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Enhanced dewaterability of waste activated sludge by Fe(II)-activated peroxymonosulfate oxidation



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HIGHLIGHTS

• Sludge dewaterability was improved by Fe(II)-PMS with high CST and SRF reduction.

- Optimal conditions were identified: PMS 0.9 mmol/gVSS, Fe(II) 0.81 mmol/gVSS, pH 6.8.
- The protein in EPS conducted a detrimental influence on sludge dewaterability.
- The release of EPS-bound water induced the enhanced sludge dewatering.

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ABSTRACT

The effect of Fe(II)-activated peroxymonosulfate (Fe(II)-PMS) oxidation on the waste activated sludge (WAS) dewatering and its mechanisms were investigated in this study. The capillary suction time (CST), specific resistance to filterability (SRF) of sludge and water content (W_C) of dewatered sludge cake were chosen as the main parameters to evaluate the sludge dewaterability. Experimental results showed that Fe(II)-PMS effectively disintegrated sludge and improved sludge dewaterability. High CST and SRF reduction (90% and 97%) was achieved at the optimal conditions of PMS (HSO₅⁻) 0.9 mmol/gVSS, Fe(II) 0.81 mmol/gVSS, and pH 6.8. Extracellular polymeric substances (EPS) and three-dimensional excitation–emission matrix (3D-EEM) fluorescence spectroscopy before and after Fe(II)-PMS oxidation were determined to explain the enhanced dewatering mechanism. The release of EPS-bound water induced by the destruction of EPS was the primary reason for the improvement of sludge dewaterability during Fe(II)-PMS oxidation.

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1. Introduction

Activated sludge processes and its derived processes are important technologies for wastewater treatment, but these biological processes generate large amounts of waste activated sludge (WAS) (Feng et al., 2009). The treatment and disposal of excess sludge generated by a conventional activated sludge treatment plant usually accounts for 50–60% of the total operating expense (Ning et al., 2014; Zhou et al., 2015b). Sludge dewatering is a promising approach in reducing sludge volume and cost of sludge transport and ultimate disposal (Zhen et al., 2012a). Various methods have been investigated to enhance sludge dewaterability, such

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as the addition of polyelectrolyte and surfactants (Yuan et al., 2011), Fenton pretreatment (Lu et al., 2003; Zhou et al., 2014; Liang et al., 2015), alkaline pretreatment (Li et al., 2009), ultrasound conditioning (Feng et al., 2009), microwave irradiation (Yu et al., 2009), and electrolysis (Yuan et al., 2011; Zhen et al., 2013).

Recent progress in wastewater treatment technologies has led to the development of advanced oxidation processes (AOPs), which are based in the generation of extremely reactive species like hydroxyl radicals (·OH) and sulfate radicals (SO₄⁻) (Shi et al., 2012). Nowadays, SO₄⁻ based AOPs using persulfate (PS, S₂O₈²⁻) or peroxymonosulfate (PMS, HSO₅⁻) as oxidant have attracted great interest in the area of water treatment and other environmental applications (Yang et al., 2008). Compared to ·OH (1.8–2.7 V), SO₄⁻ owns a higher redox potential (2.5–3.1 V), a longer life time (30–40 µs) and a stronger degradation ability for most organic pollutants over a wide pH range (4 < pH < 9) (Ren et al., 2015). SO₄⁻



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can be generated by activating PS or PMS with heat, UV or transition metals (Fe^{2+} , Co^{2+} , Ag^+) (Li et al., 2015; Cai et al., 2015). Compared with other transition metals, Fe^{2+} has the advantages of being inexpensive and nontoxic, resulting in its widely application as the high-efficiency PMS activating agent (Lin et al., 2013), via Eq. (1) (Cai et al., 2015).

$$\mathrm{Fe}^{2+} + \mathrm{HSO}_5^- \to \mathrm{Fe}^{3+} + \mathrm{SO}_4^- + \mathrm{OH}^- \tag{1}$$

Zhen et al. (2012a,b) used Fe(II)-activated persulfate (Fe(II)-PS) oxidation to condition WAS and the sludge dewaterability was obviously improved. Experimental results showed that the capillary suction time (CST) reduced 88.8% within 1 min. PMS, a type of (bi)sulfite, can participate in degradation processes with more efficient way than PS (Chen et al., 2012), and maybe have a higher efficiency on sludge dewatering than PS. However, to date, the report of using PMS radicals-based oxidation process to improve WAS dewaterability could hardly be found. The scientific attempt on the application of PMS oxidation to sludge dewatering process should be useful to enrich the theory of sludge treatment and disposal.

In this laboratory-scale study, the feasibility of Fe(II)-activated PMS oxidation on enhanced WAS dewaterability was investigated. Effect of initial pH, molar ratio of Fe^{2+}/HSO_5^- and HSO_5^- concentration on the sludge dewaterability was evaluated and the optimal experimental conditions were identified. In addition, the enhanced dewatering mechanism behind the observed experimental data was explored by three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectra.

2. Methods

2.1. Materials

The WAS used in this study was obtained in the summer from the secondary sedimentation tank of a municipal wastewater treatment plant (WWTP) of Changsha, China. The collected sludge was concentrated for 24 h by settling at 4 °C before use. The main characteristics of sludge are as follows: pH 6.8 ± 0.1, total suspended solids (TSS) 12.3 ± 0.8 g/L, volatile suspended solids (VSS) 7.6 ± 0.4 g/L, water content of sludge 97.86 ± 0.21%, CST 201.8 ± 2.0s, specific resistance to filterability (SRF) of sludge (9.52 ± 0.8) × 10¹³ m/kg, W_C of dewatered sludge cake 88.12% (Error bars show 95% confidence intervals). Potassium peroxymonsulfate triple salt (KHSO₅, >47%) and ferrous sulphate heptahydrate (FeSO₄·7H₂O, >99.0%) were purchased from Sinopharm Chemical Reagents Co. (Shanghai, China). The chemical reagents were of analytical grade and used as received without further purification.

2.2. Experimental procedure

Three series of bench-scale experiments were conducted in 500 mL conical flasks with the sludge sample of 300 mL to investigate the effect of initial pH, Fe²⁺/HSO₅⁻ and PMS concentration on sludge dewaterability. The initial pH was adjusted to 3.0, 5.0, 6.8, 8.0 and 10.0 by 2.0 M sulfuric acid or 2.0 M sodium hydroxide solutions and then 0.81 mmol/gVSS Fe²⁺ and 0.9 mmol/gVSS HSO₅⁻ was added into the reactors simultaneously. A fixed 0.9 mmol/gVSS HSO₅⁻ with different dosage Fe²⁺, controlling the molar ratio of Fe²⁺/HSO₅⁻ 0.1, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, respectively, was added into the reactor at initial pH 6.8 to evaluate the influence of Fe²⁺/HSO₅⁻. Effect of PMS concentration was conducted in six identical reactors adding 0.3, 0.6, 0.9, 1.2, 1.5, 1.8 mmol/gVSS HSO₅⁻ at fixed 0.9 of Fe²⁺/HSO₅⁻ molar ratio. The reaction was initiated immediately with adding an appropriate amount of PMS (HSO₅⁻) into the reactor once a specified Fe(II) was applied. Then the sludge

was continuously agitated by a constant temperature-magnetic stirrer with a speed of 120 rpm at 25 °C. At predetermined time intervals, a 5.0-mL sample was collected to measure CST. 100 mL sample were taken out after 20 min to analyze SRF and W_C of dewatered sludge cake. Reproducibility of the measurements was determined in triplicates, and the average values were used.

2.3. Analytical methods

2.3.1. CST, SRF and W_C determination

The CST was evaluated with a CST instrument (model 304B, Triton, UK) equipped with an 18 mm diameter funnel and Whatman No.17 chromatography-grade paper.

The SRF was measured by vacuum filtration method: 100 mL treated sludge was poured into a 9 cm standard Buchner funnel fitted with pre-wetted 1.2 μ m glass fiber filter paper, and a constant vacuum pressure (P) of 50 kPa was applied for 10 min. Both the filtrate volume (V) and the filtration time (t) were recorded to assess sludge SRF. The SRF was then calculated via Eq. (2) (Lu et al., 2003).

$$SRF = \frac{2PA^2b}{\mu W}$$
(2)

where SRF is specific resistance of sludge (m/kg), *P* is filtration pressure (N/m²), *A* is the filter area (m²), μ is the viscosity of the filtrate (N's/m²), *W* is the weight of cake solids per unit volume of filtrate (kg/m³), *b* can be calculated from the slope of filtrate discharge curve (*V* as the *X* axis, *t*/*V* as the Y axis) (s/m⁶).

The W_C of dewatered sludge cake trapped by the filter paper in the process of SRF measurement was identified in accordance with standard methods (APHA, 1998).

2.3.2. Extraction of EPS

EPS of sludge samples was extracted according to the procedures similar to the previous literature (Zhou et al., 2015b). In brief, sludge was firstly centrifuged at 4000g for 15 min at 4 °C to separate soluble EPS (S-EPS) in the sludge supernatant. The sludge pellet left in the centrifuge tube was then re-suspended to its original volume by adding 0.05% NaCl solution. Then, the sludge suspension was sheared with a vortex mixer for 1 min at 70 °C, followed by centrifugation at 4000g at 4 °C for 10 min. The organic matter in the supernatant was regarded as the loosely bound EPS (LB-EPS). The sludge pellet left in the centrifuge tube was again resuspended to its original volume by adding 0.05% NaCl solution and placed in a water bath at 60 °C for 30 min, and then the sludge mixture was centrifuged at 4000g at 4 °C for 15 min. The collected supernatant was referred to as the tightly bound EPS (TB-EPS).

2.3.3. Three-dimensional excitation–emission matrix (3D-EEM) fluorescence spectroscopy

All EEM fluorescence spectra were measured using a luminescence spectrometry (F-4600 FL spectrophotometer, Hitachi, Japan). The EEM spectra of EPS were gathered with corresponding scanning emission (Em) spectra from 200 nm to 550 nm at 3 nm increments by varying the excitation (Ex) wavelength from 200 nm to 500 nm at 3 nm increments. The excitation and emission slits were both maintained at 5 nm, and the scanning speed was set at 4800 nm/min for all the measurements. A 290 nm emission cutoff filter was used in scanning to eliminate the second order raleigh light scattering. The spectrum of deionized (DI) water was recorded as the blank. The software Origin 8.5 (Origin Lab Inc., USA) was employed to handle the EEM data. EEM spectra are plotted as the elliptical shape of contours. The X-axis represents the emission spectra from 200 to 550 nm while the Y-axis represents the excitation spectra from 200 to 500 nm, and the third dimension, i.e., the contour line, is given to express the fluorescence intensity.

2.3.4. Other item analysis

TSS and VSS of raw sludge were measured following Standard methods (APHA, 1998). pH was measured using a digital pH-meter (pHs-3C, Leici Co., Ltd., Shanghai, China). Soluble protein was determined by the Lowry–Folin method with Bull Serum Albumin (BSA) as the standard, and soluble polysaccharide was determined by the phenol–sulfuric method with glucose as the standard (Lowry et al., 1951; Herbert et al., 1971).

3. Results and discussion

3.1. Effect of initial pH

The effect of initial pH on sludge dewatering performance was explored at five different initial pH levels (3.0, 5.0, 6.8 (raw sludge), 8.0, 10.0) with HSO₅⁻ concentration 0.9 mmol/gVSS and n(Fe²⁺)/n (HSO₅⁻) 0.9. The corresponding CST, SRF and W_C at different initial pH were illustrated in Fig. 1.

It can be clearly seen from Fig. 1 that all the possible reduction of CST was almost happened within 1 min, and high CST reduction efficiency (over 80%) was achieved at investigated initial pH except for pH 10. These results agreed with those reported by Zhen et al. (2012a,b), who studied the Fe(II)-activated persulfate oxidation for sludge dewatering. The values of CST and SRF decreased slightly



Fig. 1. Effect of initial pH on sludge dewaterability. (a) The corresponding CST with time at different pH level. (b) The corresponding SRF and W_C at different pH level after 20 min-reaction. Experimental conditions: $[HSO_5^-] = 0.9 \text{ mmol/gVSS}$, n (Fe²⁺)/n (HSO_5^-) = 0.9.

when pH was ranged from 3.0 to 6.8, and reached the maximum reduction rate of 90% and 97% respectively at pH 6.8 after 20 min. Contrarily, W_C of dewatered sludge cake increased slowly with the increase of initial pH and the maximum reduction rate of 27% was achieved at pH 3.0. This is most likely because SO_4^- generated by Fe(II)-activated PMS caused the decomposition of sludge and dissolving of EPS, which enhanced the sludge dewaterability (Zhou et al., 2015a). Compared to the acidic and neutral conditions, alkaline initial pH exhibited apparent inhibition to the PMS activation and the CST, SRF values increased obviously at pH 10.0 (Fig.1). At alkaline condition, the decrease of soluble iron catalyst induced by Fe(II) precipitation to Fe(OH)_{2(s)} can be the main cause of the reduction in the sludge dewatering efficiency (Rastogi et al., 2009). Simultaneously, the 'OH formed easily in alkaline medium, which also inhibited the generation of SO_4^- (Guan et al., 2011).

3.2. Effect of molar ratio of Fe^{2+}/HSO_5^{-}

The effect of molar ratio of $\text{Fe}^{2+}/\text{HSO}_5^-$ on sludge dewaterability was investigated at initial pH 6.8 and 25 °C. HSO_5^- was added at fixed dosage (0.9 mmol/gVSS) and the dosage of Fe^{2+} was in the range of 0.09–1.62 mmol/gVSS, in which $n(\text{Fe}^{2+})/n(\text{HSO}_5^-)$ was 0.1, 0.3, 0.6, 0.9, 1.2, 1.5, 1.8, respectively. The variation of sludge dewaterability in term of CST, SRF and W_C of dewatered sludge cake is presented in Fig. 2. It can be found that $n(\text{Fe}^{2+})/n(\text{HSO}_5^-)$



Fig. 2. Effect of molar ratio of Fe^{2+}/HSO_5^- on sludge dewaterability. (a) The corresponding CST with time at different Fe^{2+}/HSO_5^- molar ratio level. (b) The corresponding SRF and W_c at different Fe^{2+}/HSO_5^- molar ratio level after 20 min-reaction. Experimental conditions: pH = 6.8, [HSO₅] = 0.9 mmol/gVSS.

have a remarkable influence on the CST and SRF value. With $n(Fe^{2+})/n(HSO_5^-)$ increasing from 0.1 to 0.9, the value of CST and SRF decreased rapidly and it tended to stable when $n(Fe^{2+})/n(HSO_5^-)$ further increased to 1.8. Compared with the raw sludge, the CST and SRF declined from 201.8s to 19.5s and from 95.2 $\times 10^{12}$ m/kg to 3.5×10^{12} m/kg respectively at $n(Fe^{2+})/n(HSO_5^-)$ 0.9 and the drop for both was more than 90%. The variation trend of W_C of dewatered sludge cake was different from CST and SRF. When the $n(Fe^{2+})/n(HSO_5^-)$ exceeded 0.9, W_C of dewatered sludge cake was only 63.62% at $n(Fe^{2+})/n(HSO_5^-)$ 0.9 and the reduction rate reached 28% compared with raw WAS (88.12%).

As an initiator, Fe(II) activates the PMS, yields the SO_4^- and consequently accelerates the disintegration of sludge floc, resulting in the reduction of CST, SRF and W_c . Hence, the increase of Fe²⁺ dosage is favorable to improvement of sludge dewaterability. However, the excess Fe²⁺ may quench SO_4^- according to Eq (3). The unfavorable consumption of SO_4^- caused the deterioration of sludge dewaterability, for example the increase of W_c of dewatered sludge cake.

$$Fe^{2+} + SO_4^{-} \rightarrow Fe^{3+} + SO_4^{2-}$$
 (3)

3.3. Effect of PMS concentration

The influence of the concentration of PMS was discussed at pH 6.8 and constant Fe²⁺/HSO₅⁻ molar ratio (0.9). Different concentration of HSO₅ was added in the range of 0.3–1.8 mmol/L. The experimental results are shown in Fig. 3. When HSO₅⁻ concentration increased from 0.3 to 0.9 mmol/gVSS, the CST value obviously decreased. The CST declined from 201.8s (raw WAS) to 20s at HSO₅⁻ concentration 0.9 mmol/gVSS. With HSO₅⁻ concentration further increasing to 1.8 mmol/gVSS, the reduction of CST became slight. The variation trend of SRF and W_C of dewatered sludge cake was similar to CST and both decreased from 95.2 × 10¹² m/kg and 88.12% (raw sludge) to 3.15×10^{12} m/kg and 64.21% respectively at HSO₅⁻ concentration 0.9 mmol/gVSS.

PMS is the source of $SO_4^{-\cdot}$ in Fe(II)-activated PMS oxidation system and more reactive radicals would be generated at higher PMS concentration (Cai et al., 2015). Hence, it is reasonable that the increasing PMS dosage is in favor of enhancing sludge dewatering. In this study, it was found that the dewaterability of sludge changed slightly when PMS concentration was over 1.8 mmol/gVSS. This might attribute to the unfavorable consumption of $SO_4^{-\cdot}$ led by the excess HSO_5^{-} . Based on Eq. (4), excess HSO_5^{-} not only resulted in the scavenging of $SO_4^{-\cdot}$, but also generated the less reactive $SO_5^{-\cdot}$. Even the radical-radical reaction may occur according to Eq. (5) (Cai et al., 2015).

$$SO_4^{-} + HSO_5^{-} \rightarrow SO_5^{-} + SO_4^{2-} + H^+$$
 (4)

$$\mathrm{SO}_4^{-\cdot} + \mathrm{SO}_4^{-\cdot} \to \mathrm{S}_2\mathrm{O}_8^{2-} \tag{5}$$

3.4. Possible mechanisms of improved sludge dewaterability

3.4.1. The content of protein and polysaccharide in EPS

Extracellular polymeric substances (EPS) secreted by the various microorganisms are the major components of sludge floc matrixes, mainly consisting of proteins, polysaccharides (Zhen et al., 2012b). They are regarded as one of the most important factors that influence the dewaterablity of sludge (Yu et al., 2009).

In this study, the experimental conditions were maintained as Fe^{2+} concentration of 0.81 mmol/gVSS, HSO_5^- concentration of 0.9 mmol/gVSS, and original pH. EPS was extracted after 20 min of conditioning and analyzed the concentration of soluble protein



Fig. 3. Effect of PMS concentration on sludge dewaterability. (a) The corresponding CST with time at different PMS concentration level. (b) The corresponding SRF and W_c at different PMS concentration level after 20 min-reaction. Experimental conditions: pH = 6.8, n (Fe²⁺)/n (HSO₅⁻) = 0.9.

and polysaccharide. The experimental results in Fig. 4 showed that raw sludge contained a large amount of protein and polysaccharide. Their concentrations reached approximately 360 mg/L and 50 mg/L respectively, most of which presented in S-EPS and TB-EPS. After Fe(II)-PMS oxidation treatment, the soluble protein



Fig. 4. The content of protein and polysaccharide in different fractions of EPS (S-EPS, LB-EPS, TB-EPS) before and after 20 min treatment by Fe(II)-PMS oxidation process. Experimental conditions: pH = 6.8, $[HSO_5^-] = 0.9 \text{ mmol/gVSS}$, n $(Fe^{2+})/n$ $(HSO_5^-) = 0.9$.

decreased rapidly to 80 mg/L meanwhile the concentration of polysaccharide slightly increased to 60 mg/L. Considering that the large reduction of protein was in line with the improvement of sludge dewaterability, it was assumed that the protein in EPS conducted a detrimental influence on sludge dewaterability. Liu et al. (2011) also found that protein-like substances in EPS contributed more to the filtration resistance of membrane in MBRs. Compared to protein, polysaccharide shows little influence on sludge dewaterability. As shown in Fig. 4, the protein content in S-EPS, LB-EPS and TB-EPS all decreased to a great extent. It suggested that the SO_4^{-} generated from Fe(II)-PMS system possess powerful oxidizing capacity, which can not only degrade S-EPS and LB-EPS, but also destroy difficult-degradation TB-EPS. Ren et al. (2015) investigated the effects of sulfate radical oxidation pretreatment on the disintegration of waste activated sludge using the peroxymonosulfate (PMS) as the sulfate radical oxidant. They found that SCOD concentration in the supernatant raised with PMS dosage increasing, but began decrease when PMS dosage exceeded 30 mg/gSS. The phenomena demonstrated that the moderate PMS could improve the sludge solubility, but dissolved COD maybe mineralized of by oxidants when dosage exceeded the threshold value.

3.4.2. EEM spectra of different EPS fractions

3D-EEM fluorescence spectroscopy is a rapid and sensitive technique to determine the fluorescence compounds in EPS and explore the possible mechanisms of improved sludge dewaterability. Typical EEM fluorescence spectra of EPS and their corresponding fractions for the raw WAS and sludge samples treated by Fe(II)-PMS are depicted in Fig. 5. Two main peaks could be identified from fluorescence spectra of EPS in raw sludge, which located at the excitation/emission wavelengths (Ex/Em) of 218–224/293–305 nm (Peak A) and 254–263/287–296 nm (Peak B) in EEM spectra. The two peaks with high fluorescence intensity were associated with the protein-like substances (Chen et al., 2003; Sheng and Yu, 2006; Wang et al., 2009). The results is agree with the conclusion that the large amount of protein existed in raw sludge. After Fe (II)-PMS oxidation treatment, five peaks with much lower fluorescence intensity were indentified at the excitation/emission (Ex/ Em) of 221-227/302-308 nm (Peak A), 275/302 nm (Peak B), 224-245/362-386 nm (Peak C), 275/365 nm (Peak D) and 323/371 nm (Peak E) in S-EPS and LB-EPS. According to the five regions of EEM divided by Chen et al. (2003), Peak C was referred to as aromatic protein (Region II), Peak D and Peak E indicates soluble microbial byproduct (SMP)-like substances (Region IV). Moreover, four peaks with much lower fluorescence intensity were found at the excitation/emission (Ex/Em) of 224/302 nm (Peak A), 275/302 nm (Peak B), 278/440 nm (Peak F) and 353/440 nm (Peak G) in TB-EPS after Fe(II)-PMS treatment. Peak F and G are related to humic-like substance (Chen et al., 2003; Wang et al., 2009: Liu et al., 2011). The locations of Peaks A and B for different EPS fractions (e.g., S-, LB- and TB-EPS) after pretreatment were all red shifted to a certain extent than those of the raw sludge EPS. A red shift should attribute to the increase of carbonyl, hydroxyl, alkoxyl, amino, and carboxyl groups in the structures of fluorophores (Chen et al., 2003; Liu et al., 2011; Zhen et al., 2012b).

Generally, intensity reduction of the fluorescence peak before and after Fe(II)-PMS oxidation treatment is an indication for oxidation of fluorescing materials. It can be seen from Fig. 5 that the fluorescence intensities of the peaks in EEM spectra of EPS were decreased significantly for the Fe(II)-PMS oxidation, which was in line with the variation tendency of sludge dewaterability in term of CST, SRF and W_C. It revealed that the fluorescence components (mainly protein) in sludge S-EPS, LB-EPS, as well as TB-EPS together affected the sludge dewaterability. The investigations in this study implied that the improved sludge dewaterability was closely related to the degradation and removal of fluorescence components present in sludge EPS. The powerful oxidation of SO_4^- from Fe(II)-PMS system actually destroyed the particular functional groups of fluorescing substances in sludge EPS and caused cleavage



Fig. 5. EEM spectra of different EPS fractions (S-EPS, LB-EPS, TB-EPS) before and after 20 min treatment by Fe(II)-PMS oxidation process. Experimental conditions: pH = 6.8, [HSO₅] = 0.9 mmol/gVSS, n (Fe²⁺)/n (HSO₅) = 0.9.

 Table 1

 Comparison of different AOPs for sludge dewatering.

AOPs	TSS (g/L)	CST		SRF		W _C of sludge	Oxidant dosage	pН	Total cost	References
		Raw sludge (s)	Reduction rate (%)	Raw sludge (m/kg)	Reduction rate (%)	cake (%)			(USD/t DS)	
Fenton	8.3	_	-	1.17×10^{13}	90.0	75.20	Fe(II) 6 g/L H ₂ O ₂ 3 g/L	3.0	250.60	Lu et al., 2003
Fenton	20.0	30.5	48.5	9.16×10^{10}	93.3	-	Fe(II) 5 g/L H ₂ O ₂ 6 g/L	3.0	288.45	Buyukkamaci (2004)
Fe(II)-PS	16.1	210.0	88.8	-	-	-	Fe(II) 1.5 mmol/gVSS $S_2O_8^{2-}$ 1.2 mmol/gVSS	6.9	323.70	Zhen et al., 2012a
Fe(II)-PMS	12.3	201.8	90.1	9.52×10^{13}	97	64.21	Fe(II) 0.81 mmol/gVSS HSO ₅ 0.9 mmol/gVSS	6.8	336.23	This study

of linkages in the polymeric backbone, thereby causing the release of EPS-bound water and subsequent enhancing the sludge dewatering.

3.5. Comparison of different AOPs for sludge dewatering

Table 1 presents the comparison of Fe(II)-PMS oxidation on enhancing sludge dewatering with Fe(II)-PS oxidation and Fenton oxidation from the technical and economical point of view. Fe (II)-PMS oxidation exhibits a similar sludge dewatering efficiency (90.1% vs 88.8% CST reduction) as well as less oxidant dosage than Fe(II)-PS oxidation. However, Fe(II)-PMS oxidation can achieve a higher CST and SRF reduction efficiency, and a lower W_C of dewatered sludge cake than Fenton oxidation. In addition, Fenton oxidation generally works in the acidic conditions, while Fe(II)-PMS and Fe(II)-PS oxidation conduct better sludge dewatering performance in a wide pH range from 3.0 to 8.0, especially in a neutral condition (pH 6.8), which save the operation cost. Therefore, compared to other AOPs, Fe(II)-PMS oxidation has many advantages, such as higher dewatering efficiency, lower oxidant dosage and wide pH applied range and is a potential technology to improve sludge dewaterability.

Total cost estimate listed in Table 1 shows that oxidant cost of Fe(II)-PMS and Fe(II)-PS oxidation is much higher than Fenton oxidation, which is because the prices of oxidant PMS and PS are more expensive than Fenton. However, the more excellent enhanced dewatering performance maybe compensate the higher operation cost and make sulfate radicals-based oxidation technology a great potential to be the effective alternates for sludge dewatering.

4. Conclusions

The Fe(II)-activated peroxymonosulfate oxidation was verified to be effective in enhancing sludge dewaterability. Optimum conditions were found to be pH 6.8, Fe(II) concentration 0.81 mmol/ gVSS, HSO_5^- concentration 0.9 mmol/gVSS. The most important mechanisms were proposed to be the degradation of EPS, especially the protein in EPS. EEM analysis confirmed that the powerful oxidation of SO_4^- generated from Fe(II)-PMS system destroyed the particular functional groups of fluorescing substances in EPS causing the release of EPS-bound water and the subsequent improvement of sludge dewaterability.

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