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Dewaterability improvement and environmental risk mitigation of waste activated sludge using peroxymonosulfate activated by zero-valent metals: Fe⁰ vs. Al⁰

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HIGHLIGHTS

- PMS activation by Fe⁰ and Al⁰ catalysts were compared for WAS dewatering.
- Fe⁰ outperformed Al⁰ for PMS activation and reactive radical production.
- Fe⁰/PMS more effectively enhanced WAS dewaterability and reduced costs.
- Fe⁰/PMS facilitated strong oxidation and flocculation for WAS dewatering.
- PMS activated by Fe⁰/Al⁰ effectively stabilized WAS and reduced environmental risk.

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GRAPHICAL ABSTRACT



ABSTRACT

The stabilization and dewaterability of waste activated sludge (WAS) are essential factors for downstream disposal or reuse. Herein, two types of zero-valent metals, zero-valent iron (Fe⁰) and zero-valent aluminum (Al⁰), were compared for their ability to activate peroxymonosulfate (PMS) during the WAS conditioning process, with the effects of PMS activation by these two metals on WAS dewaterability and the potential environmental risks evaluated. Results showed that compared to Al⁰/PMS treatment, Fe⁰/ PMS treatment achieved superior WAS dewaterability and reduced operational costs. Using PMS combined with Fe⁰ and Al⁰ treatments under optimal conditions, the water content (Wc) of dewatered sludge decreased to 55.7 \pm 2.7 wt% and 59.4 \pm 1.3 wt%, respectively. Meanwhile, application of the Fe⁰/PMS





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Keywords: Waste activated sludge dewaterability Zero-valent iron Zero-valent aluminum Peroxymonosulfate Heavy metals treatment system reduced the total annual cost by approximately 33.1%, compared to the Al⁰/PMS treatment. Analysis of the dewatering mechanism demonstrated that in the Fe⁰/PMS treatment, Fe³⁺/Fe²⁺ flocculation played an important role in the enhancement of WAS dewatering, while sulfate radical (SO_4^{--}) oxidation was the dominant factor for WAS dewaterability improvement in Al⁰/PMS treatment. The greater enhancement of WAS dewaterability by Fe⁰/PMS treatment, was mainly attributed to more efficient reduction of hydrophilic extracellular polymeric substances (EPS) and an increase in surface charge neutralization. Environmental risk evaluation results indicated that Fe⁰/PMS and Al⁰/PMS treatments both effectively alleviated the environmental risks of heavy metals and faecal coliforms in dewatered sludge. Overall, this study proposes a novel perspective for the selection of an optimal PMS activator in sludge treatment.

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1. Introduction

Conventional activated sludge wastewater treatment plants (WWTPs) have been facing a major challenge when handling excessive volumes of waste activated sludge (WAS) due to the high moisture content (~99 wt%) of WAS presenting a serious burden in subsequent sludge treatment and disposal (Wan et al., 2013; Chen et al., 2020; Masihi and Gholikandi, 2020). The high-cost of WAS treatment and disposal (approximately 50–60% of the total operational costs) has become the foremost challenge affecting the operation of WWTPs (Liu, 2019). Therefore, efficient sludge dewatering processes need to be developed, which can significantly reduce the costs associated with subsequent sludge treatment and disposal.

Extracellular polymeric substances (EPS) are main components of WAS, containing an abundance of hydrophilic substances and functional groups, which bind strongly with water and consequently cause considerable difficulty in sludge dewatering (Li et al., 2019; Zhang et al., 2020a). In order to achieve effective WAS dewaterability, efficient removal of hydrophilic EPS and its functional groups is a critical step (Xiao et al., 2017; Liang et al., 2020). Recently, persulfate-based advanced oxidation processes (PS-AOPs) have been found to be a feasible method to enhance WAS dewaterability, by generating a series of reactive species, such as sulfate radicals $(SO_4^{\bullet-})$ or hydroxyl radicals $(\bullet OH)$, which can efficiently disrupt sludge flocs and remove hydrophilic EPS (Zhen et al., 2018; Liu et al., 2020; Wang et al., 2020a). Peroxymonosulfate (PMS) contains a peroxide O-O bond, which can be easily activated and transformed into $SO_{4}^{\bullet-}$ or $\bullet OH$ using thermal treatment, ultraviolet irradiation, ultrasound, or treatment with alkalis and transition metals (Ghanbari and Moradi, 2017). Among these methods, Fe^{2+} is a promising catalyst for PMS activation, which has been intensively investigated for WAS treatment due to its elemental abundance and high efficiency (Liu et al., 2016; Xiao et al., 2017). However, due to the high operating costs (Liu et al., 2020), the occurrence of quenching between radicals and Fe²⁺ (Zhou et al., 2018), and the abundant formation of iron deposits (Liang et al., 2020), the development and utilization of homogenous PMS-AOP systems are generally limited.

Currently, heterogeneous reactions using zero-valent iron (Fe⁰) based PMS-AOPs have been developed to treat WAS, due to the higher stability, better reusability, and wider effective pH range compared to Fe²⁺ based PMS-AOPs (Li et al., 2018; Ni et al., 2019; Liu et al., 2020). For example, Li et al. (2018) reported that Fe⁰/PMS treatment achieved efficient and stable enhancement of sludge dewaterability, with two treatment cycles resulting in an 81.5% reduction in specific resistance of filtration (SRF). Liu et al. (2020) demonstrated that under neutral conditions, the reduction in capillary suction time (CST) reached 89.2% after combined

ultrasound and Fe⁰/PMS treatment. Although Fe⁰ has been proven to be more efficient than Fe²⁺ in PMS-AOPs across a wider pH range, the aggregation and immediate corrosion (Eq. (1)) of Fe^0 powder during the reaction, can hinder electron transfer efficiency (Trujillo-Reyes et al., 2014) and therefore, WAS dewaterability. Alternatively, zero-valent aluminum (Al⁰) possesses a more negative standard reduction potential $(E^0(Al^{3+}/Al^0) = -1.662 \text{ V})$ and is a highly efficient electronic donor (Arslan-Alaton et al., 2017), which can directly produce $SO_4^{\bullet-}$ via Eq. (2). Accordingly, Al⁰ based PMS-AOPs are considered to be promising for the remediation of contaminated wastewater and groundwater (Arslan-Alaton et al., 2017; Nidheesh et al., 2018). However, to the best of our knowledge, it remains unclear whether Al⁰ can replace Fe⁰ to serve as an efficient catalyst in PMS-AOPs for achieving high-level sludge dewatering, as the complex composition of sludge (i.e., EPS, metal ions, and inorganic salts) may inhibit the electron transfer rate. Furthermore, to reduce the cost of acidification and subsequent neutralization, a minimal pH adjustment (weak acidic conditions) in PMS-AOPs is highly recommended. However, weak acidic conditions (pH ~5.0) might not effectively promote Al⁰ corrosion due to the thin oxide layer on the Al⁰ surface, which could influence the reactivity of Al⁰ and its catalytic efficiency in the Al⁰/PMS system (Nidheesh et al., 2018). Therefore, whether Al⁰ can effectively enhance WAS dewatering under weak acidic conditions, also remains to be confirmed.

$$Fe^{0} + HSO_{5}^{-} + 2H^{+} \rightarrow Fe^{2+} + HSO_{4}^{-} + H_{2}O$$
 (1)

$$Al^{0} + 3HSO_{5}^{-} + 3H^{+} \rightarrow Al^{3+} + 3SO_{4}^{\bullet-} + 3H_{2}O$$
 (2)

After conditioning, dewatered sludge cake generally contains toxic heavy metals (i.e., As, Cd, Cr, Cu, Ni, Pb, and Zn) and faecal coliforms (Zhang et al., 2020b), which pose a potential threat to the ecological environment and human heath (Liu, 2019), restricting the feasibility of sludge reuse. Accordingly, in addition to sludge dewaterability, evaluation of the environmental risks of faecal coliforms and heavy metals in dewatered sludge is necessary prior to downstream treatment. However, it remains unknown if the use of PMS-AOPs can efficiently alleviate the environmental risks of heavy metals and faecal coliforms present in dewatered sludge.

Therefore, the objectives of this study were to (a) optimize the operating factors in Fe^0/PMS and Al^0/PMS treatments, (b) compare the WAS dewaterability of treatment systems using PMS activated by the two types of zero-valent metals (ZVM), Fe^0 and Al^0 , (c) explore the physiochemical characteristics of WAS under different treatment conditions to clarify the WAS dewatering mechanism, (d) evaluate the environmental risk of dewatered sludge cake and assess the economic feasibility of these systems.

2. Materials and methods

2.1. Sludge source and chemicals

20 samples of WAS were collected from a secondary sedimentation tank once a week at a local WWTP in Guangzhou, China, from January 2019–June 2019. Prior to tests, the WAS samples were settled by gravity for 24 h to increase the solid content of samples and then stored in a 4 °C refrigerator. The main characteristics of the thickened sludge were as follows: water content (Wc) = 97.4 ± 0.5 wt%, pH = 6.75 ± 0.31, total suspend solids (TSS) = 26.59 ± 0.26 g L⁻¹, volatile suspend solids (VSS) = 11.27 ± 0.10 g L⁻¹, and SRF = 5.85 ± 0.05 × 10¹² m kg⁻¹. Fe⁰ powder (~400 mesh diameter), Al⁰ powder (~400 mesh

diameter), Al^o powder (~400 mesn diameter), Al^o powder (~400 mesn diameter), and potassium peroxymonosulfate were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were of analytical grade.

2.2. Experimental procedures

In order to optimize the critical operational factors in ZVM/PMS treatment (Fe⁰ dosage, Al⁰ dosage, PMS dosage, and initial pH), a series of batch tests were performed in 500 mL beakers containing 350 mL of WAS samples. All batch tests were performed in triplicate. Prior to batch tests, Fe⁰ and Al⁰ powders were pre-treated to remove the oxide layer, using a thermal treatment and acidwashing method previously reported by Liang et al. (2020). Briefly, the Fe⁰ and Al⁰ powders were soaked in 0.1 M H₂SO₄ solution at 45 °C for 15 min, with continual agitation at a speed of 180 rpm. Detailed experimental procedures are described below. Firstly, the initial pH was adjusted to values of 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0. Secondly, different dosages of Fe^0 or Al^0 (0, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 mM g^{-1} TSS⁻¹) were added to the sludge with a mixing speed of 300 rpm applied for 1 min. Thirdly, PMS was added to the sludge at concentrations of 0, 0.1, 0.2, 0.3, 0.4, and 0.5 mM g^{-1} TSS⁻¹ with a mixing speed of 300 rpm applied for 15 min. After conditioning, samples were collected to determine WAS dewaterability, bound water content, EPS content, zeta potential, and particle size.

Quenching tests were performed by adding TBA (100 mM) and phenol (100 mM) (Ghanbari and Moradi, 2017; Li et al., 2019) to samples, to identify the contributions of metal ions, SO_4^- and • *OH* in the ZVM/PMS systems. Comprehensive details on the calculation of quenching contributions are shown in Text S1. The conditioned sludge samples were collected and pumped into a filter press to assess the Wc as an indicator of dewatering performance (Liang et al., 2020). All experiments were performed at room temperature (~25 °C).

2.3. Analytical methods

2.3.1. Waste activated sludge characteristics

The SRF was assessed using a vacuum filtration method, as described by Qi et al. (2011). The Wc of the sludge cake was measured as per APHA (2005). A reduction in the SRF values of the WAS and the Wc of the sludge cake indicated the improvement of WAS dewaterability. A filter press was used to evaluate the water removal rate of sludge, as described by Liang et al. (2020). A higher value of water removal rate indicated improved sludge dewaterability. The bound water content of sludge was determined using a centrifugal method described by Xiao et al. (2017). The functional groups and secondary structures of the protein (PN) in the freezedried sludge samples, were characterized using Fourier transform infrared (FT-IR) spectroscopy (Nicolet iS5, Thermo Fisher Scientific, Massachusetts, US) as per You et al. (2017). The faecal coliform

content of sludge samples was determined according to the method of Wei et al. (2018). A modified heat extraction method was used to extract soluble EPS (S-EPS), loosely bound EPS (LB-EPS), and tightly bound EPS (TB-EPS) from sludge, following the methods of Yu et al. (2008) and Pang et al. (2020). The total organic carbon (TOC) content in the three EPS lavers was measured using a TOC analyzer (TOC-VCPH, Shimadzu, Kvoto, Japan). The PN content in the three EPS lavers was measured using a modified Bradford method (Bradford, 1976). The PN secondary structures were analyzed according to the method of You et al. (2017). The polysaccharide (PS) content in the three EPS layers was determined based on the method of Frolund et al. (1996). Organic matter in the three EPS layers was characterized by three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy (F-4600, Hitachi, Tokyo, Japan), with spectra divided into five regions (Table S1; Chen et al., 2003). Zeta potential was analyzed using a Zeta PALS zetasizer analyzer (Brookhaven Instruments, New York, US). A laser diffraction instrument (Mastersizer 3000, Malvern Panalytical, Malvern, UK) was used to analyze the particle size distribution of sludge. According to the standard method (APHA, 2005), TSS and VSS were evaluated. The pH was measured using a pH analyzer (STARTER 2100, OHAUS Corp., New Jersey, US).

2.3.2. Extraction and analysis of heavy metals

The sludge was freeze-dried at $-60 \degree C$ for 72 h, then ground and passed through a 100-mesh sieve (Wang et al., 2020a). A toxicity characteristic leaching procedure (TCLP) was used to access the toxicity of heavy metals present in the dewatered sludge (Xiong et al., 2018). The Community Bureau of Reference (BCR) sequential extraction procedure was used to establish the transition of chemical speciation of heavy metals in dewatered sludge, as described by Rauret et al. (1999) and Wang et al. (2020a), with four fractions of heavy metal species extracted, F1 (exchangeable fraction), F2 (reducible fraction), F3 (oxidizable fraction), and F4 (residual fraction). The availability and mobility of different fractions followed the ranked order of F1 > F2 > F3 > F4 (Liu, 2019). The risk assessment code was used to evaluate the environmental risk posed by heavy metals in sludge cake, with the risk assessment code criterion determined as reported by Liu (2019). The concentrations of metals were measured using inductively coupled plasma atomic emission spectroscopy (Prodigy 7, Teledyne Instruments, California, US).

3. Results and discussion

3.1. Optimization of the main factors affecting ZVM/PMS treatment for WAS dewaterability

3.1.1. Zero-valent iron/zero-valent aluminum dosages

Fig. 1a shows the changes in WAS dewaterability after activated-PMS oxidation with Fe⁰ or Al⁰ at varying metal concentrations. The SRF value of WAS treated by PMS alone decreased slightly by 23.3%, as compared to the control sample (SRF of $5.85 \pm 0.05 \times 10^{12}$ m kg⁻¹). This insufficient promotion of WAS dewaterability was mainly due to the weak oxidation capacity of PMS alone (Wang et al., 2020a). When either Fe⁰ or Al⁰ was present, WAS dewaterability by both Fe⁰/PMS and Al⁰/PMS treatments notably improved. Following Fe⁰/PMS conditioning, the SRF of WAS decreased significantly from $4.49 \pm 0.14 \times 10^{12}$ m kg⁻¹ to $0.98 \pm 0.15 \times 10^{12}$ m kg⁻¹ as the Fe⁰ dosage increased from 0 to 3.0 mM Fe⁰ g⁻¹ TSS⁻¹ (Fig. 1a). However, no additional decrease in SRF was observed when the Fe^0 concentration further increased from 3.0 to 6.0 mM Fe^0 g⁻¹ TSS⁻¹, which might be because excessive Fe⁰ addition generated superabundant Fe²⁺, which consumed $SO_{4}^{\bullet-}$ and consequently inhibited WAS dewatering (Kusic et al.,

2011; Ni et al., 2019). Following Al⁰/PMS treatment, the SRF of WAS gradually decreased from $4.49 \pm 0.14 \times 10^{12}$ m kg⁻¹ at 0 mM Al⁰ g⁻¹ TSS⁻¹, to a minimum of $1.11 \pm 0.08 \times 10^{12}$ m kg⁻¹ at 5.0 mM Al⁰ g⁻¹ TSS⁻¹, followed by a marginal increase to $1.13 \pm 0.06 \times 10^{12}$ m kg⁻¹ at 6.0 mM Al⁰ g⁻¹ TSS⁻¹ (Fig. 1a). This trend may occur because the excessive electrons result in quenching of free radicals, limiting the capacity for WAS dewatering (Hoa et al., 2020). Under the optimal ZVM dosage conditions, Fe⁰/PMS treatment achieved better dewaterability (SRF decrease of 83.3%) compared to Al⁰/PMS treatment (SRF decrease of 81.0%). This was attributed to the *in-situ* formation of Fe³⁺ from the Fe⁰/PMS system (Eq. (3)-(6)) with superior coagulation efficiency, efficiently enhancing WAS dewaterability (Yu et al., 2016; Wang et al., 2020a).

$$2Fe^{0} + 2H_{2}O + O_{2} \rightarrow 2Fe^{2+} + 4OH^{-}$$
(3)

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{4}$$

$$Fe^{2+} + HSO_5^- \rightarrow Fe^{3+} + SO_4^{\bullet-} + OH^-$$
(5)

$$Fe^{2+} + SO_4^{\bullet-} \to Fe^{3+} + SO_4^{2-}$$
 (6)

3.1.2. Peroxymonosulfate dosage

The effects of varying PMS dosage with fixed dosages of Fe⁰ and Al⁰ on WAS dewaterability are shown in Fig. 1b. Compared to the SRF value of the control sample, the SRF values of WAS treated using Fe⁰ and Al⁰ only systems decreased by 47.7% and 40.3%, respectively, indicating unsatisfied sludge dewatering efficiency (Li et al., 2019). The presence of PMS in the Fe⁰/PMS and Al⁰/PMS processes apparently improved WAS dewaterability, likely due to the accelerated generation of $SO_4^{\bullet-}$ and $\bullet OH$ (Eqs. (2)–(5) and (7)) (Arslan-Alaton et al., 2017; Pang et al., 2019). In the Fe⁰/PMS and Al⁰/PMS systems, with an increase in PMS dosage, WAS dewaterability substantially increased and then gradually decreased (Fig. 1b). At high PMS levels (> 0.4 mM PMS g^{-1} TSS⁻¹), significant inhibition of dewatering was observed, which could probably be attributed to the consumption of $SO_4^{\bullet-}$ by excess PMS (Eq. (8)) (Zou et al., 2013). Results showed that at a PMS dosage of 0.2 mM PMS g⁻¹ TSS⁻¹, the Fe⁰/PMS treatment exhibited optimal WAS dewatering efficiency, as indicated by the lower SRF of 0.62 \pm 0.10 \times 10^{12} m kg^{-1}. Likewise, in the Al⁰/PMS treatment system, optimal WAS dewaterability was observed at a PMS dosage of 0.3 mM PMS g^{-1} TSS⁻¹, resulting in a lower SRF of 0.86 \pm 0.26 \times 10¹² m kg⁻¹. Notably, the Fe⁰/PMS treatment exhibited a superior WAS dewatering capability (SRF decrease of 89.4%) than the Al⁰/PMS treatment (SRF decrease of 85.0%), likely attributing to the efficient EPS removal and strong flocculation efficiency in the Fe⁰/PMS treatment process (Yu et al., 2016; Liang et al., 2019; Liu et al., 2020; Wang et al., 2020a).

$$SO_4^{\bullet-} + 2H_2O \to SO_4^{2-} + H^+ + \bullet OH$$
 (7)

$$HSO_5^- + SO_4^{\bullet-} \to SO_5^{\bullet-} + SO_4^{2-} + H^+$$
 (8)

3.1.3. Initial pH

The effects of initial pH on WAS dewaterability were investigated over a pH range of 3.0–8.0, as shown in Fig. 1c. With a decrease in WAS pH value, the SRF gradually decreased in both the Fe⁰/PMS and Al⁰/PMS processes, suggesting that acidic conditions favored the improvement of WAS dewatering in both processes. This phenomenon is likely due to the strong corrosion of ZVM and the subsequent release of metal ions (i.e., Fe^{2+} or Al^{3+}) (Hoa et al., 2020), enhancing the production of active radicals (i.e., $SO_4^{\bullet-}$ and •OH) (Arslan-Alaton et al., 2017; Pang et al., 2019). As shown in Fig. 1c, the Fe⁰/PMS treatment and Al⁰/PMS treatment could both effectively enhance WAS dewaterability under weak acidic conditions (pH \sim 5.0) (SRF reduction rate > 86.8%), which is comparable to the results of ethylenediaminetetraacetic acid (EDTA) chelated- Fe^{2+}/PMS treatment (SRF reduction rate of 70.5%) as reported by Wang et al. (2019). The optimum pH was 3.0–4.0 for the Fe⁰/PMS treatment (SRF from 0.39 \pm 0.09 \times 10¹² m kg⁻¹ to 0.42 \pm 0.05 \times 10¹² m kg⁻¹), while the optimum pH was 3.0 for the Al^{0}/PMS process (SRF of 0.59 ± 0.06 × 10¹² m kg⁻¹) (Fig. 1c), indicating a wider effective pH range for the Fe⁰/PMS treatment. The reduction in SRF of WAS treated by the Fe⁰/PMS process was > 90.0% at pH of 3.0-4.0, exhibiting an excellent level of WAS dewaterability (Yu et al., 2016; Li et al., 2018). Considering the costs of chemicals, the optimal pH for WAS dewatering in the Fe⁰/PMS process was pH 4.0.

3.2. Waste activated sludge dewatering efficiency using PMS-AOPs: Fe^0 vs. Al^0 catalysis

Based on the established optimal conditions for Fe^0/PMS and AI^0/PMS treatment processes (Table S2), a series of batch tests were conducted using a filter press to comprehensively compare the WAS dewatering efficiency of the Fe^0/PMS and AI^0/PMS treatment processes.

3.2.1. Sludge dewatering efficiency and bound water

The water filtration rate of sludge was only 60.0% in the control sample, while WAS conditioned by Fe⁰/PMS treatment had the highest water filtration rate (94.1%), followed by the Al⁰/PMS treatment (89.7%) and PMS-only treatment (72.4%) (Fig. 2a). These results verify that the ZVM/PMS treatments exhibited higher sludge water removal rates compared to the PMS-only treatment, probably on account of the efficient breakdown of flocs and biopolymer removal after ZVM/PMS treatment (Ni et al., 2019). Noticeably, the water removal rate for WAS conditioned by the Fe⁰/PMS system was 4.9% higher than with the Al⁰/PMS treatment system. The preferable dewaterability achieved with the Fe⁰/PMS process could be attributed to the higher EPS removal efficiency (Liu et al., 2020), increased flocculation effect (Masihi and Gholikandi, 2020), and the lower Lewis acid-base interaction energy and electrostatic interaction energy of sludge flocs (Yu et al., 2021).

The Wc values of WAS conditioned by PMS-only, Fe⁰/PMS, and Al^{0} /PMS decreased to 87.4 ± 2.1 wt%, 55.7 ± 2.7 wt%, and 59.4 \pm 1.3 wt%, respectively (Fig. 2b), indicating that the Fe⁰/PMS treatment exhibited optimal WAS dewatering efficiency compared to the PMS-only and Al⁰/PMS treatments. Results show that the WAS dewaterability of the Fe⁰/PMS treatment was superior to the established Fe²⁺/PMS method (Wc of 64.2 wt% as reported by Liu et al. (2016)) and electrochemical/Fe⁰/H₂O₂ treatment method (Wc of 65.4 wt% as reported by Cai et al. (2019)), confirming that the Fe⁰/PMS system can achieve efficient and effective WAS dewatering. Similarly to the trend in Wc values (Fig. 2b), the results of bound water content analysis confirmed that the Fe⁰/PMS treatment could more effectively remove bound water (6.41 \pm 0.15 g g^{-1} TSS⁻¹) compared with the Al⁰/PMS treatment (7.06 \pm 0.21 g g⁻¹ TSS⁻¹). This might be explained by the more efficient EPS removal (Liu et al., 2020) and effective reduction in interfacial free energy (Yu et al., 2021).



Fig. 1. Effects of the main factors on WAS dewaterability in the Fe⁰/PMS and Al⁰/PMS systems: (a) zero-valent metal dosages (Constant conditions: PMS dosage = 0.1 mM g⁻¹ TSS⁻¹, initial pH = 5.0), (b) PMS dosages (Constant conditions: Fe⁰ dosage = 3.0 mM g⁻¹ TSS⁻¹, Al⁰ dosage = 5.0 mM g⁻¹ TSS⁻¹, initial pH = 5.0), and (c) initial pH (Constant conditions: Fe⁰ dosage = 3.0 mM g⁻¹ TSS⁻¹, PMS dosage = 0.2 mM g⁻¹ TSS⁻¹; Al⁰ dosage = 5.0 mM g⁻¹ TSS⁻¹, PMS dosage = 0.3 mM g⁻¹ TSS⁻¹).

3.2.2. Radical analysis

Quenching tests were conducted to identify the main radical species present in the Fe⁰/PMS and Al⁰/PMS systems. The Wc reduction rate decreased from $38.2 \pm 1.1\%$ in the Fe⁰/PMS treatment to $16.4 \pm 0.3\%$ in the Fe⁰/PMS-phenol treatment and to $27.6 \pm 0.9\%$ in the Fe⁰/PMS-TBA treatment (Fig. 2c), exhibiting a significant deterioration in WAS dewatering in the presence of quenching chemicals (Liu et al., 2020). The reduction in WAS dewatering can be attributed to active radical quenching reactions, with phenol used for quenching of $SO_4^{\bullet-}$ and $\bullet OH$ (Li et al., 2019), while TBA quenches •OH (Ghanbari and Moradi, 2017). Accordingly, analysis of the contributions of the main radical species in the Fe^U/PMS system to WAS dewaterability, showed that •OH was the dominant radical species in the Fe⁰/PMS system (contribution of • $OH = 32.3 \pm 0.2\%$ vs. contribution of $SO_4^{\bullet-} = 25.2 \pm 0.5\%$) (Fig. 2d), which was consistent with the previous results of Liu et al. (2020). Importantly, the highest contribution to Wc reduction rate was Fe^{3+}/Fe^{2+} (42.5 \pm 0.2%), suggesting that in the Fe^{0}/PMS treatment system, Fe^{3+}/Fe^{2+} flocculation played a crucial role in improving WAS dewatering (Yu et al., 2016).

Similarly, in the presence of phenol and TBA, the Wc reduction rate of Al⁰/PMS treatment decreased significantly to 11.6 \pm 0.5% and 26.4 \pm 1.0%, respectively (Fig. 2c). The contributions of Al³⁺, SO₄⁻⁻, and •OH to WAS dewaterability in the Al⁰/PMS were ranked in the descending order $SO_4^{\bullet-} > Al^{3+} > \bullet OH$ (Fig. 2d), suggesting that $SO_4^{\bullet-}$ and Al³⁺ were the main contributors to the improvement in WAS dewaterability. This phenomenon is likely due to EPS removal by $SO_4^{\bullet-}$ (Liu, 2019) and flocculation by Al³⁺ (Masihi and Gholikandi, 2020). Overall, $SO_4^{\bullet-}$ oxidation was the dominant factor for improved WAS dewaterability in the Al⁰/PMS treatment, while in the Fe⁰/PMS treatment system, Fe³⁺/Fe²⁺ flocculation was dominant in the enhancement of WAS dewatering. This difference may partly account for the improved WAS dewatering performance of the Fe⁰/PMS treatment system, compared to the Al⁰/PMS treatment system.

3.3. The influence of different treatments on WAS characteristics

3.3.1. Extracellular polymeric substances

Extracellular polymeric substances contain an abundance of hydrophilic components (i.e., PN and PS) and hydrophilic functional groups capable of retaining bound water within sludge (Wu et al., 2020) and affecting sludge flocculation and dewaterability (Li et al., 2019). Therefore, it is essential to establish variations in EPS under different treatment conditions.

Compared to the control sample, the main components (i.e., PN and PS) of the TB-EPS in treated WAS decreased, while the S-EPS and LB-EPS content of treated WAS increased (Fig. 3a and b), indicating that some insoluble organic matter was dissolved from the inside layer to the outside layer after the PMS-AOPs treatment (Xiao et al., 2017). Compared to the control, the PN content of the TB-EPS of WAS treated by PMS-only, Fe⁰/PMS, and Al⁰/PMS reduced by 38.5%, 72.8%, and 64.2%, respectively. Similarly, the PS content of TB-EPS decreased by 24.4%, 60.5%, and 45.1%, after the PMS-only, Fe⁰/PMS, and Al⁰/PMS treatments, respectively. These results indicate that the ZVM/PMS treatments cause a more significant decrease in the PN and PS content of TB-EPS than the PMS-only treatment, likely due to the high removal of macromolecular organic matter by active radical species in the ZVM/PMS systems (Ni et al., 2019). It is of note, that the Fe⁰/PMS treatment exhibited a more efficient decrease in the PN and PS content of TB-EPS than the Al⁰/PMS treatment system. This was probably due to the greater EPS binding ability (Yu et al., 2021) and the better oxidation effect (Li et al., 2019) of the Fe⁰/PMS treatment system, which could efficiently destroy the hydrophilic structures of EPS and consequently enhance WAS dewatering. Moreover, the variations in TOC concentration of EPS (Fig. 3c) were similar to the trends observed in PN and PS concentrations, which also confirms that Fe⁰/PMS treatment caused the most effective decomposition of TB-EPS.

Organic matter release after different treatments was examined by 3D-EEM spectroscopy. Previous studies have reported that the high levels of tyrosine-like/tryptophan-like PN in EPS contain an abundance of hydrophilic functional groups, which block permeable channels and reduce sludge dewaterability (Li et al., 2019; Ni et al., 2019). After ZVM/PMS treatments, the fluorescent region intensities (FRI) of tyrosine-like/tryptophan-like PN in S-EPS, LB-EPS, and TB-EPS fractions were distinctly lower than that of the control sample and the PMS-only treatment sample (Fig. 3d, e, and f; Fig. S1), which is likely due to the stronger oxidation of active radical species (Li et al., 2019). Furthermore, compared to the Al⁰/ PMS treatment, a more obvious decrease in the FRI of the tyrosinelike/tryptophan-like PN of EPS was observed after the Fe⁰/PMS treatment, suggesting that the Fe⁰/PMS treatment effectively destroyed floc structures, inducing cell lysis and enhancing tyrosine-like/tryptophan-like PN removal, which confirms the aforementioned results for PN and TOC (Fig. 3a and c). This may be a main contributing factor to the efficient enhancement of WAS dewatering by Fe⁰/PMS treatment.



Fig. 2. Profiles in water removal rate of sludge (a), water content, and bound water content (b) of WAS treated by PMS, Fe⁰/PMS, and Al⁰/PMS; Effects of different radical quenching chemicals in the Fe⁰/PMS and Al⁰/PMS systems on Wc reduction rate (c) and contribution of the main components in the Fe⁰/PMS and Al⁰/PMS systems to improve the WAS dewaterability (d). (Constant conditions: Fe⁰ dosage = 3.0 mM g⁻¹ TSS⁻¹, PMS dosage = 0.2 mM g⁻¹ TSS⁻¹, initial pH = 4.0; Al⁰ dosage = 5.0 mM g⁻¹ TSS⁻¹, PMS dosage = 0.3 mM g⁻¹ TSS⁻¹, initial pH = 3.0; phenol dosage = 100 mM, TBA dosage = 100 mM).

3.3.2. FT-IR analysis

FT-IR spectra in the range of 400-4000 cm⁻¹ was used to investigate the hydrophilicity/hydrophobicity of the sludge surface, as an indicator of sludge dewaterability (Zhang et al., 2020a). The Fe⁰/PMS treatment significantly strengthened the transmittance of absorption peaks on the sludge surface (Fig. 4a) as compared with the other treatments, indicating a larger magnitude of release of hydrophilic functional groups (i.e., C-OH and C-O associated with PS; C=O stretch, C-H, C-N stretch, and C=O symmetric stretching associated with PN) (Table S3; You et al. (2017)). To further confirm the changes in hydrophilicity/hydrophobicity of the sludge surface, the PN secondary structures were analyzed. Previous studies by You et al. (2017) and Li et al. (2019) have reported that a decrease in the ratio of α -helix/(β -Sheet + Random coil) indicates a looser PN molecular structure, resulting in the sludge surface being more hydrophobic. Results show that the Fe⁰/PMS treatment effectively weakened the ratio of α -helix/(β -Sheet + Random coil) (< 29.0%) compared with the other treatments (Fig. 4b, Fig. S2, and Table S4). This suggests that the Fe⁰/PMS treatment could effectively induce loosening of the PN molecular structure and the hydrophobic sludge surface (You et al., 2017), consequently increasing the release of water.

3.3.3. Zeta potential and particle size

Sludge dewaterability was closely related to the floc structure of sludge, indicated by the zeta potential and particle size of sludge (Li et al., 2019). The addition of Fe⁰/PMS and Al⁰/PMS increased the zeta potential of sludge from -21.5 ± 0.9 mV in the control sample to -1.6 ± 0.8 mV and -3.1 ± 2.3 mV, respectively (Fig. 4c), indicating that ZVM/PMS could effectively neutralize the negative charge and compress the double layer of sludge (Liu et al., 2020). Compared to the Al⁰/PMS treatment, the Fe⁰/PMS treatment induced a greater degree of charge neutralization (Fig. 4c). A possible reason for this is that Fe³⁺ could more efficiently reduce the interfacial free energy and the electrostatic interactions between sludge flocs than Al³⁺ (Yu et al., 2021).

The particle sizes with D50 of WAS conditioned by PMS-only, Fe⁰/PMS, and Al⁰/PMS decreased to 47.9 \pm 0.6 μ m, 40.5 \pm 1.0 μ m, and 43.2 \pm 0.3 μ m, respectively, compared to the control sample (D50 of 53.7 \pm 1.2 μ m) (Fig. 4d), indicating that PMS-AOPs caused sludge flocs to disperse and formed a compact and dense floc structure (Liang et al., 2020). Furthermore, compared to the Al⁰/PMS treatment, the particle size of WAS conditioned by Fe⁰/PMS was smaller, likely due to the Fe⁰/PMS treatment effectively destroying the gel-networks surrounding flocs via oxidation by active radical species (Liu et al., 2020).

3.4. Environmental risk evaluation

3.4.1. Speciation distribution and leaching behaviour of heavy metals

The chemical speciation distribution of heavy metals was used to evaluate their availability and mobility, reflecting the environmental risk of heavy metals present in sludge (Liu, 2019). As shown in Fig. 5a and f. Cd and Zn mainly existed in the reducible fraction (F2) in the control sample (> 37.0% in the F2 fraction), indicating high environmental risk (Xiong et al., 2018). After treatment, the F2 fraction content of Cd and Zn decreased, while the residual fraction (F4) content significantly increased, indicating that Cd and Zn became more immobilized in the sludge cake. It should be noted that after treatment with Fe⁰/PMS, the increase in F4 fraction content of Cd and Zn was higher than with PMS-only or Al⁰/PMS treatments, exhibiting an enhanced level of risk reduction and immobilization of heavy metals. This effect could be due to the efficient removal of EPS by active radical species (Xiong et al., 2018). Cr and Cu were mostly distributed among oxidizable fraction (F3) and F4 fractions in the control sample (> 90.0%), while an obvious increase in the F4 fraction content of Cr and Cu was observed after the Fe⁰/PMS and Al⁰/PMS treatments (Fig. 5b and c), indicating enhanced Cr and Cu stabilization. After conditioning by both Fe⁰/ PMS and Al⁰/PMS treatments, the F3 and F4 fractions of Ni and As increased compared with the control sample (Fig. 5d and g), indicating enhanced stabilization of these metals. Notably, the Al⁰/PMS treatment more effectively enhanced the immobilization of Ni. while Fe⁰/PMS treatment more efficiently reduced the eco-toxicity of As. In both the control and treated samples. Pb was mainly distributed in the F3 and F4 fractions (Fig. 5e), which indicates the high stability of Pb in the WAS. Additionally, the results of risk assessment code and TCLP analysis (Table S5 and Table S6) show that after Fe⁰/PMS and Al⁰/PMS treatments, the leaching toxicity and environment risk of these heavy metals in dewatered sludge cake, were significantly reduced. Compared to the Al^0/PMS treatment, WAS treated by Fe^0/PMS treatment presented a lower environmental risk from these heavy metals in sludge cake, likely due to the effective destruction of flocs and EPS (Liu, 2019). Overall, these results show that the Fe⁰/PMS treatment was more effective at enhancing the stabilization of heavy metals and lightning the leaching toxicity and environmental risk of heavy metals in treated sludge.

3.4.2. Faecal coliforms

Faecal coliform content is an important factor that determines the degree of sludge stabilization and suitability for agricultural use and sanitary landfill (Zeng et al., 2019). As such, the biomass specific most probable number (MPN) of E. coli was examined as an indicator. The MPN value of faecal coliforms decreased from 5.5 \pm 0.2 log (MPN g^{-1} TSS⁻¹) to 3.3 \pm 0.1 log (MPN g^{-1} TSS⁻¹) with PMSonly treatment, 2.3 \pm 0.1 log (MPN g⁻¹ TSS⁻¹) with Fe⁰/PMS treatment, and 2.2 \pm 0.1 log (MPN g⁻¹ TSS⁻¹) with Al⁰/PMS treatment (Fig. S3). These results showed that the faecal coliform MPN values of WAS treated by the ZVM/PMS systems were sufficiently lower than the standard sanitary level required by the US EPA (3.0 $\log (MPN g^{-1} TSS^{-1}))$ (Ruiz-Hernando et al., 2014), indicating effective faecal coliform inactivation. It should be noted that the level of faecal coliform inactivation by Fe⁰/PMS treatment was close to that of Al⁰/PMS, which might be due to the fact that active radical species can efficiently destroy the structure of these pathogenic microorganisms (Wordofa et al., 2017).

3.5. Mechanisms of WAS dewaterability with Fe^0/PMS and Al^0/PMS treatments

Based on the discussed results, a two-step mechanism of oxidation and flocculation is proposed for WAS conditioning by Fe^{0} / PMS and Al^{0} /PMS (Fig. 6).



Fig. 3. Changes in (a) PN concentrations, (b) PS concentrations, and (c) TOC concentrations during the Fe⁰/PMS and Al⁰/PMS systems and variations in the FRI values in the (d) S-EPS, (e) LB-EPS, and (f) TB-EPS during the Fe⁰/PMS and Al⁰/PMS systems. (Constant conditions: Fe⁰ dosage = 3.0 mM g⁻¹ TSS⁻¹, PMS dosage = 0.2 mM g⁻¹ TSS⁻¹, initial pH = 4.0; Al⁰ dosage = 5.0 mM g⁻¹ TSS⁻¹, PMS dosage = 0.3 mM g⁻¹ TSS⁻¹, initial pH = 3.0).



Fig. 4. (a) FT-IR spectrum of the raw and treated WAS, (b) Profiles in α -Helix/(β -Sheet + Random coil) of the PN secondary structures, (c) Changes in zeta potential of WAS treated by PMS, Fe⁰/PMS, and Al⁰/PMS, and Al⁰/

In the Fe⁰/PMS treatment process, large amounts of active SO_4^{-1} and •*OH* radicals were generated. These active radicals could efficiently destroy floc structures, decomposing PN and PS biopolymers present in EPS and removing hydrophilic functional groups (i.e., C–OH and C–O associated with PS; C=O stretch, C–H, C–N stretch, and C=O symmetric stretching associated with PN) on the sludge surface. This results in cell lysis and a significant decrease in EPS concentration, particle size, bound water content, as well as the availability and mobility of heavy metals. Meanwhile, Fe³⁺/Fe²⁺ with a strong flocculation ability could effectively form compact flocs through negative charge neutralization and electrostatic interaction energy mitigation. Accordingly, a high level of WAS dewaterability was achieved. Overall, in the Fe⁰/PMS process, Fe³⁺/Fe²⁺ flocculation likely played a significant role in the improvement of WAS dewaterability.

In the Al⁰/PMS conditioning process, less active SO_4^- and • *OH* radicals were produced, capable of removing a portion of the EPS and hydrophilic functional groups on the sludge surface. This relatively moderate degree of oxidation resulted in less structural damage to flocs and a lower decrease in particle size, bound water content, as well as the availability and mobility of heavy metals. Furthermore, Al³⁺ exhibits moderate flocculation ability with WAS, which could not efficiently reassemble the dissociated flocs. As a result, a moderate level of WAS dewaterability could be obtained. Overall, in the Al⁰/PMS process, oxidation was the dominant

process for the enhancement of WAS dewaterability.

3.6. Cost-benefit analysis and environmental implications

In order to evaluate the feasibility of Fe⁰/PMS and Al⁰/PMS treatments, a comparative cost-benefit analysis was performed under the scenario of a WWTP (400,000 m³ day⁻¹) with an annual WAS production of 21.600.0 ton TSS. The total annual cost of Fe⁰/ PMS and Al⁰/PMS treatments for WAS conditioning were calculated to be 2,633,420 USD\$ year⁻¹ and 3,933,606 USD\$ year⁻¹, respectively (Table 1), both of which are significantly lower than the reported costs for the Fe²⁺/PMS system (7,592,400 USD\$ year⁻¹, Liu et al., 2016), Fe²⁺/persulfate system (7,322,400 USD\$ year⁻¹, Zhen et al., 2012), and Fenton system (5,743,440 USD year⁻¹, Lu et al., 2003). The total annual cost of Fe⁰/PMS and Al⁰/PMS treatments were found to be comparable to the reported costs for electrolysis + Fe⁰/persulfate treatment (3,220,560 USD\$ year⁻¹, Li et al., 2016) and vanadium-titanium magnetite/PMS treatment (2,982,960 USD\$ year⁻¹, Liu, 2019) (Table 1). These results indicated that the proposed ZVM/PMS treatments could efficiently enhance WAS dewaterability whilst achieving significant economic advantages. Furthermore, these results also showed that application of the Fe⁰/PMS treatment system could save approximately 33.1% of the total cost annually, compared to the Al⁰/PMS treatment, while the Wc of WAS treated by Fe⁰/PMS (Wc of 55.7 wt%) was also the



Fig. 5. Chemical species distribution of (a) Cd, (b) Cr, (c) Cu, (d) Ni, (e) Pb, (f) Zn, and (g) As in the dewatered sludge cake of control sample and treated samples after PMS, Fe⁰/PMS, and Al⁰/PMS treatments.

lowest compared to all other treatments (Table 1). Collectively, these findings indicate that Fe^0/PMS treatment is the most

economically-feasible technique for enhancing WAS dewaterability and promoting the sludge disposal capacity.



Fig. 6. Proposed mechanisms for improving the WAS dewaterability treated by the Fe⁰/PMS treatment and the Al⁰/PMS process.

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Table 1

Cost estimation of Fe ⁰ /PMS treatmen	t, Al ⁰ /PMS process	, and different AOPs for th	e enhancement of sludge	dewaterability.
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Process	Chemical agents	Unit price ^a	Reagents cost	Energy cost ^b	Total cost	Annual cost ^c (USD\$ year ⁻¹)	Wc of dewatered sludge
		(USD\$ ton ⁻¹)	(USD\$ ton ⁻¹ TSS ⁻¹)	$(\text{USD}\ \text{ton}^{-1}\ \text{TSS}^{-1})$	$(\text{USD}\ \text{ton}^{-1}\ \text{TSS}^{-1})$		(wt.%)
Fe ⁰ /PMS	H ₂ SO ₄ Fe ⁰ PMS	78.0 170.0	105.4	16.5	121.9	2,633,420	55.7
Al ⁰ /PMS	H_2SO_4 Al^0	78.0 750.0	165.6	16.5	182.1	3,933,606	59.4
Fe ²⁺ /PMS ^d	FeSO ₄ ·7H ₂ O PMS	64.7 600.0	336.2	15.3	351.5	7,592,400	64.2
Fe ²⁺ /persulfate ^e	FeSO ₄ ·7H ₂ O potassium persulfate	64.7 600.0	323.7	15.3	339.0	7,322,400	-
$Fe^{2+}/H_2O_2{}^{\rm f}$	H_2SO_4 FeSO ₄ ·7 H_2O H_2O_2	78.0 64.7 200.0	250.6	15.3	265.9	5,743,440	75.2
$Electrolysis + Fe^0/persulfate^g \\$	Fe ⁰ potassium persulfate	170.0 600.0	83.8	65.3	149.1	3,220,560	73.6
Vanadium-titanium magnetite/PMS ^h	Vanadium-titanium magnetite PMS	87.0 600.0	122.8	15.3	138.1	2,982,960	72.9

Unit price of chemicals was determined according to http://www.alibaba.com/.

^b Energy cost was calculated as per Xiao et al. (2017).
 ^c Scenario of a 400,000 m³ day⁻¹ WWTP with a daily sludge production of 60.0 ton TSS was used to calculate the total annual cost.

^d Refer to Liu et al. (2016).

^e Refer to Zhen et al. (2012).

^f Refer to Lu et al. (2003).

^g Refer to Li et al. (2016).

^h Refer to Liu (2019).

Zero-valent metals act as efficient catalysts for PMS activation in WAS dewatering (Wc < 60.0 wt%), significantly improving WAS dewaterability, mitigating the risks presented by heavy metals and faecal coliforms, while also lowering operational costs. However, the feasibility of implementing these technologies for improving sludge dewaterability has previously only been evaluated in labscale tests, while the feasibility of full-scale applications should also be assessed in terms of technical and economic feasibility. Furthermore, the Fe⁰/PMS and Al⁰/PMS treatments also have the issue of low pH requirement. Accordingly, to overcome this challenge in the full-scale applications, future studies should be worthy to optimize the operational conditions of Fe⁰/PMS and Al⁰/PMS treatments to achieve efficient sludge dewaterability under neutral pH conditions.

Compared to Al⁰/PMS treatment, Fe⁰/PMS treatment appears to be superior for the treatment of WAS, achieving increased WAS dewaterability, lower operational costs, and greater reduction of environmental risks presented by heavy metals and faecal coliforms. Furthermore, according to the study of Lu et al. (2020), Fe⁰/ PMS conditioning methods could effectively remove antibiotic resistance genes (ARGs) from WAS, further reducing the environmental burden. These advantages increase the potential for subsequent resource utilization, in applications such as an iron-rich fertilizer for land use (Wang et al., 2020b) and phosphorus recovery via the formation of FePO₄ crystals (Wilfert et al., 2015). Moreover, prior to WAS conditioning, Fe⁰ could be added to the anerobic digestion tank, promoting VSS reduction and CH₄ production (Yan et al., 2020) and consequently strengthening the practicability of effective Fe⁰/PMS treatment. It is of note, that although the Al⁰/PMS treatment exhibited a lower dewatering capability and cost-benefit than the Fe⁰/PMS treatment, the Al⁰/PMS treatment still exhibited a better dewatering efficiency and lower operational costs compared to the established Fe^{2+}/PMS system (Table 1). Furthermore, in scenarios where Al-rich precipitating reagents are utilized in WWTPs (Ottosen et al., 2013), Al⁰/PMS treatment could be a

preferred option to treat WAS, as the residual Al could be used as a catalyst for the Al⁰/PMS process. Also, to further minimize operational costs, scrap Al⁰ from beverage cans could be applied as an alternative to Al⁰ powder. However, the feasibility of use scrap Al⁰ in the Al⁰/PMS system must be researched further, due to the bigger particle sizes. Furthermore, aluminum exposure via the dewatering liquid should be taken into consideration before future applications, due to the potential environmental toxicity of Al (Xie et al., 2015).

4. Conclusions

In this study, WAS dewaterability, physiochemical characteristics, and the potential environmental risks of both Fe⁰/PMS and Al⁰/ PMS treatments, were systematically compared. The main conclusions can be summarized as follows:

- (1) Fe⁰/PMS treatment achieved higher WAS dewaterability than Al^{0}/PMS treatment. The Wc values of WAS treated by Fe⁰/ PMS and Al⁰/PMS were 55.7 \pm 2.7 wt% and 59.4 \pm 1.3 wt%, respectively.
- (2) The key factors contributing to the enhancement of WAS dewaterability, were Fe³⁺/Fe²⁺ flocculation in the Fe⁰/PMS treatment, while in the Al⁰/PMS treatment, SO_4^{--} oxidation was the dominant factor.
- (3) Compared to the Al⁰/PMS treatment, Fe⁰/PMS treatment conditioning achieved greater reduction of hydrophilic EPS and particle size, with an enhanced increase in zeta potential.
- Both the Fe⁰/PMS and Al⁰/PMS treatment processes effec-(4)tively reduced the environmental risks presented by heavy metals and faecal coliforms in dewatered sludge. Moreover, the Fe⁰/PMS treatment exhibited greater cost savings than the Al⁰/PMS treatment process.

In summary, this study provides a solid baseline for the selection

of effective PMS activator during the sludge conditioning and dewatering processes, with mechanistic information allowing system optimization depending on WAS characteristics.

Declaration of competing interest

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

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Appendix A. Supplementary data

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Author statement

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