Enhancing dewaterability of waste activated sludge by combined oxidative conditioning process with zero-valent iron and peroxymonosulfate
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ABSTRACT
The enhancement of sludge dewaterability is of great importance for facilitating the sludge disposal during the operation of wastewater treatment plants. In this study, a novel oxidative conditioning approach was applied to enhance the dewaterability of waste activated sludge by the combination of zero-valent iron (ZVI) and peroxymonosulfate (PMS). It was found that the dewaterability of sludge was significantly improved after the addition of ZVI (0–4 g/g TSS) (TSS: total suspended solids) and PMS (0–1 g/g TSS). The optimal addition amount of ZVI and PMS was 0.25 g/g TSS and 0.1 g/g TSS, respectively, under which the capillary suction time of the sludge was reduced by approximately 50%. The decomposition of sludge flocs could contribute to the improved sludge dewaterability. Economic analysis demonstrated that the proposed conditioning process with ZVI and PMS was more economical than the ZVI + peroxodisulfate and the traditional Fenton conditioning processes.

Key words | dewaterability, oxidative conditioning process, peroxymonosulfate, waste activated sludge, zero-valent iron

INTRODUCTION
The activated sludge process has been demonstrated as an effective and environmentally friendly method for the treatment of wastewater for a long time. However, huge volumes of excess sludge produced from the operation of the wastewater treatment process added great economic burden for disposal, which could constitute 60% of the total operating costs for a wastewater treatment plant (WWTP) (Wang et al. 2017; Wei et al. 2017).

To reduce the volume of the sludge and save the disposal cost, pretreatment processes including conditioning and dewatering should be conducted before the final disposal. The conditioning process is to improve the dewaterability of waste activated sludge (WAS) by facilitating the separation of bound water, attached by capillary forces and chemical bonds, from sludge flocs (Lee & Liu 2000). After that, the water could be separated mechanically by a dewatering process.

Nowadays, advanced oxidation processes have been widely applied to sludge conditioning, including classical Fenton reagent, Fenton-like reagent and other kinds of...
strong oxidants (ozone, ferrate, etc.) (Sievers & Schaefer 2007; Liu et al. 2016). The classical Fenton reaction is comprised of a series of reactions between Fe(II) and hydrogen peroxide in the acid condition, which produce hydroxyl radicals. The hydroxyl radicals are highly oxidizing, and could decompose the sludge flocs and release the bound water from sludge structure (Buyukkamaci 2004; Liu et al. 2012). However, the chemical instability of Fe(II) and hydrogen peroxide as well as the employing of corrosive acid limited the application of the classical Fenton reagent.

More recently, modified Fenton-like methods were applied to overcome the drawbacks of the classical Fenton reagent (Xu & Wang 2012; Bokare & Choi 2014). For example, the combination of zero-valent iron (ZVI) and persulfate salt was used as an alternative reagent for the oxidization process (Hussain et al. 2014). Zhou et al. found that peroxydisulfate (PDS), a kind of persulfate salt, could react with ZVI in the neutral condition and then increase the dewaterability of sludge efficiently (Zhou et al. 2015b). The highly oxidizing sulfate radicals could be produced by ZVI-PDS reactions. Peroxymonosulfate (PMS), another kind of persulfate salt, was also found to be an effective oxidant (Yang et al. 2010). Similar to the ZVI-PDS system, the combination of PMS and ZVI could also produce sulfate radicals (Equations (1)–(3)) (Volpe et al. 2013):

\[
\begin{align*}
\text{Fe} + \text{HSO}_5^- + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{HSO}_4^- + \text{H}_2\text{O} \quad (1) \\
\text{Fe}^{2+} + \text{HSO}_5^- & \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \quad (2) \\
\text{Fe}^{2+} + \text{SO}_4^- & \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} \quad (3)
\end{align*}
\]

Compared with the hydroxyl radicals, sulfate radicals were more stable and had higher oxidation potential (Liang & Su 2009). The ZVI-PMS system was applied to decompose the refractory organics and remove the hexavalent chromium from industrial wastewaters. Sun et al. primarily applied ZVI and PMS to decompose the phenol in liquid (Sun et al. 2012). Ghanbari et al. reported that the removal rate of chemical oxygen demand (COD) from textile wastewater could reach 74.6% with the addition of 3,000 mg/L ZVI and 20 mM PMS (Ghanbari et al. 2014). Volpe et al. also found that Cr(VI) and surfactants brij 35 could be removed simultaneously in the presence of ZVI and PMS (Volpe et al. 2013).

However, no study has been conducted on changes of WAS characteristics by the treatment of a ZVI-PMS system. To investigate the feasibility of the ZVI-PMS system on the sludge conditioning process, we examined its oxidization effect on the dewaterability of WAS systematically for the first time. Capillary suction time (CST) was used as the main indicator of dewaterability, which was measured before and after ZVI-PMS treatment. Other parameters such as dissolved iron concentration from ZVI and the soluble COD in the mixture were also measured to study the related mechanisms. Economic analysis was also applied to evaluate the economic potential of the proposed oxidization process.

### METHODS

#### Sludge source and chemicals

The WAS used in this study was collected from a local WWTP (Shenzhen, China). For increasing the concentration before the experiments, the sludge was settled for 48 h in a temperature-controlled cold room (−4 °C). The cold room was to avoid the sludge degradation during the 48 h settling process. Indeed, the sludge degradation was observed to be negligible during the settling process, which was confirmed by the similar (p > 0.05) total suspended solids (TSS) and volatile suspended solids (VSS) concentrations before and after settling. The TSS and VSS of the WAS were 23.4 ± 0.4 g/L and 11.5 ± 0.1 g/L, respectively. The CST was 48.6 ± 0.7 s, and the pH was 6.5.

Analytical grade reduced iron powder (Macklin Co.) with the size of 100 mesh and Oxone (2KHSO₅·KHSO₄·K₂SO₄) (Macklin Co.) were used for the tests.

#### Batch tests

For studying the effect of PMS and ZVI concentrations on sludge dewaterability, two groups of batch tests were designed (Table 1). Test group (I) was to examine the effect of PMS concentration (0–1 g/g TSS, as shown in Table 1) on sludge dewaterability while the ZVI concentration was kept at 2 g/g TSS. Test group (II) was to investigate the effect of ZVI concentration (0–4 g/g TSS, as shown in Table 1) on sludge dewaterability while the PMS concentration was kept at 0.1 g/g TSS. The concentration of ZVI in group (I) and the concentration range of PMS and ZVI in both groups were selected based on our previous studies (Zhou et al. 2015b; Song et al. 2016). The PMS concentration in group (II) was selected according to the optimum results of group (I). All the batch tests were operated in duplicate.
Before the beginning of each batch test, 100 mL WAS was added into a 250 mL flask. After that, ZVI powder and PMS were transferred into the flasks. The samples in the flasks were then mixed with an orbital shaker at 150 rpm for 30 min. After the treatment, the sludge was sampled for measuring CST, which is described in the ‘Analytical methods’ section. Then the un-dissolved ZVI particles in the sludge were recycled by the operation of magnetic stirrers for 3 min. The ZVI powder adhered onto the magnetic stirrer bar and was removed from the sludge. Finally, the concentrations of dissolved iron were measured by the method described under ‘Analytical methods’. The soluble chemical oxygen demand (SCOD) concentrations in WAS before and after ZVI-PMS treatment were also measured.

### Analytical methods

CST was measured by a capillary suction timer (Triton-WPRL, Type 304). The measurement of CST is widely used as the standard method for indicating sludge dewaterability. CST is applied as a quantitative index for the evaluation of the dewatering performance, which stands for the time needed for sludge to complete the filtration process.

The concentration of dissolved iron in sludge was measured with coupled plasma optical emission spectroscopy (Optimal 8000). For the preparation of samples, the sludge was mixed with analytical grade nitric acid and digested with a microwave oven (MARS Xpress) for 20 min. The TSS and VSS concentrations of the original sludge and the SCOD concentration in sludge filtrate were measured by Standard Methods (American Public Health Association et al. 1998).

### Data analysis

Reduction percentage, R (%), of CST was applied as the indicator of the enhancement of sludge dewaterability, which is calculated as follows:

$$R(\%) = \frac{CST_0 - CST_e}{CST_0} \times 100\%$$ (4)

where $CST_0$ was the CST of the original sludge (s); $CST_e$ was the CST after treatment (s).

The dissolved iron from ZVI was evaluated as below:

$$\text{dissolved iron from ZVI} = Iron_e - Iron_o$$ (5)

The dissolved rate of ZVI is the dissolved ZVI during the treatment process, which is calculated as follows:

$$\text{ZVI dissolved rate (\%)} = \frac{Iron_e - Iron_o}{ZVI_0} \times 100\%$$ (6)

where $Iron_o$ was the iron concentration of original sludge (mg/L); $ZVI_0$ was the addition amount of ZVI in sludge (mg/L); $Iron_e$ was the residual iron concentration in sludge after the un-dissolved ZVI was removed (mg/L).

### RESULTS AND DISCUSSION

#### Effect of PMS concentration on WAS dewaterability

Figure 1 shows the effect of PMS concentration on WAS dewaterability. The dewaterability of WAS was enhanced...
significantly after the oxidation treatment by the ZVI-PMS system. The CST reduction rate was increased from 20% to 52% while the PMS concentrations increased from 0 g/g TSS to 0.1 g/g TSS at a ZVI concentration of 2 g/g TSS. Meanwhile, the dissolved iron from ZVI also increased from 23 mg/L to 670 mg/L with the increased PMS concentrations from 0 g/g TSS to 0.1 g/g TSS while the addition amount of ZVI was kept at 2 g/g TSS.

According to Equation (1), ZVI could be dissolved and formed Fe(II) in the presence of PMS. As shown in Equation (2), Fe(II) was the catalyst for the generation of sulfate radicals. Obviously, the increased addition of PMS led to the higher release of Fe(II), which further transformed more PMS ion into sulfate radicals. Therefore, the increased production of sulfate radicals could oxidize sludge flocs and increase the dewaterability of WAS accordingly.

However, a further increase of PMS addition did not lead to the obvious enhancement of sludge dewaterability. When the addition of PMS increased from 0.1 g/g TSS to 0.25 g/g TSS, the reduction rate of CST did not significantly increase \( (p > 0.05) \) and remained at around 52%. Interestingly, the reduction rate of CST was found to decrease from 52% to 40% while the concentration of PMS was further increased from 0.25 g/g TSS to 1 g/g TSS although the dissolved iron concentration increased from 2,470 mg/L to 8,870 mg/L. It is possibly due to the fact that excess addition of PMS ion could be consumed by the reaction with Fe(0) (see Equation (1)), and therefore less PMS ion would be available for sulfate radicals production and Fe(II) consumption (see Equation (2)).

It was also found that the CST reduction rate reached 20% while only 2 g/g TSS of ZVI was added in WAS (i.e. in the absence of PMS). A similar phenomenon was also reported by previous studies \( (Zhou \ et \ al. \ 2015b) \). This was possibly due to the reductive characteristics of ZVI, which could react with sludge flocs and transform the sludge structures.

In summary, the optimum addition of PMS was 0.1 g/g TSS while the concentration of ZVI was 2 g/g TSS, under which the reduction rate of CST was 52%. However, the increased addition of PMS (from 0.1 to 0.25 g/g TSS) did not significantly increase CST reduction rate \( (p > 0.05) \).

**Effect of ZVI concentration on WAS dewaterability**

According to Figure 1, 0.1 g/g TSS PMS was the optimum concentration for the enhancement of WAS. Thus, the effect of ZVI concentration on WAS dewaterability was investigated at a PMS concentration of 0.1 g/g TSS. Figure 2 shows that the reduction of CST increased \( (p < 0.05) \) from 20% to 50% while the addition of ZVI was increased from 0 to 0.25 g/g TSS. But further increase of ZVI did not lead to significant increase of sludge dewaterability \( (p > 0.05) \). The results implied that the optimum addition of ZVI and PMS was 0.25 g/g TSS and 0.1 g/g TSS, respectively. The reduction rate of WAS could be comparable to other kinds of oxidation conditioning process, such as the classical Fenton and ZVI-PDS system \( (Buyukkamaci \ 2004; \ Zhou \ et \ al. \ 2015b) \). The dissolved iron from ZVI only slightly increased from 438 mg/L to 700 mg/L while the ZVI concentrations ranged between 0.25 g/g TSS and 4 g/g TSS at a PMS concentration of 0.1 g/g TSS. Obviously, the relatively low concentration of PMS limited the dissolution of ZVI and excess addition of ZVI could not be oxidized. Therefore, limited sulfate radicals were generated due to the fact that no further Fe(II) ion could be produced to catalyze the PMS ion (see Equation (2)).

Furthermore, it was also found that the reduction rate of CST attained 12% in the presence of PMS only (i.e. 0.1 g PMS/g TSS in the absence of ZVI). The phenomenon is likely due to the fact that PMS itself is a kind of oxidant. Also, the dissolved iron in the sludge could possibly react with oxidant and generate radicals. Therefore, the PMS could decompose the sludge structure and then increase sludge dewaterability.

**Oxidation of sludge**

The SCOD concentrations in sludge filtrate were measured to investigate the change of sludge characteristics before and after oxidation treatment by the ZVI-PMS system. In our previous studies, we found that the increase of sludge dewaterability was primarily due to the destruction of sludge structure (i.e. extracellular polymeric substances...
and cell from sludge) during the oxidation conditioning treatment with Fenton reagent, while other mechanisms (i.e. flocculation by Fe(III)) played minor roles (Zhou et al. 2015a). Similarly, the release of SCOD could also indicate the change of sludge structure during the oxidation conditioning process with the ZVI-PMS system. The concentration of PMS influenced the release of SCOD significantly. Compared with the original sludge, the SCOD increased from 66 mg/L to 700 mg/L while the addition of PMS and ZVI was 0.25 g/g TSS and 2 g/g TSS, respectively. However, although the release of SCOD further increased to 2,080 mg/L while the addition of PMS was 1 g/g TSS, the sludge dewaterability deteriorated. This is likely due to the fact that moderate addition of oxidation reagent could decompose the sludge structure, thereby facilitating the release of bound water contained in sludge. However, excess addition of oxidation reagent could further decompose the sludge structure and release more mini-size fragments from sludge flocs, which could influence the sludge dewaterability negatively. A similar phenomenon was also reported by other researchers (Huan et al. 2009; Yu et al. 2009).

ZVI recovery and economical analysis of the proposed ZVI-PMS conditioning process

In contrast with traditional advanced oxidation processes activated by Fe(II), ZVI has a more stable chemical property as well as much lower price. During the Fe(II) activated oxidation conditioning processes, Fe(II) will be oxidized to Fe(III) completely and mixed with sludge. Hence, it could never be recycled. However, besides the dissolved iron during the oxidation conditioning process, the remaining part of the added ZVI could be separated and recovered (Zhou et al. 2015b).

As shown in Figures 1 and 2, when the concentration of PMS increased from 0.05 g/g TSS to 1 g/g TSS, the dissolved rate of ZVI ranged from 0.4% to 18.3% while the addition of ZVI was 2 g/g TSS (Figure 3(a)). On the other hand, when the concentration of PMS was kept at 0.1 g/g TSS, the dissolved fraction of ZVI ranged from 7.5% to 0.8% while the addition of ZVI was between 0.25 g/g TSS and 4 g/g TSS (Figure 3(b)). When the optimum amount of ZVI and PMS was added (0.25 g/g TSS and 0.1 g/g TSS), the dissolved iron was only 438 mg/L (i.e. dissolved rate of 7.5%). The results implied that only a small amount of iron could be consumed during the process. Considering the recycle of the remaining ZVI, the actual usage of ZVI is very low. It should be noted that the iron recovery could be achieved by the magnetic separation method, which has been reported in other literature (Li et al. 2010; Yang et al. 2011). Therefore, the application of ZVI could lead to significant cost-cutting.

The proposed ZVI-PMS technology is shown in Figure S1 (available with the online version of this paper). The produced WAS from the wastewater treatment process goes to a tiny ZVI-PMS conditioning reactor, where the WAS dewaterability was able to be improved. After that, the ZVI-PMS treated WAS is ready for dewatering, during which less volume of sludge would be generated in comparison to the WAS without ZVI-PMS treatment. Therefore, the proposed technology could substantially reduce the cost of sludge transport and disposal later. However, it should be noted that the proposed technology demonstrated in this study is only applicable to the small
WWTPs where an anaerobic digester does not exist. In the large WWTPs with the anaerobic digester, the WAS would first go to the anaerobic digester prior to dewatering, and thus anaerobically digested sludge will be produced and then subject to dewatering. Therefore, anaerobically digested sludge instead of WAS should be used as the sludge source to evaluate the feasibility of ZVI + PMS conditioning in the large WWTPs. After sludge treatment, the PMS will be consumed and ZVI will be converted to ferric/ferrous and/or recovered. Therefore, ZVI + PMS treatment will not produce any by-product that will affect the final sludge quality and cause any issues with land application. In addition, the nutrient availability of ZVI + PMS treated sludge would not be affected either. In contrast, a synthetic polymeric conditioner could be difficult to decompose and therefore might pose potential environmental issues (Tony et al. 2008; Zhou et al. 2014).

To compare the economic cost of the ZVI + PMS conditioning process with the previously proposed ZVI + PDS (Zhou et al. 2015b) and the traditional Fenton (Buyukkamaci 2004) conditioning processes, a desktop scaling-up study was performed based on a WWTP with a population equivalent of 200,000. In the economic analysis, it was assumed that three types of conditioning processes had the same efficiency for the enhancement of sludge dewaterability (i.e. 50% reduction in CST). Therefore, the economic comparison was primarily based on chemical cost. According to the results (see Table S1, available with the online version of this paper; costs given in Australian dollars), the ZVI + PMS conditioning process could save up to 200% ($509,600 per year) and 320% ($823,000 per year) of the costs compared with the ZVI + PDS and the traditional Fenton conditioning processes, respectively. However, it should be noted that the proposed ZVI + PMS conditioning process ($170/dry tonne sludge per year) is more expensive compared with the organic (e.g. polyacrylamide) and inorganic (e.g. aluminum salt) conditioners ($10–40/dry tonne sludge per year) (Metcalf & Eddy 2003). Therefore, further study in this area is still required to reduce its cost.

CONCLUSIONS

The feasibility of the enhancement of sludge dewaterability based on a novel oxidation conditioning process with combination of ZVI and PMS was investigated by a series of batch tests. The results showed that the sludge dewaterability could be significantly enhanced, with CST being reduced by 50% while the optimum addition of ZVI and PMS was 0.25 g/g TSS and 0.1 g/g TSS, respectively. The enhanced sludge dewaterability could be attributed to the decomposition of sludge flocs. Compared to the ZVI + PDS and the traditional Fenton conditioning processes, the combined ZVI + PMS conditioning process could save the up to 200% and 320% of the costs, respectively.

ACKNOWLEDGEMENTS

Authors Xu Zhou and Wenbiao Jin contributed equally to this work. The authors acknowledge the support of Shenzhen Science and Technology Innovation Projects (JCYJ20150529114024254, JCYJ20170307150223308). Dr Qilin Wang acknowledges the support of Australian Research Council (ARC) Discovery Early Career Researcher Award (DE160100667).

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First received 5 April 2017; accepted in revised form 26 June 2017. Available online 10 July 2017.