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Combined zero valent iron and hydrogen peroxide conditioning significantly enhances the dewaterability of anaerobic digestate

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ABSTRACT

The importance of enhancing sludge dewaterability is increasing due to the considerable impact of excess sludge volume on disposal costs and on overall sludge management. This study presents an innovative approach to enhance dewaterability of anaerobic digestate (AD) harvested from a wastewater treatment plant. The combination of zero valent iron (ZVI, 0–4.0 g/g total solids (TS)) and hydrogen peroxide (HP, 0–90 mg/g TS) under pH 3.0 significantly enhanced the AD dewaterability. The largest enhancement of AD dewaterability was achieved at 18 mg HP/g TS and 2.0 g ZVI/g TS, with the capillary suction time reduced by up to 90%. Economic analysis suggested that the proposed HP and ZVI treatment has more economic benefits in comparison with the classical Fenton reaction process. The destruction of extracellular polymeric substances and cells as well as the decrease of particle size were supposed to contribute to the enhanced AD dewaterability by HP + ZVI conditioning.

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Introduction

The most commonly used technology for wastewater treatment is the activated sludge process. However, a huge amount of excess sludge is generated in this process, which causes environmental problem (Foladori et al., 2010; Wang et al., 2013a, 2013b; Zhao et al., 2016). Nowadays, excess sludge management is one of the major challenges in wastewater

treatment plants (WWTPs). In fact, treatment and disposal of excess sludge incurs large expenditures, which occupy up to 30%–60% of the total cost of a WWTP (Foladori et al., 2010; Wang et al., 2017).

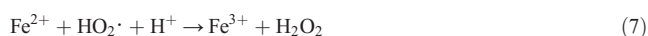
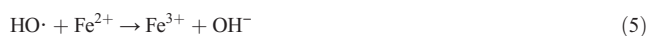
The sludge treatment and disposal procedure usually encompasses thickening, stabilization, conditioning, dewatering and disposal (Foladori et al., 2010). Dewatering has been proven to be an efficient method to reduce sludge volume, cutting sludge

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transport and disposal cost. Since sludge has poor dewaterability, conditioning process is commonly used to enhance the sludge dewaterability prior to dewatering (Wang et al., 2013c). Sludge comprises free water and bound water. The free water combines with the sludge structure in a loose manner and hence is able to be removed much more easily during the dewatering process. On the contrary, the bound water is combined with the sludge via capillary forces or chemical bonds, which is much more difficult to be eliminated compared with the free water. Sludge conditioning could transform the bound water in sludge into the free water to enhance sludge dewaterability (Wang et al., 2014; Li et al., 2016; Liu et al., 2016a, 2016b; Zhang et al., 2016).

Until now, a number of approaches for sludge conditioning have been investigated. They include classical Fenton reaction treatment, alkaline or acid treatment, flocculation agent addition, freezing and heat treatment (Wang et al., 2014; Gong et al., 2015; Li et al., 2016; Liu et al., 2016a, 2016b; Zhang et al., 2016). Amongst them, Fenton reaction is an excellent approach because it is striking in improving sludge dewaterability (Liang et al., 2015; He et al., 2015). The classical Fenton reaction is composed of a series of reactions between Fe^{2+} and hydrogen peroxide (HP) under acid condition (Eqs. (2)–(8)) (Pignatello et al., 2006). In these reactions, huge amount of hydroxyl radical ($\text{HO}\cdot$) is generated (Eq. (2)), which is a much stronger oxidant in comparison to HP (Neyens et al., 2003). When the sludge contacts with hydroxyl radicals, the structure of the sludge is effectively changed and microorganisms would be decomposed by oxidation. This will improve the sludge dewaterability by facilitating the sludge conditioning (Tony et al., 2008; Fontmorin and Sillanpaa, 2015).



Nevertheless, the Fe^{2+} is instable compared with zero valent iron (ZVI). ZVI was able to be oxidized to Fe^{2+} by acid as a result of its highly reductive characteristics (Eq. (1)). Therefore, ZVI was also able to get involved in the Fenton-like reactions at acidic condition (Eqs. (1)–(8)). Recently, the

HP-ZVI system has been investigated to enhance the excess sludge dewaterability (Zhou et al., 2014). The capillary suction time (CST) of excess sludge, which is an indicator of sludge dewaterability, was decreased by around 50% using combined HP and ZVI conditioning (Zhou et al., 2014). However, excess sludge usually undergoes anaerobic digestion before dewatering in most WWTPs, to produce biogas and reduce excess sludge (Foladori et al., 2010; Bacenetti et al., 2013). After this, huge quantities of anaerobic digestate (AD) are still produced, which needs to be dewatered before its final disposal. Nevertheless, the dewatering performance of AD is of great difference compared with that of excess sludge because of the different characteristics between AD and excess sludge (Foladori et al., 2010; Zhang et al., 2015). Therefore, the efficient conditioning approach for enhancing AD dewaterability deserves to be explored.

This work aims to systematically evaluate the effectiveness of the HP-ZVI conditioning in the AD dewaterability. To the best of our knowledge, it is the first time that the HP-ZVI treatment is employed as an AD conditioning approach to improve AD dewaterability. The AD dewaterability indicator, that is CST, was measured before and after HP-ZVI conditioning. The concentrations of dissolved iron in AD were determined before ZVI-HP conditioning and after ZVI recovery. Soluble chemical oxygen demand (SCOD) concentration in AD was also measured after HP-ZVI conditioning. The economic potential of the HP-ZVI conditioning approach was determined.

1. Materials and methods

1.1. Sludge and chemicals

The AD was collected from the anaerobic sludge digester of a local biological nutrient removal WWTP. The main characteristics of AD are as following: iron 320 ± 5 mg/L, total solids (TS) 22.3 ± 0.4 g/L, volatile solids (VS) 19.1 ± 0.2 g/L, solid content $2.23\% \pm 0.04\%$, moisture content $97.77\% \pm 0.04\%$, chemical oxygen demand (COD) 22.1 ± 0.2 g/L, CST 115.6 ± 0.7 sec, and pH 7.72.

ZVI power (size: 80 meshes; Australian Metal Powder Supplies Pty Ltd.) was adopted in this work. The concentration of HP stock solution (Ajax Finechem Co.) was 33%. 30% sulfuric acid was utilized to adjust the AD pH.

1.2. Batch experiments

Two groups of batch experiments were carried out to investigate the effects of HP and ZVI levels on the dewaterability of AD, which is shown in Table 1. The first group was to evaluate the effect of ZVI concentrations (0–4.0 g/g TS) when HP concentration was kept at 90 mg/g TS. The second group aimed to evaluate the effect of HP concentrations (0–90 mg/g TS) while the concentration of ZVI was kept at 2.0 g/g TS. All the experiments were prepared and analyzed in duplicate in this work.

During each experiment, 200 mL of AD was transferred to a 350 mL glass flask. pH of the AD was adjusted to 3.0 by dosing sulfuric acid (30%). Afterwards, varying concentrations of ZVI and HP were added to the glass flasks based on Table 1. The glass flasks were then placed in a shaker at 140 r/min to mix

Table 1 – Experimental conditions used in the hydrogen peroxide-zero valent iron (HP-ZVI) enhanced anaerobic digestate (AD) dewaterability experiments.

Group	HP concentration (mg/g TS)	ZVI concentration (g/g TS)
I. Effect of ZVI concentration	90	0
	90	0.25
	90	0.5
	90	1.0
	90	2.0
	90	4.0
II. Effect of HP concentration	0	2.0
	18	2.0
	45	2.0
	90	2.0

AD and HP-ZVI for 30 min. The CST and SCOD were then determined according to the method as detailed described in Section 1.3. Meanwhile, a stirrer bar was added into each glass flask and was then promptly rotated by the magnetic stirrer at 140 r/min for 5 min. The residual un-dissolved ZVI particles would be attached to the stirrer bar via magnetic force, which were then recovered from AD. Afterwards, the stirrer bar together with the attached residual un-dissolved ZVI particles was separated from AD, thereby recovering ZVI. The concentrations of iron in both the ZVI-recovered and original AD were measured according to the method as detailed in Section 1.3.

1.3. Analyzing methods

The AD dewaterability was indicated by the capillary suction timer (Triton-WPRL, Type 304). The sludge dewaterability is commonly reflected by CST (Chen et al., 1996), which could stand for the time needed for the sludge to complete the filtration process. During the filtration process, AD was transferred to a stainless steel funnel which stands on the filter paper. Thereafter, the capillary suction timer determined the time for the water to permeate from AD to the filter paper.

Before measuring the iron concentration, the AD samples were firstly digested with 70% nitric acid (HNO₃) for 15 min. The concentration of iron in the AD was then measured by inductively coupled plasma optical emission spectrometry (ICP-OES). TS, VS, COD and SCOD concentrations were measured according to the standard methods (Cleceri et al., 1998).

The enhancement of AD dewaterability was indicated by CST reduction percentage (%), which is determined as below:

$$\text{CST} = \frac{\text{CST}_0 - \text{CST}_a}{\text{CST}_0} \times 100\% \quad (9)$$

where, CST_a (sec) means the CST for the HP-ZVI treated AD; CST₀ (sec) means the CST for the AD before HP-ZVI treatment.

The concentration of iron dissolved from ZVI (ZVI_{dis}) is determined as follows:

$$\text{ZVI}_{\text{dis}} = \text{Iron}_a - \text{Iron}_0 \quad (10)$$

where Iron_a (mg/L) means the iron concentration in AD after recovering ZVI via stirrer bar; Iron₀ (mg/L) means the iron concentration in AD before HP-ZVI treatment.

The recovery percentage of ZVI (ZVI_r) is determined as follows:

$$\text{ZVI}_r = \frac{\text{Iron}_0 + \text{ZVI}_0 - \text{Iron}_a}{\text{ZVI}_0} \times 100\% \quad (11)$$

where, ZVI₀ (mg/L) is the external ZVI added in AD.

2. Results and discussion

2.1. Effect of ZVI concentration on AD dewaterability

The effect of ZVI concentration on the dewaterability of AD is demonstrated in Fig. 1. The AD dewaterability was enhanced significantly when both HP and ZVI were present. The CST reduction percentage rose from around 60% to 80% ($p < 0.05$) while the concentration of ZVI increased from 0 to 2.0 g/g TS at an HP concentration of 90 mg/g TS at pH 3.0. Meanwhile, the concentration of iron arising from the dissolution of ZVI also increased from 0 to 55 mg/g TS ($p < 0.05$). This caused the increased production of hydroxyl radicals (Eq. (2)). The generated hydroxyl radicals could oxidize the sludge flocs and decompose the microorganisms, where the bound water was transformed into the free water, thereby enhancing the AD dewaterability (Zhang et al., 2015). It should be noted that CST was reduced by 60% even in the absence of ZVI when HP concentration was 90 mg/g TS at pH 3.0. This might still be caused by classical Fenton reactions because AD itself contains iron at around 320 mg/L.

Likewise, the increased ZVI concentration from 0 to 2.0 g/g TS also resulted in the decreased SCOD concentration (from 1750 to 1200 mg/L, see Fig. 2) ($p < 0.05$). This might be due to the increased oxidization capacity of the HP-ZVI system, which is consistent with the CST result.

However, the AD dewaterability failed to improve further ($p > 0.05$) while the ZVI concentration further rose from 2.0 to 4.0 g/g TS. This might be caused by the fact that the iron dissolved from ZVI remained relatively stable (around 55 mg/g TS) ($p > 0.05$) and thus no more hydroxyl radicals were generated (Eq. (2)). This also corresponded to the SCOD result (Fig. 2), where the SCOD concentration did not further decrease ($p > 0.05$) when the ZVI concentration increased from 2.0 to 4.0 g/g TS.

2.2. Effect of HP concentration on AD dewaterability

It was adequate to enhance AD dewaterability with ZVI concentration at 2.0 g/g TS according to Fig. 1. Consequently, the effect of HP concentrations on AD dewaterability was explored with the ZVI concentration kept at 2.0 g/g TS. Fig. 3 shows that the CST reduction percentage increased from 45% to 90% ($p < 0.05$) when the HP concentration increased from 0 to 18 mg/g TS at pH 3.0. This suggested that the proposed treatment is capable of enhancing AD dewaterability. The CST reduction percentage of 45% in the absence of HP (i.e., HP = 0 mg/g TS) at pH 3.0 was probably caused by acid treatment (i.e., pH 3.0) instead of classical Fenton reactions. This was because that Fenton reactions would not happen in that case due to the absence of HP. Chen et al. (2001) have already demonstrated that pH 3.0 is effective in improving

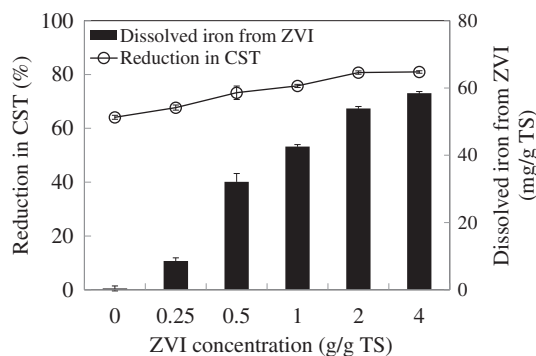


Fig. 1 – Effect of ZVI concentrations on AD dewaterability, along with the concentration of dissolved iron from ZVI. The hydrogen peroxide (HP) concentration was 90 mg/g TS. The capillary suction time (CST) of AD without HP-ZVI treatment served as the reference.

sludge dewaterability although the excess sludge rather than the AD was used in their study. The potential reason for the improved dewaterability by acid treatment was the decrease of extracellular polymeric substances (EPS), which has been demonstrated in the study of Chen et al. (2001). And EPS was reported to prevent the water release (Mikkelsen and Keiding, 2002; Liu and Fang, 2003). Also, it was interesting that the CST reduction percentage in this study (up to 90%) was substantially larger compared to that achieved in the previous work (50%), in which HP-ZVI was adopted to enhance the excess sludge dewaterability (Zhou et al., 2014). The different characteristics between excess sludge and AD could be the important reason for that and therefore resulted in the different dewaterability. For instance, the CST of AD in this work was 115.6 sec. In contrast, the CST of excess sludge was only 31.2 sec. This is also why this work was conducted.

However, when the HP concentration further rose from 18 to 90 mg/g TS, the AD dewaterability declined significantly with the CST reduction percentage decreasing from 90% to 80% ($p < 0.05$) although dissolved iron concentration from ZVI was still increasing (from 10 to 20 mg/g TS) ($p < 0.05$). This is probably because that the excess amount of HP could consume hydroxyl radical (Eq. (4)) and thus weaken the hydroxyl

radical induced advanced oxidation reaction. Due to the weakness of the advanced oxidation reaction, SCOD also increased accordingly from 1000 to 1350 mg/L ($p < 0.05$) when the concentration of HP increased from 18 to 90 mg/g TS (Fig. 4).

2.3. Recovering ZVI in the HP-ZVI approach

In the HP-ZVI conditioning, the amount of dissolved ZVI was quite tiny and the majority of the ZVI particles could be recovered and reused. Fig. 5 shows that the recovery percentage of ZVI was above 95% at the conditions performed in this work (0.25–4.0 g ZVI/g TS and 0–90 mg HP/g TS). As a result, ZVI could be recycled under the HP-ZVI method applied in this work. This revealed that HP-ZVI treatment process could attain substantial savings while improving AD dewaterability. In addition, ZVI used in this work might be replaced by waste scrap iron from industrial waste (Zhang et al., 2014), which would further decrease the cost of the proposed conditioning strategy. It should be noted that although Fe(III) oxides are stable and often used as the reagent for the Fenton-like reactions (Lin and Gurol, 1998; Kwan and Voelker, 2003), they would be difficult to be recovered after conditioning process. Therefore, ZVI was used in this study.

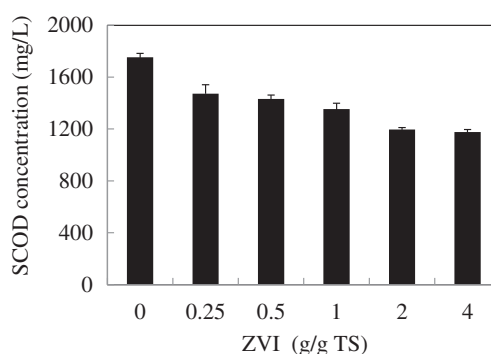


Fig. 2 – Effect of ZVI concentrations on soluble chemical oxygen demand (SCOD) concentration. The HP concentration was 90 mg/g TS.

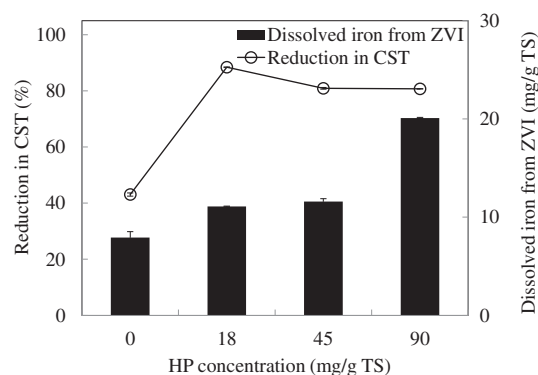


Fig. 3 – Effect of HP concentrations on AD dewaterability, along with the concentration of dissolved iron from ZVI. The ZVI concentration was 2.0 g/g TS. The capillary suction time (CST) of AD without HP-ZVI treatment served as the reference.

2.4. HP-ZVI conditioning as a potential approach for enhancing AD dewaterability

In this study, it is the first time that the HP-ZVI conditioning was demonstrated to be an effective approach for enhancing AD dewaterability substantially. This was experimentally revealed by a series of laboratory batch tests on AD dewaterability.

The proposed HP-ZVI approach is shown in Fig. 6. The produced excess sludge from the wastewater treatment process first undergoes the anaerobic sludge digestion, during which AD is generated. AD is then transferred to a tiny HP-ZVI conditioning reactor, where the AD dewaterability was able to be enhanced. Afterwards, the HP-ZVI treated AD is ready for dewatering, in which less volume of sludge would be generated in comparison to the AD without HP-ZVI treatment and therefore the proposed approach could substantially reduce the cost of sludge transport and disposal later.

Zhang et al. (2015) reported that the highest CST reduction percentage for AD could reach 90% when the classical Fenton reaction conditioning process was applied, which is in accordance with the result in this work (approximately 90%). In addition, both ADs employed in Zhang et al. (2015) and in this study were harvested from anaerobic sludge digesters with

comparable characteristics. As a result, classical Fenton reaction conditioning and HP-ZVI conditioning were hypothesized to have identical effect on the AD dewaterability enhancement in the economic analysis (see Table 2). Since the key difference between the classical Fenton reaction conditioning process and HP-ZVI conditioning lies in the use of iron (Fe^{2+} versus ZVI), the primary cost difference between these two conditioning processes could be attributed to the different cost of Fe^{2+} and ZVI. Therefore, the economic analysis focused on the cost of Fe^{2+} and ZVI. The results of economic analysis indicated that the ZVI-HP conditioning process could save the annual cost by up to \$167,000 in a WWTP with a population equivalent of 100,000 compared with the classical Fenton reaction conditioning process (see Table 2). However, it should be pointed out that this work is only the first step to investigate the proposed method for enhancing AD dewaterability and only as a proof of concept study. Therefore, the values of cost and benefit presented here should only be regarded as indicative and preliminary reference. Full-scale analyses are needed to better assess HP-ZVI method in the future. It also should be noticed that the main purpose of this study was to see the feasibility of the HP-ZVI conditioning method for improving AD dewaterability and optimization of the proposed approach was not yet conducted. Therefore, HP and ZVI concentrations, conditioning

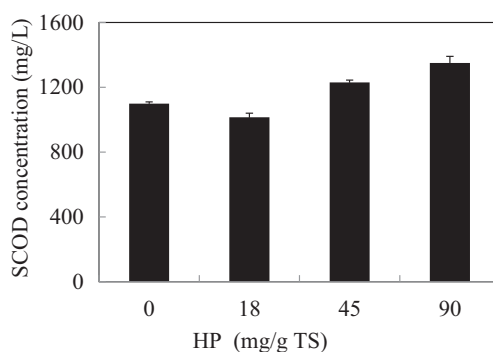
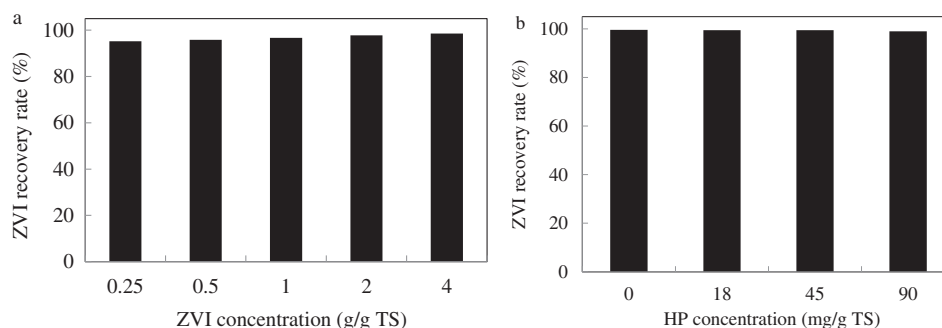


Fig. 4 – Effect of HP concentrations on soluble chemical oxygen demand (SCOD) concentration. The ZVI concentration was 2.0 g/g TS.



time and other technology optimizations would be required to get better AD dewaterability enhancement in the future.

It should be noted that excess sludge is generally not treated in the small size WWTPs, and will be dewatered on site and then transported to the large size WWTPs. As a result, Zhou et al. (2014) developed the HP-ZVI conditioning method to enhance the dewaterability of excess sludge. This primarily targets the small size WWTPs. Nevertheless, in the large size WWTPs, the excess sludge generated on site and transported from the small size WWTPs would undergo anaerobic sludge digestion and hence AD would be generated. The AD would then be dewatered before sludge transport and disposal. It should be pointed out that anaerobic sludge digestion changes the sludge structural characteristics substantially, making the solid/liquid separation of AD more difficult in comparison with excess sludge (Ye et al., 2014). In addition, the other properties of excess sludge and AD are tremendously different. For example, the chemical compositions (*e.g.*, concentration of polysaccharide and protein) of intracellular substances and EPS between excess sludge and AD are different (Mikkelsen and Keiding, 2002; Tomei et al., 2011; Zhang et al., 2015). Excess sludge and AD also have different

shear sensitivity (Mikkelsen and Keiding, 2002; Tomei et al., 2011; Zhang et al., 2015). Therefore, excess sludge and AD have different filterability and dewaterability performances (Mikkelsen and Keiding, 2002; Tomei et al., 2011; Zhang et al., 2015). The chemical composition of EPS has also been reported to play an important role in the performance of sludge dewaterability (Cetin and Erdinciler, 2004; Lu et al., 2015). Thus, the effectiveness of ZVI-HP in the improvement of AD dewaterability was studied separately in this work. This was mainly for the large WWTPs.

2.5. Mechanisms for HP-ZVI enhanced AD dewaterability

EPS, which account for a large fraction of sludge mass, have been reported to play a crucial role in binding bound water, keeping the structure of hydrated sludge and preventing the water release (Mikkelsen and Keiding, 2002; Liu and Fang, 2003). Zhang and Yang (2014) clearly demonstrated that bound water was released and transformed into free water because of the EPS degradation. As a result, the EPS degradation is supposed to be of great importance in improving the water release from sludge flocs (Neyens et al., 2004). Also, cells contain water and therefore cell

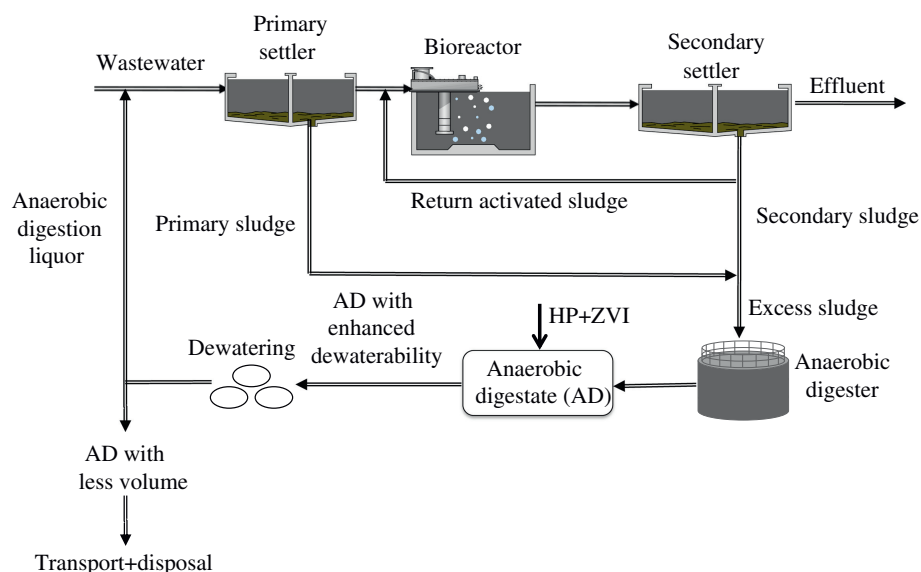


Fig. 6 – Conceptual diagram of the proposed HP-ZVI conditioning method in a typical wastewater treatment plant.

Table 2 – Economic benefit comparison of the HP-ZVI and classical Fenton conditioning processes for the AD dewaterability enhancement in an assumed wastewater treatment plant (WWTP) with a population equivalent of 100,000.

General parameter	Values
Size of the WWTP (population equivalent — PE)	100,000
Size of the WWTP (m ³ wastewater/day)	25,000
Influent chemical oxygen demand (COD) (mg/L)	600 ^a
Influent biochemical oxygen demand (BOD) (mg/L)	320 ^a
Influent Total Kjeldahl Nitrogen (TKN) (mg N/L)	55 ^a
Influent ammonium nitrogen (mg N/L)	35 ^a
Influent total suspended solids (mg/L)	200 ^a
Decay coefficient of heterotrophic biomass (day ⁻¹)	0.2 ^b
Decay coefficient of nitrifying biomass (day ⁻¹)	0.1 ^b
Yield coefficient of heterotrophic biomass (g COD/g COD)	0.625 ^b
Yield coefficient of nitrifying biomass (g COD/g N)	0.24 ^b
Fraction of inert COD generated in biomass decay (g COD/g COD)	0.2 ^b
Sludge retention time in the bioreactor of the WWTP (day)	12 ^a
Mixed liquor suspended solid concentration in the bioreactor (mg/L)	4,000 ^a
Mixed liquor volatile suspended solid concentration in the bioreactor (mg/L)	3,200 ^a
Hydraulic retention time of the anaerobic digester (day)	20 ^b
Degradation of excess sludge in anaerobic digester (on a dry vs basis)	35% ^a
Price of ferrous sulfate (\$/tonne)	100 ^c
Price of ZVI (\$/tonne)	400 ^c
Traditional Fenton conditioning (HP + Fe ²⁺) ^d	AD subject to conditioning (dry tonne/y) 560 Reduction percentage of CST 90% Ferrous sulfate cost (\$/year) 180,000 AD subject to conditioning (dry tonne/y) 560 Reduction percentage of CST 90% ZVI cost (\$/year) 13,000 ^e Saving with HP-ZVI conditioning (compared to traditional Fenton conditioning) (\$/year) 167,000
HP-ZVI conditioning ^d	

^a Personal communication with industry partners.

^b Refer to Metcalf and Eddy (2003).

^c <http://www.alibaba.com/>.

^d Since the key difference between the classical Fenton conditioning and HP-ZVI conditioning lies in the use of iron (Fe²⁺ versus ZVI), the primary cost difference between these two conditioning approaches could be attributed to the different cost of Fe²⁺ and ZVI. Thus, the economic analysis focused on the cost of Fe²⁺ and ZVI.

^e ZVI recovery percentage was 97%.

destruction would also play a crucial role in water release. Zhou et al. (2015) have found that both EPS and cells from excess sludge were oxidized and degraded by the Fenton's reagent ($\text{Fe}^{2+} + \text{HP}$). He et al. (2015) also reported that Fenton-like reaction resulted in EPS destruction and the lysis of the sludge cells. As ZVI + HP system at pH 3.0 could also stimulate Fenton reaction (Eqs. (1)–(3)), EPS and cell destruction could be the reason for the enhanced AD dewaterability. In addition, it was reported that sludge particles became smaller and thinner after Fenton reagent conditioning (Liang et al., 2015). This structure could facilitate the formation of outflow channels for releasing free water. Our work also observed the decrease of particle size after ZVI-HP conditioning, as indicated by the decreased volume median diameter (d_{50}) (d_{50} decreased by 15%). This might contribute to the improved AD dewaterability as well. It should be noted that this was a proof-of-concept study, which focused on the demonstration of the effectiveness of ZVI + HP in enhancing dewaterability of anaerobic digestate. Therefore, the production of $\text{HO} \cdot$ and the station of the ions (e.g., Fe^{3+}) were not investigated and measured in this work. They would be assessed in the future to get more insight into the mechanisms.

3. Conclusions

Anaerobic digestion is the commonly used stabilization process for the excess sludge. Improving the dewaterability of AD is a promising way to save the cost of sludge treatment and disposal in most wastewater treatment plants. In this study, an innovative approach for enhancing dewaterability of AD using combined ZVI and HP conditioning at pH 3.0 was performed. A series of batch experiments conducted in this study implied that combined HP and ZVI conditioning is capable of enhancing AD dewaterability. The highest enhancement of AD dewaterability was obtained at 2.0 g ZVI/g TS and 18 mg HP/g TS, with the reduction percentage of capillary suction time being up to 90% compared with the AD without ZVI and HP treatment. In comparison to the classical Fenton reaction process, the proposed conditioning combined ZVI and HP treatment has more economic benefits, with the saving being up to \$167,000 per year in a WWTP with a population equivalent of 100,000.

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