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Short Communication

A novel conditioning process for enhancing dewaterability of waste activated sludge by combination of zero-valent iron and persulfate

Xu Zhou, Qilin Wang, Guangming Jiang, Peng Liu, Zhiguo Yuan $*$

Advanced Water Management Centre, The University of Queensland, St. Lucia, Queensland 4072, Australia

highlights

- Combined conditioning by ZVI and persulfate enhanced sludge dewaterability effectively.

- The improvement of sludge dewaterability was over 50%.

- Cost saving was up to 29% with ZVI–persulfate conditioning in comparison to classical method.

article info

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ABSTRACT

Improvement of sludge dewaterability is crucial for reducing the costs of sludge disposal in wastewater treatment plants. This study presents a novel conditioning method for improving waste activated sludge dewaterability by combination of persulfate and zero-valent iron. The combination of zero-valent iron $(0-30 g/L)$ and persulfate $(0-6 g/L)$ under neutral pH substantially enhanced the sludge dewaterability due to the advanced oxidization reactions. The highest enhancement of sludge dewaterability was achieved at 4 g persulfate/L and 15 g zero-valent iron/L, with which the capillary suction time was reduced by over 50%. The release of soluble chemical oxygen demand during the conditioning process implied the decomposition of sludge structure and microorganisms, which facilitated the improvement of dewaterability due to the release of bound water that was included in sludge structure and microorganism. Economic analysis showed that the proposed conditioning process with persulfate and ZVI is more economically favorable for improving WAS dewaterability than classical Fenton reagent.

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1. Introduction

The activated sludge process is the most widely used wastewater treatment technology [\(Peng et al., 2015\)](#page--1-0). Despite its high efficiency in removing organic substances and macronutrient, substantial amounts of waste activated sludge (WAS) are also produced, which must be treated and disposed of. However, WAS treatment and disposal is expensive, representing up to 60% of the total operating costs of a wastewater treatment plant (WWTP) [\(Canales et al., 1994; Hao et al., 2010, 2011; Gao et al.,](#page--1-0) [2015\)](#page--1-0).

The typical WAS treatment and disposal process consists of thickening, stabilization, conditioning, dewatering and disposal. Among them, conditioning is conducted to improve the WAS dewaterability. The improved WAS dewaterability will facilitate the separation of water from WAS flocs, thereby reducing the WAS volume that needs to be disposed of and thus reducing WAS disposal costs. Nowadays, many techniques have been developed for sludge conditioning, including heating, freezing/thawing, acid/alkaline treatment, flocculation agent addition and advanced oxidization [\(Feng et al., 2009; Yuan et al., 2011; Chen and Yang,](#page--1-0) [2012\)](#page--1-0). Among them, advanced oxidization process is a promising technique due to its high efficiency and economical advantage ([Neyens et al., 2003; Dewil et al., 2005; Zhen et al., 2013\)](#page--1-0).

Classical Fenton reaction is a common advanced oxidization method. Fenton reaction includes a series of reactions between Fe(II) and hydrogen peroxide under acidic condition. The reaction generates large amounts of hydroxyl radicals (HO⁻), which are highly reactive oxidants ([Zhou et al., 2015\)](#page--1-0). As the hydroxyl radicals could effectively change the WAS structure and decompose the microorganisms via oxidation, thereby transforming the bound water into free water, the WAS dewaterability could be improved after being exposed to hydroxyl radicals. This is because that the free water can be removed much more easily during the dewatering process compared with the bound water. However, the classical Fenton methods have several drawbacks, such as the instability of the chemicals (i.e. Fe(II) and hydrogen peroxide), the requirement

[⇑] Corresponding author. Tel.: +61 7 3365 4374; fax: +61 7 3365 4726. E-mail address: zhiguo@awmc.uq.edu.au (Z. Yuan).

of the harsh operating conditions (i.e. pH at 3.0) and the corrosion caused by hydrogen peroxide [\(Zhou et al., 2014a](#page--1-0)). Compared to hydrogen peroxide, persulfate salts are safer and easier to store and transport. Furthermore, it could be catalyzed by iron under neutral pH condition rather than under acidic condition ([Zhen](#page--1-0) [et al., 2012](#page--1-0)). Similarly, zero valent iron (ZVI) is also more stable and economical than the Fe(II) salt [\(Liu et al., 2011, 2012; Zhou](#page--1-0) [et al., 2014b](#page--1-0)). Both persulfate and ZVI could be applied to advanced oxidization reaction system. In the persulfate–ZVI system, the persulfate ions could oxidize ZVI to Fe(II) (Eq. (1)). After that, Fe(II) could reduce persulfate ions, with the simultaneous generation of the strong oxydic sulfate radicals (Eq. (2)):

$$
Fe + S_2O_8^{2-} \rightarrow Fe(II) + 2SO_4^{2-}
$$
 (1)

$$
Fe(II) + S_2O_8^{2-} \rightarrow Fe(III) + SO_4^{2-} + S_4O_4^{-}
$$
 (2)

Compared to hydroxyl radicals, the sulfate radicals ($SO₄$) has a higher oxidation potential ([Zhen et al., 2012\)](#page--1-0), which makes the oxidization reactions with WAS easy to start. In recent years, the persulfate–ZVI system has been used to decompose refractory organics in liquid, such as dyes and p-chloroaniline (PCA). For example, [Hussain et al. \(2012\)](#page--1-0) reported that 100% of the PCA in solution could be degraded with the addition of 2.5 mM persulfate and 5 g/L ZVI. [Le et al. \(2011\)](#page--1-0) also found that the color removal efficiency of dye (RB19) could be up to 100% and the total organic carbon removal could reach 54% with the addition of 10 mM persulfate and 0.8 g/L ZVI.

We hypothesize that the combined ZVI–persulfate system could improve the sludge dewaterability based on its oxidization characteristics. To verify this hypothesis, this study systematically investigated the effect of the ZVI–persulfate system on the dewaterability of WAS. This is for the first time that the ZVI–persulfate system was applied to sludge conditioning for improving WAS dewaterability. Capillary suction time (CST), which is an indicator of dewaterability, was measured before and after treatment. Dissolved iron concentration and soluble COD were measured. Economic analysis was also performed to assess its economic potential.

2. Methods

2.1. Sludge sources and chemicals

The WAS used in this study was collected from a local biological nutrient removal WWTP (Brisbane, Australia). To increase the concentration, the WAS was settled by gravity for 48 h. The total solids (TS) and volatile solids (VS) of the WAS were 7.9 ± 0.2 g/L and 6.6 ± 0.3 g/L, respectively. The total chemical oxygen demand (TCOD) was 7.9 g/L. The CST was 20.5 ± 0.9 s, and the pH was 6.70. The solid retention time (SRT) was 15 d ([Wang et al., 2013\)](#page--1-0) and the organic load to the WWTP was 0.22 kg BOD/kg MLVSS/d.

Analytical grade of ZVI powder (Alfa-Aesar Co.) and potassium persulfate (Sigma–Aldrich Co.) were used for the tests.

2.2. Batch tests

To investigate the effect of the ZVI and persulfate concentrations on sludge dewaterability, two groups of tests were designed (Table 1). Test group I was to investigate the effect of ZVI concentration (0-30 g/L , see Table 1) while the concentration of persulfate was kept at 4 g/L. Test group II was to explore the effect of persulfate concentration (0–6 g/L, see Table 1) while the concentration of ZVI was kept at 15 g/L. The persulfate and ZVI concentration ranges were selected based on [Zhen et al. \(2012\)](#page--1-0) [and Le et al. \(2011\).](#page--1-0) All the tests were performed in duplicate.

For each test, 100 mL of WAS was transferred into a 250 mL flask, following which ZVI and persulfate were added into the flask. The flasks were then mixed with an orbital shaker at 100 rpm for 30 min. After the treatment, the CST was measured according to the methods detailed in Section 2.3. The flasks were then transferred onto the magnetic stirrers (Heindolph Model MR 3000R, 100 rpm), and a stirrer bar was added in each flask for 3 min to recover the residual un-dissolved ZVI particles what could be attached on the stirrer bar by magnetic force. After that, the attached residual ZVI particles were removed from the sludge with the stirrer bar. The dissolved iron concentrations were then measured according to the methods described in Section 2.3.

2.3. Analytical methods

A capillary suction timer (Trition-WPRL, Type 304) was applied to indicate the sludge dewaterability. CST is commonly used as an indicator of the sludge dewaterability, which could assess the time needed while the water in sludge permeated the filter paper.

Inductive Coupled Plasma-Optical Emission Spectroscopy instrument (ICP-OES) was used to measure the total iron concentration in the sludge samples. Before performing the measurement, the samples were digested by 50% nitric acid for 15 min.

The TS and TVS concentrations of the WAS were measured according to the APHA standard methods ([APHA et al., 1998\)](#page--1-0). COD was measured with COD cuvette tests (Merck, range 500– 10,000 mg/L). The COD samples were pre-treated by oxidization and heating, then measured with a spectrophotometer.

2.4. Data analysis

The enhancement of sludge dewaterability was presented as the reduction percentage R (%) of CST, which is calculated as below:

$$
R\text{ }(\%) = \frac{\text{CST}_0 - \text{CST}_e}{\text{CST}_0} \times 100\% \tag{3}
$$

where CST_0 is the original CST value before treatment; CST_e is the CST after the treatment.

The dissolved iron from ZVI (mg/L) is calculated as follows:

The dissolved iron from $ZVI = Iron_e - Iron_0$

In this equation, Iron $₀$ stands for the indigenous iron concentra-</sub> tion in the original sludge (mg/L), and Iron $_e$ is the total iron concentration in the mixture after the removal of ZVI with the stirrer bar (mg/L) .

The percentage of ZVI that was dissolved is calculated as follows:

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