., 2010). However, the proposed PS-ZVI conditioning would not have significant impact on the choice of sludge disposal. The PS and dissolved iron would be primarily in forms of sulfate and ferric in the aerobically digested sludge after the treatment. These un-harmful ions could be easily dissolved and largely removed through sludge dewatering (Sun et al., 2017). Thus, the proposed PS-ZVI conditioning technique was unlikely to introduce harmful compounds to sludge, which also supported the ecological

feasibility of the proposed method. On the other hand, the water generated by sludge dewatering was usually recycled to the beginning of the WWTP and concentrations of sulfate and iron could be largely diluted by the WWTP influent, as this part of water usually only accounted for approximately 1% of total flow in a WWTP (Van et al., 2001). Therefore, the PS-ZVI conditioning technique would not lead to any adverse impact on the mainstream wastewater treatment, which further supported the sustainability and of the method.

In this study, the highest CST reduction was around 80%. However, it should be noted that the aim of this study was to evaluate the feasibility of improving the dewaterability of aerobically digested sludge through PS-ZVI conditioning, while the optimization of the proposed technique was not included in this study. The optimizations of PS and ZVI dosage, ZVI particle size, reaction time, and other operational parameters are worthy to be investigated in future. It is possible that with the optimization, a better enhancement in the dewaterability of aerobically digested sludge could be achieved. It is also possible that special floc structure and EPS compositions of the aerobically digested sludge restrained further improvement of the dewaterability. Studies have been proven that the oxidation efficiency of PS-ZVI system could be improved by applying weak magnetic field on the system or using pre-magnetization ZVI (Pan et al., 2016; Xiong et al., 2014). These approaches are also worthy to be included in the future investigation in order to further improve the dewaterability of the aerobically digested sludge.

483

484 **4. Conclusions**

485 Aerobic digestion followed by dewatering is a commonly used method for sludge
486 stabilization and reduction in decentralized wastewater treatment plant with small scales.

487 In this study, the feasibility of enhancing dewaterability of the aerobically digested
488 sludge by persulfate (PS) and zero valent iron (ZVI) conditioning was evaluated and
489 following conclusions could be drawn:

- 490 • The PS-ZVI conditioning approach could effectively enhance the dewaterability of
491 the aerobically digested sludge. The reduction of capillary suction time could
492 reach >80% under the tested treatment conditions.
- 493 • PS-ZVI treatment could reduce the proteins, polysaccharides and humic acids-like
494 compounds in the tightly bounded extracellular polymeric substances of the
495 aerobically digested sludge, resulted in the release of bound water in sludge flocs.
- 496 • The proposed PS-ZVI conditioning combined with aerobic digestion was proven to
497 be a sustainable approach for sludge treatment for decentralized WWTPs as the
498 ZVI particles could be recovered and no adverse effect would be induced for
499 mainstream wastewater treatment. By applying this approach, the cost for sludge
500 disposal could be effectively reduced.

501

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References

- Buyukkamaci, N., 2004. Biological sludge conditioning by Fenton's reagent. *Process Biochem* 39(11), 1503-1506.
- Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ Sci Technol* 37(24), 5701-5710.
- Dai, Q., Ma, L., Ren, N., Ning, P., Guo, Z., Xie, L., Gao, H., 2018. Investigation on extracellular polymeric substances, sludge flocs morphology, bound water release and dewatering performance of sewage sludge under pretreatment with modified phosphogypsum. *Water Res* 142, 337-346.
- Dai, X., Hu, C., Zhang, D., Chen, Y., 2017. A new method for the simultaneous enhancement of methane yield and reduction of hydrogen sulfide production in the anaerobic digestion of waste activated sludge. *Bioresource Technol* 243, 914-921.
- Dong, B., Xia, Z., Sun, J., Dai, X., Chen, X., Ni, B.-J., 2019. The inhibitory impacts of nano-graphene oxide on methane production from waste activated sludge in anaerobic digestion. *Sci Total Environ* 646, 1376-1384.
- Foladori, P., Andreottola, G., Ziglio, G., 2010. Sludge Reduction Technologies in Wastewater Treatment Plants. *Water Intelligence Online*.
- Frølund, B., Griebe, T., Nielsen, P.H., 1995. Enzymatic activity in the activated-sludge floc matrix. *Applied Microbiology & Biotechnology* 43(4), 755-761.
- He, D.-Q., Wang, L.-F., Jiang, H., Yu, H.-Q., 2015. A Fenton-like process for the enhanced activated sludge dewatering. *Chem Eng J* 272, 128-134.
- 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. *Environ Sci Technol* 50(13), 7106-7115.
- Kuutti, L., Haavisto, S., Hyvarinen, S., Mikkonen, H., 2011. Properties and flocculation efficiency of cationized biopolymers and their applicability in papermaking and in conditioning of pulp and paper sludge. *Bioresources* 6(3), 2836-2850.
- Li, X.Y., Yang, S.F., 2007. Influence of loosely bound extracellular polymeric substances (EPS) on the flocculation, sedimentation and dewaterability of activated sludge. *Water Res* 41(5), 1022-1030.

- 540 Liang, C., Bruell, C.J., Marley, M.C., Sperry, K.L., 2004. Persulfate oxidation for in situ
541 remediation of TCE. II. Activated by chelated ferrous ion. *Chemosphere* 55(9),
542 1225-1233.
- 543 Liang, C., Guo, Y.Y., 2010. Mass transfer and chemical oxidation of naphthalene
544 particles with zerovalent iron activated persulfate. *Environ Sci Technol* 44(21),
545 8203-8208.
- 546 Liu, T., Chen, Z.L., Yu, W.Z., You, S.J., 2011. Characterization of organic membrane
547 foulants in a submerged membrane bioreactor with pre-ozonation using
548 three-dimensional excitation-emission matrix fluorescence spectroscopy. *Water Res*
549 45(5), 2111-2121.
- 550 Liu, Y., Fang, H.H.P., 2003. Influences of Extracellular Polymeric Substances (EPS) on
551 Flocculation, Settling, and Dewatering of Activated Sludge. *Crit Rev Env Sci Tec* 33(3),
552 237-273.
- 553 Liu, Y., Gao, M., Zhang, A., Liu, Z., 2017. Strengthen effects of dominant strains on
554 aerobic digestion and stabilization of the residual sludge. *Bioresource Technol* 235,
555 202-210.
- 556 Luo, J., Chen, Y., Feng, L., 2016. Polycyclic Aromatic Hydrocarbon Affects Acetic Acid
557 Production during Anaerobic Fermentation of Waste Activated Sludge by Altering
558 Activity and Viability of Acetogen. *Environ Sci Technol* 50(13), 6921-6929.
- 559 Mayer, L.M., Schick, L.L., Iii, T.C.L., 1999. Dissolved protein fluorescence in two
560 Maine estuaries. *Mar Chem* 64(3), 171-179.
- 561 Murthy, S.N., Novak, J.T., 1999. Factors Affecting Floc Properties during Aerobic
562 Digestion: Implications for Dewatering. *Water Environ Res* 71(2), 197-202.
- 563 Ning, X.-a., Chen, H., Wu, J., Wang, Y., Liu, J., Lin, M., 2014. Effects of ultrasound
564 assisted Fenton treatment on textile dyeing sludge structure and dewaterability. *Chem*
565 *Eng J* 242, 102-108.
- 566 Novak, J.T., Sadler, M.E., Murthy, S.N., 2003. Mechanisms of floc destruction during
567 anaerobic and aerobic digestion and the effect on conditioning and dewatering of
568 biosolids. *Water Res* 37(13), 3136-3144.
- 569 Pan, Y., Zhou, M., Li, X., Xu, L., Tang, Z., Sheng, X., Li, B., 2016. Highly efficient
570 persulfate oxidation process activated with pre-magnetization Fe 0. *Chem Eng J* 318.
- 571 Qian, X., Wang, Y., Zheng, H., 2016. Migration and distribution of water and organic
572 matter for activated sludge during coupling magnetic conditioning–horizontal
573 electro-dewatering (CM–HED). *Water Res* 88, 93-103.
- 574 Ruiz-Hernando, M., Simón, F.X., Labanda, J., Llorens, J., 2014. Effect of ultrasound,
575 thermal and alkali treatments on the rheological profile and water distribution of waste
576 activated sludge. *Chem Eng J* 255(7), 14-22.
- 577 Schüring, J., Schulz, H.D., Fischer, W.R., Böttcher, J., Duijnisveld, W.H.M., 2000.
578 Redox: Fundamentals, Processes and Applications. Springer.
- 579 Sheng, G.P., Yu, H.Q., 2006. Characterization of extracellular polymeric substances of
580 aerobic and anaerobic sludge using three-dimensional excitation and emission matrix
581 fluorescence spectroscopy. *Water Res* 40(6), 1233-1239.

- Song, K., Zhou, X., Liu, Y., Xie, G.J., Wang, D., Zhang, T., Liu, C., Liu, P., Zhou, B., Wang, Q., 2016. Improving dewaterability of anaerobically digested sludge by combination of persulfate and zero valent iron. *Chem Eng J* 295, 436-442.
- Sun, J., Dai, X., Liu, Y., Peng, L., Ni, B.-J., 2017. Sulfide removal and sulfur production in a membrane aerated biofilm reactor: Model evaluation. *Chem Eng J* 309, 454-462.
- Sun, J., Hu, S., Sharma, K.R., Bustamante, H., Yuan, Z., 2015a. Impact of reduced water consumption on sulfide and methane production in rising main sewers. *J Environ Manage* 154, 307-315.
- Sun, J., Pikaar, I., Sharma, K.R., Keller, J., Yuan, Z., 2015b. Feasibility of sulfide control in sewers by reuse of iron rich drinking water treatment sludge. *Water Res* 71, 150-159.
- Van, D.U., Jetten, M.S., van Loosdrecht, M.C., 2001. The SHARON-Anammox process for treatment of ammonium rich wastewater. *Water Science & Technology A Journal of the International Association on Water Pollution Research* 44(1), 153.
- Wang, Q., 2017. A Roadmap for Achieving Energy-Positive Sewage Treatment Based on Sludge Treatment Using Free Ammonia. *Acs Sustainable Chemistry & Engineering* 5(11).
- Wang, Q., Duan, H., Wei, W., Ni, B.-J., Laloo, A., Yuan, Z., 2017. Achieving Stable Mainstream Nitrogen Removal via the Nitrite Pathway by Sludge Treatment Using Free Ammonia. *Environ Sci Technol* 51(17), 9800-9807.
- Wang, Q., Song, K., Hao, X., Wei, J., Pijuan, M., van Loosdrecht, M.C.M., Zhao, H., 2018. Evaluating death and activity decay of Anammox bacteria during anaerobic and aerobic starvation. *Chemosphere* 201, 25-31.
- Wang, Q., Yuan, Z., 2015. Enhancing aerobic digestion of full-scale waste activated sludge using free nitrous acid pre-treatment. *Rsc Advances* 5(25), 19128-19134.
- Wu, B., Ni, B.-J., Horvat, K., Song, L., Chai, X., Dai, X., Mahajan, D., 2017. Occurrence State and Molecular Structure Analysis of Extracellular Proteins with Implications on the Dewaterability of Waste-Activated Sludge. *Environ Sci Technol* 51(16), 9235-9243.
- Xiong, X., Bo, S., Jing, Z., Gao, N., Shen, J., Li, J., Guan, X., 2014. Activating persulfate by Fe 0 coupling with weak magnetic field: Performance and mechanism. *Water Res* 62(7), 53-62.
- Ye, F., Liu, X., Li, Y., 2012. Effects of potassium ferrate on extracellular polymeric substances (EPS) and physicochemical properties of excess activated sludge. *J Hazard Mater* 199-200, 158-163.
- Yu, Q., Lei, H., Yu, G., Feng, X., Li, Z., Wu, Z., 2009. Influence of Microwave Irradiation on Sludge Dewaterability. *Chem Eng J* 155(1), 88-93.
- Yu, W., Yang, J., Shi, Y., Song, J., Shi, Y., Xiao, J., Li, C., Xu, X., He, S., Liang, S., 2016. Roles of iron species and pH optimization on sewage sludge conditioning with Fenton's reagent and lime. *Water Res* 95, 124-133.
- Zanetti, M., Godio, A., 2006. Recovery of foundry sands and iron fractions from an industrial waste landfill. *Resources, Conservation and Recycling* 48(4), 396-411.

- 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. *Chem Eng J* 301, 238-248.
- Zhang, W., Yang, P., Yang, X., Chen, Z., Wang, D., 2015. Insights into the respective role of acidification and oxidation for enhancing anaerobic digested sludge dewatering performance with Fenton process. *Bioresource Technol* 181, 247-253.
- Zhang, Z., Zhou, Y., Zhang, J., Xia, S., Hermanowicz, S.W., 2016. Effects of short-time aerobic digestion on extracellular polymeric substances and sludge features of waste activated sludge. *Chem Eng J* 299, 177-183.
- Zhao, L., Ji, Y., Kong, D., Lu, J., Zhou, Q., Yin, X., 2016. Simultaneous removal of bisphenol A and phosphate in zero-valent iron activated persulfate oxidation process. *Chem Eng J* 303, 458-466.
- Zhen, G., Lu, X., Li, Y., Zhao, Y., Wang, B., Song, Y., Chai, X., Niu, D., Cao, X., 2012. Novel insights into enhanced dewaterability of waste activated sludge by Fe(II)-activated persulfate oxidation. *Bioresource Technol* 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 (Fe^{2+} vs. Fe^0) in activating persulfate-based oxidation process with implications to waste activated sludge dewaterability. *Water Res* 134, 101-114.

Table and Figure Legends

Table 1. Experimental conditions applied in the sludge treatment tests.

Figure 1. The effect of ZVI concentration on CST and its reduction ratio of aerobically digested sludge.

Figure 2. The effect of persulfate concentration on CST and its reduction ratio of aerobically digested sludge.

Figure 3. The fractions of proteins, polysaccharides and HAs in the LB-EPS and TB-EPS of the aerobically digested sludge with and without persulfate-ZVI treatment.

Figure 4. Typical EEM fluorescence spectra of different EPS fractions in aerobically digested sludge. (A) LB-EPS of untreated sludge, (B) LB-EPS of persulfate-ZVI treated sludge, (C) TB-EPS of untreated sludge, (D) TB-EPS of persulfate-ZVI treated sludge.

Figure 5. (A) Effect of persulfate-ZVI treatment on COD concentration, bound water content and zeta potential of the aerobically digested sludge. (B) Comparison of particle size distribution in the aerobically digested sludge with and without persulfate-ZVI treatment.

666 **Figure 6.** The effect of ZVI concentration (A) and persulfate concentration (B) on iron
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668

669 **Figure 7.** Conceptual diagram of the proposed persulfate-ZVI conditioning combined
670 with aerobic digestion for sludge stabilization and reduction in decentralized wastewater
671 treatment plant.

Table 1. Experimental conditions applied in the sludge treatment tests

Experimental sets	Persulfate concentration (g/gTS)	ZVI concentration (g/gTS)
(I) Effect of ZVI concentration	0.5	0
	0.5	0.01
	0.5	0.05
	0.5	0.1
	0.5	0.25
	0.5	0.5
(I) Effect of persulfate concentration	0	0.05
	0.01	0.05
	0.05	0.05
	0.1	0.05
	0.2	0.05
	0.4	0.05

Figure 1. The effect of ZVI concentration on CST and its reduction ratio of aerobically digested sludge.

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Figure 7. Conceptual diagram of the proposed persulfate-ZVI conditioning combined with aerobic digestion for sludge stabilization and reduction in decentralized wastewater treatment plant.

Highlights

- Persulfate-ZVI conditioning enhanced the dewaterability of aerobically digested sludge.
- Capillary suction time reduced by 80% at 0.05 g ZVI/g TS and 0.1 g persulfate/g TS.
- Persulfate-ZVI treatment reduced the hydrophilic organic compounds in TB-EPS.
- ZVI could be recovered and the cost for sludge disposal could be reduced.

Accepted Manuscript

Persulfate and zero valent iron combined conditioning as a sustainable technique for enhancing dewaterability of aerobically digested sludge

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Graphical Abstract