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Peroxymonosulfate versus Peroxydisulfate

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Research Article

Enhancing Volatile Fatty Acid Production during Anaerobic Fermentation of Waste Activated Sludge with Persulfates: Peroxymonosulfate versus Peroxydisulfate

Wei Fang, Xuedong Zhang, Henri Spanjers, and Tao Zhang*

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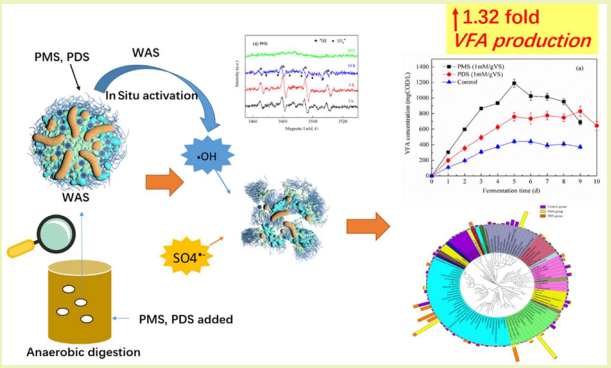
ABSTRACT: Persulfates ((peroxymonosulfate (PMS) and peroxydisulfate (PDS)) can disintegrate waste activated sludge (WAS), but their influence on volatile fatty acid (VFA) production during anaerobic fermentation is largely unclear. Particularly, it is unknown whether persulfates can improve fermentation without any preactivation. This study investigated how the direct addition of PMS and PDS into the fermenter influences VFA production from WAS, and uncovered possible mechanisms of improved VFA production. At the PMS dosage of 1.0 mM/gVS, maximum VFA yield (1025 ± 55 mg COD/L) was observed in 5 days of fermentation, which was 24% higher than that with an equimolar addition of PDS and 132% higher than that without persulfate addition. However, the cost-effectiveness of PMS in enhancing VFA production is lower than that of PDS. The in situ generated hydroxyl and sulfate radicals from persulfates in the fermenter enhanced not only WAS disintegration and solubilization but also the formation of biodegradable substances for acidification. Moreover, the direct addition of persulfates into the fermenter shifted the microbial community toward hydrolysis-acidification such as *Clostridium_sensu_stricto_10* and *Fonticella*. Results of this study also suggest that preactivation is not necessary when persulfates are applied to improve WAS fermentation.



KEYWORDS: *Waste activated sludge (WAS), Anaerobic fermentation, Volatile fatty acids, Peroxymonosulfate (PMS), Peroxydisulfate (PDS)*

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INTRODUCTION

Waste activated sludge (WAS) is the main byproduct of wastewater treatment plants (WWTPs). The large volume of WAS is a major issue to be handled in WWTPs because its management requires relatively high operation cost (up to 50% in WWTPs) and energy consumption (approximately 14%).[1] Anaerobic digestion is one of the most commonly applied approaches in WWTPs to effectively treat WAS and recover energy in the form of biogas. The biogas is a low-value product. In contrast, intermediate fermentation products such as volatile fatty acids (VFA) have higher values as stock chemicals.[2] For example, Kleerebezem et al.[3] reported that the revenue of polyhydroxyalkanoates (PHA) in the fermentative VFA is 5 times higher than that of methane produced from anaerobic digestion. The VFA production via anaerobic fermentation of WAS attracted increasing research interest in recent years.[3,4]

However, the application of anaerobic digestion or fermentation to WAS treatment is often limited by the low hydrolysis rate, which is due to the complexity of the organic matter of WAS.[5] To overcome this limitation, substantial work has been done to improve the disintegration of WAS, applying physical, chemical, biological or combined, pretreatment approaches.[6−8] According to these studies, oxidation processes generating hydroxyl radicals ($^{\bullet}OH$) are effective in destroying the complex organic matter of WAS. During the past decade, wet-oxidation, ozone, Fenton and Fenton-like processes, and UV-assisted oxidation have been investigated to improve the anaerobic biodegradability of WAS.[9−11]

Recently, sulfate radicals ($SO_4^{\bullet-}$) generated through activating persulfates (peroxymonosulfate (PMS) and peroxydisulfate (PDS)) received much attention, because $SO_4^{\bullet-}$ is a powerful and selective radical (2.5−3.1 V) with a relatively long lifetime ($t_{1/2}$ = 30−40 μs).[12] During the last several years, efforts have been made to enhance WAS disintegration and dewatering ability through persulfate activation (Liu et al.

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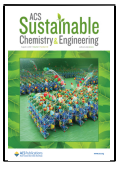

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2018[1]). It was found that more VFA was yielded from the anaerobic fermentation of WAS when pretreated with PMS at room temperature than that without PMS pretreatment.[13] For example, Yang et al. (2019) pretreated WAS by the addition of 0.09 g PMS/g TSS at room temperature for 150 min. Next, the pretreated WAS was subjected to the anaerobic fermentation to obtain a maximum VFA yield of 312 mg COD/g VSS, which was approximately 10.5 times greater than that obtained from WAS without pretreatment. It was further revealed that the free radicals, such as $SO_4^{\bullet-}$, •OH, and $^1O_2$, produced during the anaerobic fermentation promoted the sludge disintegration and improved the biodegradability of organics released, thereby providing more biodegradable substrates for subsequent VFA production. Besides, the removal of several nonbiodegradable organics in WAS such as humic substances was also contributed to the VFA production. Additionally, PMS positively enriched microbial community structure and activities of enzymes responsible for hydrolysis and VFA production.[13] It was worth notice that PMS rarely decomposes in WAS in the absence of PMS activators.[14] There will be limited decomposition of PMS during the pretreatment phase if no activator was introduced. The remaining PMS might influence VFA production during the following anaerobic fermentation phase. In the presence of activators such as iron minerals, PMS and PDS can induce cell damage and extracellular polymeric substances (EPS) decomposition.[15] In fact, if persulfates are directly introduced into the fermenter without any preactivation and reaction, it will be easy to see the direct functions of persulfates. If the direct introduction of persulfates into the fermenter works well in improving WAS disintegration and VFA production, the pretreatment step (i.e., the artificial activation of persulfate) will be unnecessary. In addition, although PDS is much cheaper than PMS ($0.74/kg vs $2.2/kg),[16] it is not as reactive as PMS due to its stable symmetric structure. Unlike those that studied PMS, few works investigated how PDS influences VFA production from WAS.

This work investigated whether and how direct introduction of PMS and PDS without any preactivation can enhance VFA production from WAS anaerobic fermentation. Specifically, the direct introduction of the two persulfates were compared for their influences on the composition and yields of VFA and volatile suspended solids (VSS). The disintegration, solubilization, and biodegradability of the WAS treated in this way were analyzed. Reactive oxidant species were identified to better understand the mechanism.

MATERIAL AND METHODS

Source of Materials. WAS used in this study was collected from a sedimentation tank of a municipal WWTP in Beijing, China. It was concentrated by settling for 24 h and then stored at 4 °C for use. The WAS has a pH of 6.9 ± 0.1, total solids (TS) of 10.9 ± 0.2 g/L, and volatile solids (VS) of 6.0 ± 0.2 g/L. The elemental composition is shown in the Supporting Information in Figure S1.

Analytical grade PMS and PDS were purchased from Sigma-Aldrich. Other chemicals were reagent grade and purchased from Sinopharm Chemical Reagent Company.

Anaerobic Fermentation of WAS. Batch tests were carried out in identical fermentative bottles with a working volume of 250 mL. Each bottle was initially fed with 200 mL of WAS and 1.0 mM/gVS of persulfate. Then, the bottles were capped and flushed with N_2 at 0.3 L/min for 5 min to remove oxygen. During anaerobic fermentation, the bottles were placed on a shaker rotating at 140 rpm, keeping the temperature at 35 ± 1 °C. Control tests without persulfate addition were also performed. All the batch tests were conducted in triplicates.

Microbial Community Analysis. Samples collected from fermenters were harvested by centrifugation and stored at −80 °C for DNA extraction. The DNA was extracted using the DNeasy UltraClean Microbial Kit (Qiagen, Hilden, Germany). The quantity and quality of extracted DNA were checked using Qubit3.0 DNA detection (dsDNA HS Assay Kit, Life Technology, USA) and agarose gel electrophoresis. The isolated DNA was subjected to a final quality check using a bioanalyzer (Agilent Technologies, Santa Clara, CA, USA), and then bacterial (V3−V4) 16S rRNA genes were amplified and subjected to high throughput sequencing using the Illumina MiSeq platform. The high-quality sequences were analyzed at NCBI Sequence Read Archive following the procedure described by Ghasimi et al.[17]

Radical Identification. Reactive radicals generated from persulfate were characterized with electron paramagnetic resonance (EPR) spectra recorded on an EMXNano electron paramagnetic resonance spectrometer (A300, Bruker, USA) after trapping with 5,5-dimethyl-1-pyrolin-*N*-oxide (DMPO). The WAS (1 mL) and DMPO (2 mL, 100 mM) were mixed and stirred in centrifuge tubes for 30 s, and then the mixture was transferred into a quartz capillary immediately. ESR parameters were set as follows: 20.004 mW of microwave power, 9.862 GHz of microwave frequency, 1.25 G of modulation amplitude, and 100 kHz of modulation frequency. The analysis of spin characters and quantification were performed using the Bruker software.

Other Analyses. Total solids (TS) and volatile solids (VS) were determined based on weight following the Standard Methods.[18] After filtration with 0.45 μm syringe filters, the samples were analyzed for soluble chemical oxygen demand (COD), volatile fatty acids (VFA), protein, and polysaccharide. Soluble COD was measured using Hach kits. VFA was measured using gas chromatography equipped with a flame ionization detector (FID) (Agilent 7890A, USA) and a DB-FFAP column (30 m × 0.25 mm × 0.25 mm). Details of VFA detection were described in one of our previous works.[19] Proteins were measured with bovine serum albumin as standards as proposed by Frølund et al.[20] Polysaccharides were quantified as glucose equivalents using the phenol−sulfuric acid method.[21]

Particle size distribution and surface area of the samples were determined using a Mastersizer 2000 particle analyzer (Malvern, UK). The elemental composition of the sludge was analyzed with an X-ray fluorescence spectrometer (XRF, Thermo, USA). Element mapping images of the sludge were obtained with a scanning electron microscope (SEM, ARM200F, Japan). The concentration of dissolved metal ions was determined with inductively coupled plasma spectrometry (ICP, Agilent 720ES, USA). Three-dimensional excitation and emission matrix fluorescence (3D-EEM) was analyzed on a luminescence spectrometer (Hitachi, Japan). The PMS concentration was determined with an ABTS colorimetric method,[22] and PDS was analyzed with iodometry.[23]

RESULTS AND DISCUSSIONS

Influence on Anaerobic Fermentation of WAS. *VFA Production.* Figure 1a shows the evolution of VFA concentration during anaerobic fermentation of WAS. The VFA concentration increased both with and without persulfate addition. A peak VFA concentration of 442 ± 21 mg COD/L was observed in 5 days without persulfate addition. The addition of PMS and PDS obviously improved VFA production all over the anaerobic fermentation. The maximum VFA concentration in the case of PMS addition was 1025 ± 55 mg COD/L on the fifth day of anaerobic fermentation, which was 132% higher than that in the absence of persulfate. This result is consistent with other studies which applied PMS for the pretreatment of WAS.[13,24] After 8 days, the VFA production significantly decreased possibly due to VFA conversion to methane.[19] Direct addition of PDS into the fermentor improved VFA production by 87.6%, but the maximum VFA yield was somewhat lower than PMS addition

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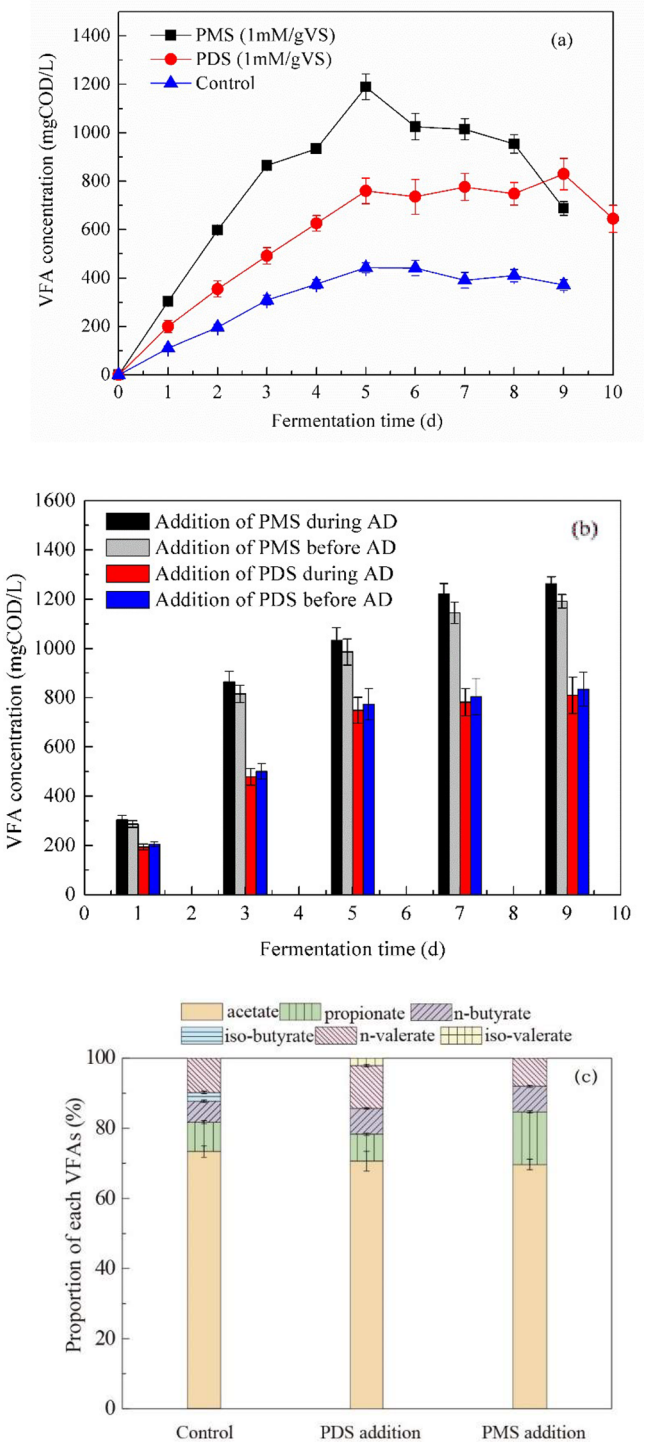

Figure 1. Influence of PMS and PDS on VFA production during anaerobic digestion: (a) VFA concentration, (b) comparison to persulfate pretreatment (PMS and PDS = 1 mM/gVS), and (c) VFA composition. Note: "iso-" and "n-" means "isomer-" and "normal-", respectively.

(829 ± 65 mg COD/L vs 1025 ± 55 mg COD/L). The peak yield of VFA in the presence of PMS occurred 4 days earlier than that of PDS, indicating that the VFA production was accelerated more significantly by PMS than by PDS. The same amounts of persulfates were also tested for the pretreatment of the sludge for 150 min before fermentation.[13] Figure 1b shows that adding persulfates before and during fermentation resulted in no significant difference in VFA production.

In terms of VFA composition, Figure 1c shows the proportion of each VFA in three tests as calculated at the maximum VFA yields. Acetate, propionate, butyrate, and valerate were all detected. Acetate was the dominant component, accounting for 73.5% ± 1.6% (in the absence of persulfate), 69.8% ± 1.3% (in the presence of PMS) and 70.8% ± 2.6% (in the presence of PDS) of total VFA production. PMS addition increased the proportion of propionate, being approximately 1.7 and 2.0 times of that without persulfate addition and with PDS addition, respectively. Meanwhile, the lowest proportion of n-valerate (7.7%) was observed with PMS addition. The results can be probably explained by reduction in chain length elongation of propionate to valerate with the addition of PMS. On the other hand, with the addition of PDS, the percentages of acetate and propionate did not change significantly compared with the control group. In contrast, Luo et al. (2020)[25] observed that the dominant VFA in the control reactor was propionate, and the addition of PMS and PDS with different metal catalysts activators into fermenters greatly improved acetate and significantly reduced the proportions of propionate. The different VFA compositions contributed to the variations of metabolic pathways and microbes by the addition of the PMS and PDS. However, detailed information regarding the influence of persulfate-assistant treatment on the pathway of VFA production is still missing, which should be further studied.

The total n-butyrate and iso-butyrate accounted for less than 8% of the total VFA yields for all the three tests. Iso-valerate composed a minor part of VFA (less than 2%) produced from the anaerobic fermentation.

Sludge Reduction. Sludge reduction by anaerobic digestion can be evaluated by VSS.[6] As measured at the end of anaerobic fermentation (on day 10), the VSS was reduced by 19.5%, 31.3%, and 28.2% without persulfate addition and with the addition of PMS and PDS, respectively. This result suggests that more organic matter of WAS was solubilized with the addition of PMS and PDS.

The VSS reduction in the presence of PMS and PDS (by 30%−50%) was comparable with conventional anaerobic digestion with and/or without pretreatment,[5,19] but the solid retention time was significantly reduced as compared with conventional anaerobic digestion (10 d vs 20−30 d). The acceleration in VSS reduction can be ascribed to the degradation of organic substances during hydrolysis and acidogenesis.[5]

Influence on WAS Hydrolysis. WAS Disintegration. The particle size distribution (PSD) of WAS usually reflects floc disintegration.[5] The PSD of the raw WAS and that collected after 24 h digestion are depicted in Figure 2a.

The size of WAS distributed in a relatively wide range of 0.1 to 1000 μm. Mikkelsen and Keiding[26] reported that the particles of WAS normally can be classified as primary particles (~2.5 μm), microflocs (~13 μm) and macro-flocs (~100 μm). In the control test, the PSD of WAS after 24 h digestion was similar to that of the raw WAS. In contrast, the size of flocs was significantly reduced upon the addition of PMS and PDS in anaerobic fermentation. Flocs with size above 100 μm disappeared in the case of PMS-assisted anaerobic fermentation, and the average size (by volume) was reduced from 50 to 10 μm. Small particles with average size of 1 μm apparently appeared. The particle median size ($D_{0.5}$) after PMS-assisted

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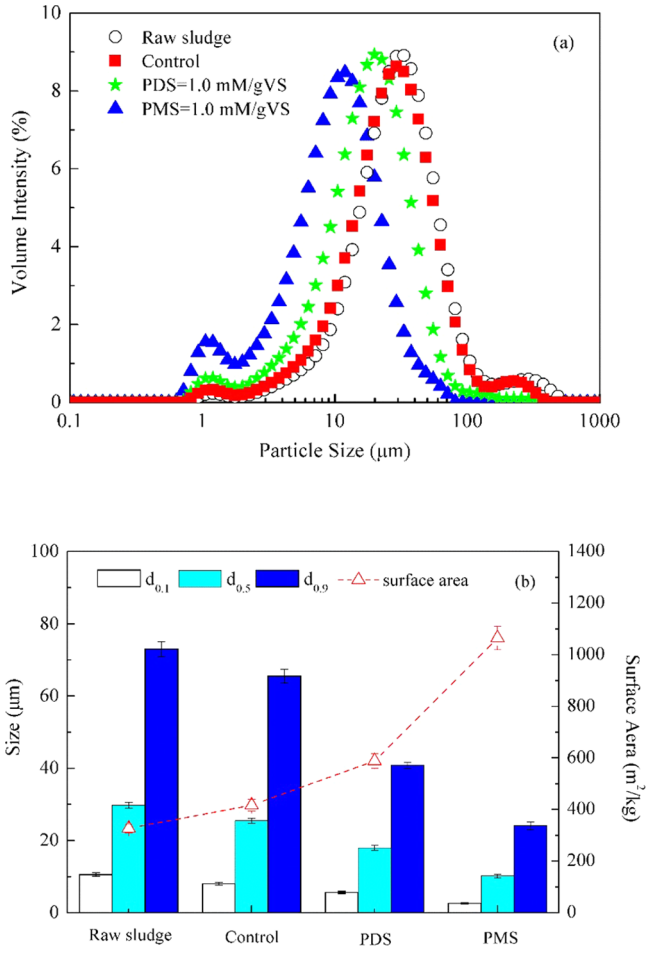

Figure 2. Influence of PMS and PDS addition on the size distribution of WAS flocs: (a) particle size distribution and (b) particle size and surface area.

fermentation was 10.2 μm, which is 39.6% and 25.1% lower than the raw sludge and the fermentation without persulfate addition (i.e., the control test), respectively. The particle size reduction of WAS upon PDS addition was less significant than that of PMS addition (Figure 2a). There was also no apparent formation of the small particles (around 1 μm) (Figure 2a).

The average surface area of WAS followed the order of PMS addition (1065 m^2/kg) > PDS addition (588.4 m^2/kg) > the control group (416.8 m^2/kg) > the raw WAS (327.1 m^2/kg) (Figure 2b and Table S1 in the Supporting Information S8). The reduction in particle size and the increase in surface area of WAS could improve the efficiency of enzymatic attack on particulate organic matter, leading to enhanced hydrolysis and biodegradation of WAS in anaerobic digestion.[5] The accelerated release of organic matter from WAS into water will provide more substrates for VFA production.[27]

Influence of Persulfate Addition on WAS Solubilization and Biodegradability. Hydrolyzing solid substrates to convert them into soluble substances is the first and the rate limiting step for anaerobic fermentation of sludge.[28] Proteins and carbohydrates are the main components of WAS, thus the increase of their concentrations in the liquid phase usually is an indicator for the extent of WAS hydrolysis.[8] As shown in Table 1, soluble proteins and carbohydrates in the supernatant increased when PMS and PDS were added. For instance, 1097 ± 22 mg COD/L of soluble protein was detected in the supernatant after 24 h PMS-assisted anaerobic fermentation, which was about 1.7 and 50 times of those detected in PDS addition and the control test, respectively. Similarly, 131 ± 3 mg COD/L of soluble carbohydrate was detected in the supernatant of PMS-assisted fermentation, which was about 2 and 6 times of those detected in PDS addition and the control test, respectively. The literature also reported higher protein production than carbohydrates in some fermentations,[29,30] which can be ascribed to the higher percentage of proteins than carbohydrates in WAS.[27]

Table 1. Soluble Protein and Carbohydrate Concentrations Observed after 24 h Fermentation

	control group	PMS-assisted	PDS-assisted
soluble proteins (mg COD/L)	22 ± 1	1097 ± 22	636 ± 29
soluble carbohydrates (mg COD/L)	22 ± 2	131 ± 3	62 ± 4
SCOD (mg/L)	217 ± 11	1767 ± 21	1486 ± 2

Figure 3 shows 3D fluorescence spectra of the supernatants obtained from the three tests. As compared to the control test, the addition of PMS and PDS increased fluorescence intensities indicating that more soluble organic matter was released into the liquid phase. This result is consistent with what was presented in Table 1. The fluorescence spectra usually can be divided into five regions, representing different fluorophores.[31] As shown in Table S2 in the Supporting Information S9, the total percentage of fluorescence corresponding to biodegradable substrates (Region I, Region II, and Region IV) in the fermenter was 66.2% for PMS addition, 71.9% for PDS addition, and 60.1% for that without persulfate addition (i.e., the control test). Correspondingly, the non-biodegradable substances such as the humic-like were largely degraded in the case of PMS and PDS addition. Previous studies confirmed that persulfates can decompose humic-like substrates due to their oxidation capability. For instance, hydroxyl and sulfate radicals were observed effective for the degradation of fulvic-like substances.[13,32] The above results suggest that the direct addition of PMS and PDS into the fermenter enhanced biodegradability of WAS.

Decomposition of Persulfate and Generation of Radicals during Anaerobic Fermentation. Generally, PMS and PDS themselves are not reactive toward WAS, only radical species generated through persulfate activation are reactive.[14] In this study, radical formation from PMS and PDS during fermentation was confirmed with electron spin resonance (ESR) spectroscopy. Figure 4 shows the signals of DMPO−OH ($\alpha^N = \alpha^H = 14.9$ G) and DMPO−SO_4^- ($\alpha^N = 13.2$ G, $\alpha^{\beta\text{-H}} = 9.6$ G, $a^{\gamma\text{-H1}} = 1.48$ G, and $\alpha^{\gamma\text{-H2}} = 0.78$ G) in the supernatant of the WAS during fermentation. These two DMPO adducts are signatures of ·OH and $SO_4^{\bullet-}$ formation during anaerobic fermentation.

In addition, the radical formation patterns for PMS and PDS were somewhat different. In the case of PMS addition, the signals of ·OH appeared in 2 h of anaerobic fermentation, and the intensities significantly increased in 9 h. As the anaerobic fermentation further proceeded, the intensity decreased and was not be obviously detected after 18 h. This result is consistent with the previous study of Yang et al.[13] who reported that no free radicals were detected after 24 h in the sludge fermenter with 0.09 g PMS/g TSS.

In contrast to that of PMS, the signals of ·OH and $SO_4^{\bullet-}$ radicals detected in PDS addition were weaker and delayed.

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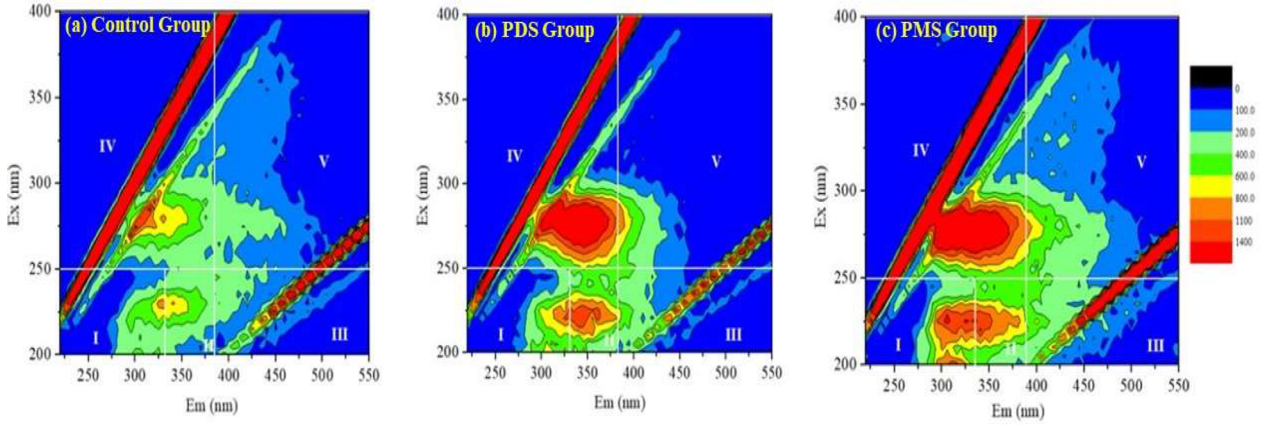

Figure 3. Fluorescence EEM spectra of the soluble organic matter of WAS after 24 h of anaerobic fermentation with (a) no persulfate addition, (b) PDS addition, (c) PMS addition. All samples were diluted by 150 times before analysis.

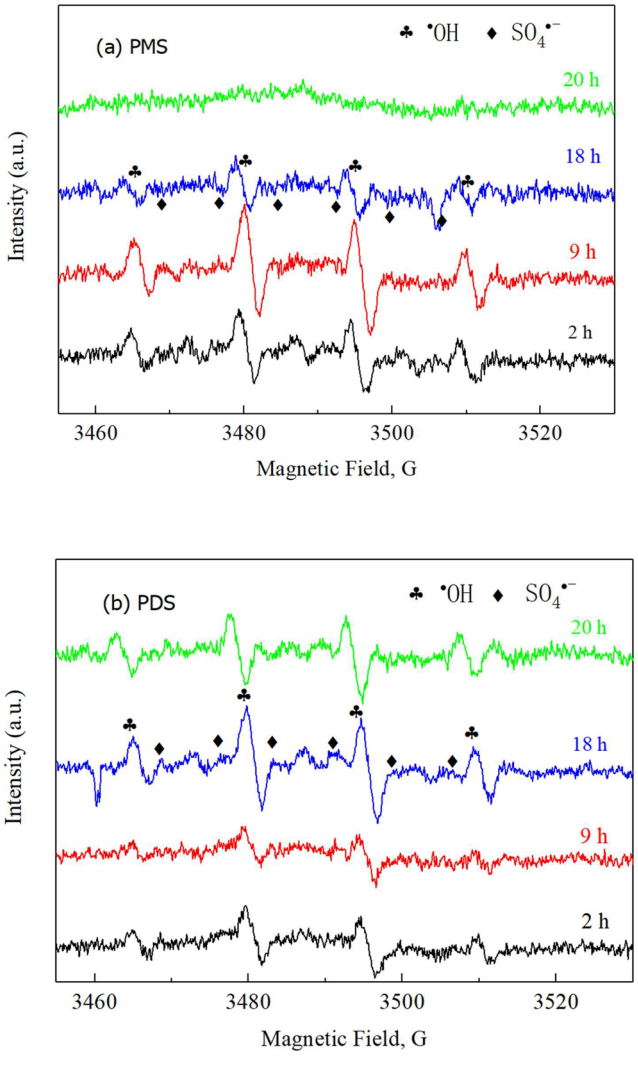

Figure 4. ESR spectra during 24 h anaerobic fermentation with (a) PMS addition and (b) PDS addition.

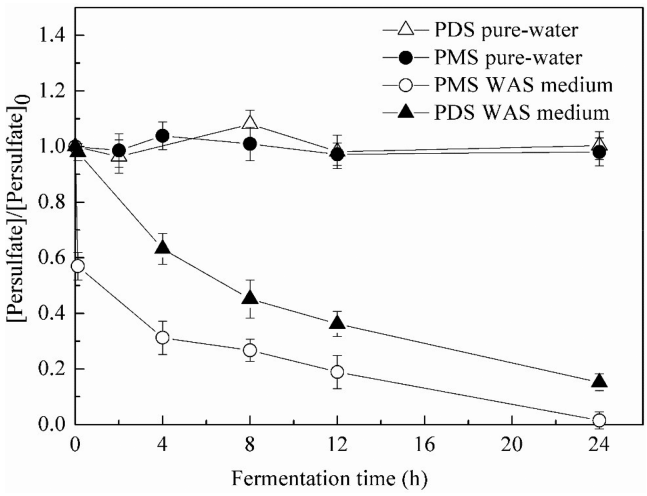

Figure 5. Decomposition of PMS and PDS in pure-water and WAS at 35 °C.

These signals were detectable in 2 h of digestion but their intensities did not obviously increase until 18 h of digestion.

Figure 5 shows the decomposition of PMS and PDS during the WAS fermentation. The decomposition of PMS can be separated into two stages, that is, the fast decomposition of 40% PMS in the first several minutes, then followed by slow decomposition. Nearly all the PMS was decomposed in 24 h. The initial fast decomposition of PMS indicates that some WAS constituents consumed PMS through direct reactions.[14] The initial fast decomposition was not observed for PDS. About 80% of PDS decomposed in 24 h. This phenomenon is consistent with the retarded radical formation from PDS as compared with PMS during the WAS fermentation.

Normally, the generation of free radicals such as $SO_4^{\bullet-}$ from persulfate requires external activation such as heating, transition metals, or UV irradiation, which can be expressed in eqs 1−3.[12]

$$HSO_5^- + e^- \text{ or heat} \rightarrow SO_4^{\bullet-} + OH^- \quad (1)$$

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{\bullet-} \quad (2)$$

$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + \bullet OH + H^+ \quad (3)$$

In the present study, the fermentation temperature was maintained at 35 ± 1 °C, and this temperature is not effective for persulfate activation (Figure 5, curves obtained for pure water). Some trace transition metal ions and minerals, and/or components released from WAS probably caused the decomposition of the persulfates. As can be seen from Figure

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S1 in Supporting Information S2, the WAS comprises 3.0% of iron, which might be a catalyst for $SO_4^{\bullet-}$ and $^{\bullet}OH$ generation from persulfates.[33] The iron concentration in the supernatant of the raw WAS was only 0.06 ± 0.01 mg/L. However, after 24 h of anaerobic digestion, the iron concentration increased to 1.28 ± 0.24 mg/L, 5.32 ± 0.49 mg/L, and 6.56 ± 0.46 mg/L in the control test, PDS addition, and PMS addition, respectively. Therefore, the addition of persulfates improved iron release from WAS to the supernatant as compared to the control test, which also can be related to the accelerated WAS dissolution in the presence of persulfate. The released iron could activate PMS and PDS to produce $SO_4^{\bullet-}$ and $^{\bullet}OH$.[15] According to the literature,[34,35] some humic substances and quinones can also activate persulfate to produce $SO_4^{\bullet-}$. Actually, WAS itself usually contains 10%−20% of humic substances in terms of COD.[5] These humic-like substrates might also contribute to the activation of persulfate during the anaerobic fermentation.[36] More insight information on radical formation during the anaerobic fermentation should be carried out in the future.

Microbial Community. To better understand the influence of persulfate on anaerobic microbes and the microbial mechanism of VFA production in these tests, the microbial community at phylum and genus levels were analyzed using the Illumina sequencing. The Alpha diversity analysis showed that the Simpson index in the control test was greater than that in the PMS and PDS addition (as shown in Figure S2 in the Supporting Information S7), revealing that the addition of PMS and PDS reduced the microbial diversity but did not largely change the microbial structure. As shown in Figure 6,

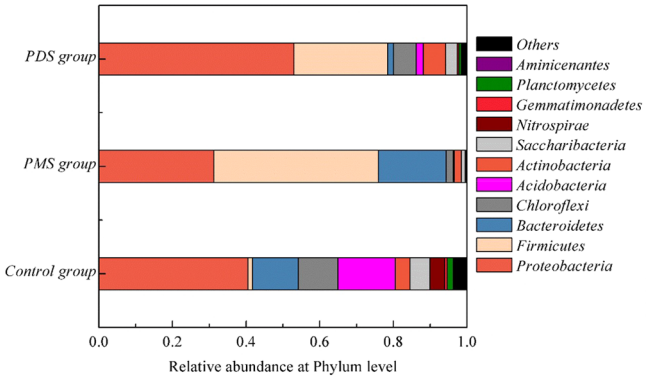

Figure 6. Relative abundances of the microbial community at the phylum level.

the most abundant phyla in the control and experimental groups were *Proteobacteria* (31.2%−52.3%), *Firmicutes* (1.2%−44.7%), *Bacteroidetes* (1.5%−18.5%) and *Chloroflexi* (2.0%−10.0%), which is consistent with the literature.[37,38]

Compared to the control test, the abundance of *Firmicutes* was enriched from 1.2% to 25.5% and 44.7% in the case of PMS and PDS addition, respectively. It was widely reported that *Firmicutes* can degrade a wide range of organic matter in WAS under anaerobic condition, and its enrichment is beneficial to organic matter degradation during hydrolysis as shown in Table 1. *Proteobacteria* and *Bacteroidetes* are important phyla in the anaerobic digestion, which accounted for 40.5% and 12.4% of the total sequences in the control and experimental groups, respectively. For the sample collected from PDS-assisted fermentation, *Proteobacteria* increased to 52.3% along with a sharp reduction of *Bacteroidetes* to 1.6%. However, only 31.2% of *Proteobacteria* and 18.5% of *Bacteroidetes* were detected in the PMS-assisted fermentation. PDS seems to lead to the enrichment of *Proteobacteria* and inhibit the growth of *Bacteroidetes*. Compared to PDS, PMS showed the opposite effect on *Proteobacteria* and *Bacteroidetes*. Additionally, *Acidobacteria* decreased from 15.5% to less than 2.0% in the persulfate-assisted fermentation.

A phylogenetic tree of the top 100 genera found in the three tests (Figure 7) was constructed with iTOL;[39] the genera are colored by phylum. The length of the outer bars represents the relative abundance of the bacteria in the genus level. This result demonstrates that the fermenters consist of various anaerobes that play significant roles in hydrolysis, acidogenesis, nitrogen cycle, and sulfate-reduction. The bacteria community compositions were not significantly changed by the addition of persulfate, but the relative abundances of certain key populations were affected.

For example, although hydrolytic bacteria such as *norank_c__Bacteroidetes_vadinHA17*, *Ferruginibacter*, and *Woodsholea* were detected in all groups, their relative abundances decreased in the presence of PMS and PDS. In contrast, other important hydrolytic bacteria such as *Bacillus* were enriched in PMS- and PDS-assisted fermentation. It has been reported that *Bacillus* is capable of degrading various organic matter and also have high tolerance to environmental stresses.[40]

The relative abundance of acidogenesis such as *Clostridium_sensu_stricto_10*, *Fonticella*, and *Macellibacteroides* were higher in persulfate-assisted fermentation. In particular, the genus *Clostridium_sensu_stricto_10* which was reported to be one of VFA producers in anaerobic fermentation was highly enriched in the PMS- and PDS-assisted fermentation with relative abundances of 3.6% and 13.8%, respectively. Moreover, *Fonticella* which degrades organic substances producing VFA via acidogenesis and acetogenesis,[41] was strengthened by the addition of PMS (2.4%) and PDS (1.4%). The total abundance of acidifiers increased from 6.9% to 22.7% and 24.2%, respectively, in the case of PMS and PDS addition. Therefore, the change of these genera can explain why more VFAs were produced in the presence of PMS and PDS.

Some types of denitrifiers such as *Thioclava*,[42] *Acinetobacter*,[43] and *Desulfotomaculum*[44] were detected in all groups, which suggests the coexistence of denitrification during WAS fermentation.[38,45] In addition, PMS and PDS addition enriched the sulfate-reduction bacteria. For example, *Thioclava* increased from 0.05% to 0.2% and 1.9% for the PMS- and PDS-assisted fermentation, respectively.

DISCUSSION

To improve VFA production from anaerobic fermentation of WAS, the ideal technology means a short treatment period and low cost for high VFA production. Compared to previous studies, which applied complex PMS activation as pretreatment,[13,24,33] this study revealed that direct addition of PMS and PDS at the beginning of the anaerobic fermentation without any preactivation allowed substantial improvement of the hydrolysis rate of WAS in anaerobic fermentation. It was worth noticing that this method obtained similar VFA production from WAS as the method of pretreatment by PMS and PDS before anaerobic fermentation. PMS has a higher efficiency in WAS hydrolysis and VFA production than

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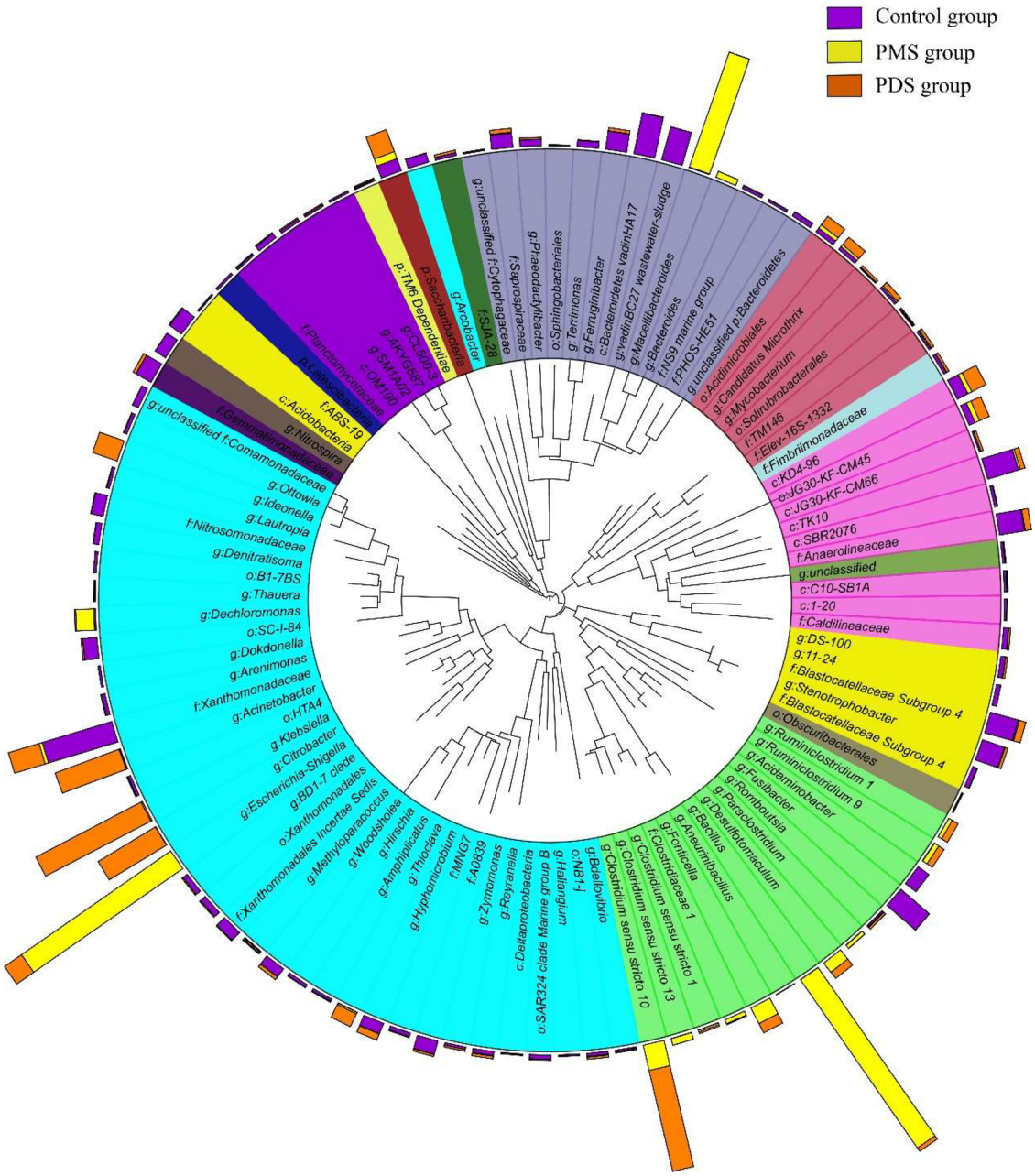

Figure 7. Evolutionary tree of the top 100 genus in different fermenters.

PDS during the anaerobic fermentation (Figure 1). However, the latter has advantages in its relatively low cost.

On the basis of further analysis, reactive oxygen species such as hydroxyl and sulfate radicals were detected during the initial 24 h of anaerobic fermentation as the consequence of the decomposition of PMS and PDS. Hydroxyl and sulfate radicals, which are strong oxidants, are capable of decomposing a number of organic substances in WAS via oxidation.[13,14] Yang et al.[13] observed that ·OH and $SO_4^{\bullet-}$ can improve the diffusion of EPS from the inner layer to the outer layer of the sludge, thus releasing remarkable organic components into the liquid phase. Besides, Li et al.[46] reported that ·OH produced by CaO_2 addition improved WAS disintegration and the removal of refractory organic contaminants. It is reasonable to infer that the released hydroxyl and sulfate radicals improved WAS disintegration and its dissolution. The consequent decrease in particle size and the increase in surface area of WAS can promote hydrolysis.[5] The increased soluble proteins and carbohydrates in the supernatant also provide more biodegradable substrates for acidifiers and the associated enzymes for subsequent VFA production.

More biodegradable substrates were available due to the enhanced WAS disintegration and solubilization by persulfate addition, and thereby functional microorganisms converting the soluble substrates to VFA played a key role in fermentation. Although addition of PMS and PDS did not substantially affect the microbial structure, it substantially increased the relative abundance of certain key bacterial phyla, such as *Firmicutes* and *Bacillus*. The versatile anaerobes are capable of degrading proteins, polymeric carbohydrates, and lipids. Their enrichment might result from the increased solubilization of protein and carbohydrates observed at 24 h of anaerobic fermentation with the addition of PMS and PDS. The result implies that the addition of PMS and PDS also

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contributed to the biodegradation of complex substrates in sludge, such as proteins. Besides, persulfate-assisted fermentation increased the proportion of VFA producers. But, the influences of PMS and PDS addition on the enrichment of VFA producers in the genus level were different. The addition of PDS enriched *Clostridium_sensu_stricto_10*, belonging to *Phylum Firmicutes* from 0% in the control group to 13.8% in the PDS group, whereas this value was only 3.6% in the PMS group. On the other hand, the addition of PMS mainly enriched *Macellibacteroides*, belonging to *Phylum Bacteroidetes* from 0.08% in the control to 16.7% in the PMS group. It can be calculated that the total abundance of acidifiers with PMS and PDS addition increased to 2.2 times of that without persulfate addition. Therefore, persulfate addition enriched hydrolytic and VFA-forming bacteria, which was another one of the main reasons for improved VFA yield. Additionally, some genera such as *Thioclava* was enriched with the presence of persulfate, reflecting that the addition of PMS and PDS stimulated the sulfate reducing bacteria during anaerobic fermentation. This result might be attributed to the increased sulfate from the decomposition of persulfates.

A brief cost-effectiveness evaluation was also performed. As mentioned above, the maximum VFA concentration obtained from the PMS-assisted fermentation was only 1.24 times that of the PDS-assisted. However, the commercial price of PMS ($2.2/kg) is nearly three times of PDS ($0.74/kg).[12] The additional cost of PMS was not compensated by its higher VFA production as compared with PDS. However, it should be stated that this comparison did not consider the cost of VFA recovery. In contrast to methane production, anaerobic fermentation for VFA production could avoid the competition between sulfate-reducing bacteria and methanogenic archaea. From the view of resource recovery, the residual sulfate could be recovered through precipitation,[47] or further treated by novel technology such as Sha Tin sewage treatment.[48] More detailed investigation (e.g., the influences of pH, temperature, and persulfate dosage) is still needed to optimize the persulfate-assisted WAS fermentation.

CONCLUSION

This study shows that direct addition of persulfates during anaerobic WAS fermentation without any preactivation steps both substantially improved the hydrolysis rate and VFA yields. The VFA yield was increased by 132% and 87.6% by PMS and PDS addition at 1.0 mM/gVS, respectively. However, the cost-effectiveness of PMS in enhancing VFA production was not comparable to that of PDS. PMS and PDS added under this condition was depleted in 24 h of fermentation, associated with the generation of ·OH and $SO_4^{\bullet-}$. The released radicals further improved the disintegration, solubilization and biodegradability of WAS. ·OH and $SO_4^{\bullet-}$ generation from PDS addition was weaker and delayed as compared with PMS addition. Both PMS and PDS addition enriched the microbial community which is responsible for VFA production.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c01781.

Two figures and tables as described in the text (PDF)

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Notes

The authors declare no competing financial interest.

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