Highly efficient enhancement of municipal sludge dewaterability using persulfate activation with nZVI/HA
Hao Li, Lei Song, Baohong Han, Hongwei Song, Runying Bai, Huidong Li, Qian Wang, Zhipeng Lin and Wenbin Hu

ABSTRACT
This study presents a sulfate radical-based oxidation method for improving municipal sludge dewaterability by combining persulfate and nanoscale zero-valent iron supported on humic acid (nZVI/HA-PS). Sludge dewaterability using persulfate activation with nZVI/HA was assessed for specific resistance to filterability (SRF), time to filter (TTF), settling volume percentage (SV30) and water content (Wc). The influencing factors, such as mass ratios of nZVI to HA, initial pH, PS dosage and nZVI/HA nanocomposite dosage, were investigated. Experimental results indicated that the SRF reduction efficiency of the sludge reached 86.47% using initial concentrations of 1.2 mmol/gVSS PS and 300 mg/L nZVI/HA. The soluble chemical oxygen demand (SCOD) of sludge supernatants increased from 79 mg/L to 710 mg/L under optimum conditioning, indicating that sludge flocs were effectively decomposed. Economic analysis demonstrated that the nZVI/HA-PS conditioning process is a potential method for improving sludge dewaterability.

Key words | advanced oxidation process, dewaterability, humic acid supported nanoscale zero-valent iron, persulfate, waste activated sludge

ABBREVIATIONS
AOPs Advanced oxidation processes
EPS Extracellular polymeric substances
HA Humic acid
nZVI Nanoscale zero-valent iron
nZVI/HA Humic acid supported nanoscale zero-valent iron
PS Persulfate
SCOD Soluble chemical oxygen demand
SRF Specific resistance to filterability
SV30 Settling volume percentage
TTF Time to filter
TSS Total suspended solids
VSS Volatile suspended solids
Wc Water content
WWTP Wastewater treatment plant

INTRODUCTION
With the accelerated development of urbanization in developing countries, an increasing amount of municipal sludge is causing serious environmental pollution and escalating operation costs in wastewater treatment plants (WWTPs) (Xiao et al. 2018). Based on reports, the expense of disposing of sludge using conventional cationic polyacrylamide (CPAM) accounted for 30–60% of total running costs in WWTPs (Ye et al. 2014; Xiao et al. 2017). Therefore, efficiency improvements in sludge dewaterability are of great importance for reducing municipal sludge transportation and disposal costs.

A number of sludge conditioning methods have been investigated for reducing sludge volume (Zhou et al. 2014). Among them, advanced oxidation processes (AOPs) are considered to be one of the most popular and powerful methods for enhancing sludge dewaterability (Yuan et al. 2018). Oxidants, such as hydrogen peroxide, calcium peroxide, ozone and ferrate have been developed for sludge conditioning (Zhen et al. 2013; Zhou et al. 2014; Chen et al. 2016; Badalians Gholikandi et al. 2018). These chemicals enhance sludge dewaterability by producing reactive species, such as hydroxyl radicals (·OH) or sulfate radicals (SO4·), which decompose sludge floc...
structure and degrade the organic compounds in extracellular polymeric substances (EPS). Compared with the above oxidants, persulfate (PS, $S_2O_8^{2-}$) is a more promising chemical, as it is inexpensive and easy to store (Zhen et al. 2016). In recent years, sulfate radical-based oxidation as an efficient sludge treatment method has received much research attention (Shi et al. 2015; Kim et al. 2016; Li et al. 2016). In general, $S_2O_8^{2-}$ is activated by the ferrous iron ($Fe^{2+}$) or zero-valent iron (ZVI, $Fe^0$) to generate $SO_4^{•-}$ with a high oxidation potential ($E_0 = 2.5–3.1$ V). Due to the small particle size, large surface area and high reactivity, nanoscale ZVI (nZVI) heightens the activation of PS (Yan et al. 2015). The reactions between PS and $Fe^{2+}$ or $Fe^0$ are as follows:

\[
S_2O_8^{2-} + Fe^0 \rightarrow Fe^{2+} + 2SO_4^{2-} \tag{1}
\]
\[
S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{•-} \tag{2}
\]
\[
2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{3}
\]

Bare nZVI has a high degree of aggregation, so it needs to be dispersed by other substances. According to research, supported nZVI can efficiently activate PS to degrade the majority of organic substances (Zhan et al. 2016; Diao et al. 2016; Hussain et al. 2017). However, few studies have adopted persulfate activation with supported nZVI in sludge conditioning. Humic acid (HA), as the major component of natural organic matter, is an inexpensive and renewable material. It is composed of a skeleton of aromatic or aliphatic structures interconnected by different oxygen-containing functional groups (Qiao et al. 2014; Xing et al. 2017).

In our previous study, HA-supported nZVI nanocomposite (nZVI/HA) was successfully synthesized (Li et al. 2018). The novel nanocomposite was adopted to activate PS for sludge conditioning (nZVI/HA-PS), and the reaction mechanisms under chemical conditioning were investigated in detail. In this study, we have evaluated various influencing factors, including nZVI to HA ratios, nZVI/HA dosage, persulfate dosage and initial pH, to find the optimum conditions for sludge treatment. Sludge dewaterability was assessed by time to filter (TTF), settling volume percentage (SV30), specific resistance to filterability (SRF) and water content (Wc) of dewatered sludge cake. Bearing in mind the possibility of applying this technology in practice, we also evaluated its economic potential through a desktop scale-up study.

## METHODS

### Sludge sources and chemicals

The municipal sludge sample was collected from a secondary settling tank in Xinxinban WWTP, located in Hohhot, China. This WWTP treats approximately 150,000 m$^3$ of sludge per day by the anaerobic-anoxic-oxic process. The raw sludge sample was stored in a 4°C cold room for 2 days to ensure no significant changes in composition. Several fundamental properties of the raw sludge are list in Table 1, which can be used as baseline background reading.

Sodium persulfate (Na$_2$S$_2$O$_8$), sodium borohydride (NaBH$_4$), ferrous sulfate (FeSO$_4$·7H$_2$O), polyethylene glycol (PEG-4000) and HA were purchased from Sinopharm Chemical Reagent Co. (Beijing, China). All reagents were of analytical grade and all solutions were prepared in ultrapure water (18.2 MΩ cm, ELGA). Ultrasonic cleaner was purchased from Ningbo Xinzhi Biotechnology Co., Ltd.

### Synthesis of nZVI/HA nanocomposite

nZVI/HA was prepared by the reduction of ferrous iron by NaBH$_4$ as shown in Figure S1 (available with the online version of this paper). First, 17.99 mM FeSO$_4$·7H$_2$O and PEG-4000 were dissolved with solution of deoxygenned ultrapure water and anhydrous ethanol (1:4 volume ratio). Second, different amounts of HA (1, 2, 3, 5 and 7 g) were added to the mixture while being continuously stirred with an electric agitator for 30 min. Third, 0.37 M of NaBH$_4$ alkali solution was added dropwise into three-necked flasks by a peristaltic pump (BT100-1L, Hebei) at the rate of 5 mL/min, while being constantly stirred for 1 hour. The entire experiment was performed under a N$_2$ atmosphere to exclude O$_2$. Finally, the nanocomposite was washed at least three times with deoxygenated ultra-pure water and ethanol, followed by sonication for 30 min, and then vacuum dried at 70°C. The reaction equation was:

\[
2Fe^{2+} + BH_4^- + 2H_2O \rightarrow 2Fe^0 + BO_2^- + 2H_2 + 4H^+ \tag{4}
\]

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characteristics of raw sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indicator</td>
<td>Water content (wt %)</td>
</tr>
<tr>
<td>Value</td>
<td>98.91</td>
</tr>
</tbody>
</table>

Downloaded from https://iwaponline.com/wst/article-pdf/79/7/1309/567556/wst079071309.pdf by guest
Five types of nZVI/HA nanocomposites were synthesized with different mass ratios of nZVI to HA of 1:1, 1:2, 1:3, 1:5 and 1:7. All the products were stored in a brown flask.

**Batch reactor experiments**

Three sets of bench-scale experiments were conducted to investigate the efficiency of sludge dewaterability. First, the effect of different mass ratios of nZVI to HA was investigated. Next, the effect of initial pH (4, 5, 6, 7, 8, 9, 10), which was adjusted by sulfuric acid or sodium hydroxide solutions, was evaluated. Finally, the effects of PS and nZVI/HA dosage were assessed (Table 2).

For each experiment, 100 ml sludge was poured into a beaker, following which PS was added into the sludge and mixed using a constant-temperature magnetic stirrer at 300 rpm for 5 min. Then, nZVI/HA nanocomposite was added, followed by stirring at 150 rpm for 10 min. Finally, we measured SRF, TTF, SV30, and Wc.

**Analytical methods**

In this study, SRF values were applied to evaluate sludge dewaterability: 100 mL sludge suspension was poured into a 9 cm standard Buchner funnel equipped with a quantitative filter paper, and a constant pressure (P) of 40 kPa was applied by a vacuum pump for 10 min. The filtrate, time (t), and filtration volume (V) were recorded for the calculation of sludge SRF (Equation (5)). In addition, the SRF reduction efficiency and Wc of dewatered sludge cakes were calculated.

\[
SRF = \frac{2PA^2b}{\mu \omega}
\]  

Where P is the filtration pressure (kg/m²); A is the unit filtration area (m²); \( \mu \) is the kinetic viscosity (kg·s/m²); \( \omega \) is the cake solid weight per unit volume of sludge on the filtrate (kg/m³); and b is the time-to-filtration ratio, which can be calculated from the slope of the curve (with V on the X axis and t/V on the Y axis) (s/m²).

TTF is defined as the time when the filtrate volume reaches 50 mL. SV30 is defined as the sludge volume after 30 min of sedimentation. The pH of the sludge sample adjusted with sulfuric acid or sodium hydroxide was measured with a pH meter (pHS-3C, Shanghai). The TSS, VSS and soluble chemical oxygen demand (SCOD) concentrations of the sludge were measured based on the standard methods (APHA 2005).

**RESULTS AND DISCUSSION**

**Effect of mass ratios of nZVI to HA on sludge dewaterability by nZVI/HA-PS**

The first set of experiments was designed to investigate the sludge dewaterability efficiency by PS activated with different ratios of nZVI/HA (1:1, 1:2, 1:3, 1:5 and 1:7). As shown in Figure 1, nZVI/HA composites combined with PS could effectively enhance sludge dewaterability. The SRF reduction efficiencies of treated sludge increased from 82.08% to 86.47% with an increase in the nZVI/HA ratio from 1:1 to 1:3, indicating that increasing mass ratios of nZVI to HA in a certain range improved the sludge dewaterability. However, with further increases in the mass ratios of...
nZVI to HA, the SRF reduction efficiencies were reduced to 77.34%. This might be due to the fact that excessive nZVI could block the reactive sites on the iron surface, resulting in a lower probability of participating in the reaction and decreasing the reducing capacity of the iron particles (Hussain et al. 2017). As a result, a mass ratio of nZVI to HA of 1:3 showed the best performance on sludge dewaterability. Therefore, we selected nZVI/HA (1:3) as the best material for subsequent experiments.

**Effect of initial pH on sludge dewaterability**

A set of tests was conducted at different initial pH levels (4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0) to investigate the effect of initial pH on sludge dewaterability. As shown in Figure 2, the initial pH of the sludge conditioning was closely related to SRF, Wc, TTF, SV30. The values of SRF and Wc were relatively low when the pH ranged from 4.0 to 7.0, and the trend of TTF and SV30 coincided with that of SRF and Wc. These results might be due to the fact that SO4\(^{-}\) could exist in acidic and neutral conditions (Liang & Su 2009). At pH = 5, TTF and SV30 were at their minimum values, indicating that extra sulfate radicals could be produced in acidic conditions based on the following equations:

\[
\text{H}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{HS}_2\text{O}_8^{-} \tag{6}
\]

\[
\text{HS}_2\text{O}_8^{-} \rightarrow \text{H}^+ + \text{SO}_4^{2-} + \text{SO}_4^{-} \tag{7}
\]

However, the sludge dewaterability became worse when the pH was greater than 7. This is most likely because the concentration of Fe\(^{2+}\) and Fe\(^{0}\) were reduced to generate Fe(OH)\(_2\) in alkaline conditions, which blocked the regeneration of soluble iron and the production of SO4\(^{-}\) (Rastogi et al. 2009). In addition, HA might have been decomposed into various macromolecules in alkaline conditions, which were released in the sludge solution. The unfavorable reaction led to the increase of sludge viscosity and deterioration of sludge dewatering.

**Effect of nZVI/HA dosage on sludge dewaterability**

The effect of nZVI/HA dosage on sludge dewaterability is shown in Figure 3. PS was added with 1.2 mmol/g VSS, and the dosage of nZVI/HA was increased from 100 mg/L to 500 mg/L. As shown in Figure 3, the effect of sludge dewaterability in terms of SRF and Wc was significant. The value of SRF dropped off considerably when nZVI/HA dosage increased from 100 mg/L to 300 mg/L, but was stable when the nZVI/HA dosage increased to 500 mg/L. Compared with the raw sludge, the value of SRF and Wc reduced from 17.3 \times 10^{12} m/kg to 2.2 \times 10^{12} m/kg and from 98.91% to 78.57% respectively when the nZVI/HA dosage was 300 mg/L. The changes in TTF and SV30 were similar to each other. These results were mainly because Fe\(^{0}\) activated PS to yield SO4\(^{-}\), which accelerated the disintegration of the sludge floc structure and enhanced sludge dewaterability. When the dosage of the nZVI/HA was increased, the contact surface area between PS and Fe\(^{2+}\) increased; thus, more Fe\(^{2+}\) was produced according to Equation (1). As an initiator, Fe\(^{2+}\) activated PS to generate the SO4\(^{-}\) (Equation (2)). However, excessive Fe\(^{2+}\) may consume SO4\(^{-}\), which resulted in the deterioration of sludge dewaterability. The findings are consistent with the study of Li et al. 2016.

**Effect of PS dosage on sludge dewaterability**

As shown in Figure 4, the effect of PS dosage on sludge dewaterability was obvious when the nZVI/HA dosage was fixed at 300 mg/L. SRF and Wc decreased sharply
when the PS dosage was in the range of 0.8–1.2 mmol/g VSS. However, few effects were observed on SRF and Wc reduction when the PS dosage was increased to 1.6 mmol/g VSS. The value of TTF and SV30 instead increased with PS dosage at 1.6 mmol/g VSS. Although PS is the source of SO4\(\cdot\), extra PS did not improve sludge dewaterability. High concentrations of SO4\(\cdot\) might act with S2O8\(\cdot\) to produce SO4\(2-\) and S2O8\(2-\), as shown in Equations (8) and (9), preventing the improvement of sludge dewaterability. These results agree with those reported by Zhen et al. 2015. This study proved that nZVI/HA has an analogous mechanism with Fe2\(\cdot\) on PS activation.

\[
\begin{align*}
\text{SO}_4\cdot + \text{S}_2\text{O}_8^- & \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^- \quad (8) \\
\text{SO}_4\cdot + \text{SO}_4\cdot & \rightarrow \text{S}_2\text{O}_8^- \quad (9)
\end{align*}
\]

**Decomposition of municipal sludge**

An optimum amount of sludge decomposition is beneficial for enhancing sludge dewaterability (Zhou et al. 2017). SO4\(\cdot\) can destroy microbial cells and floc structures, causing the release of bound water in sludge flocs and the rise of SCOD in the sludge supernatants. When nZVI/HA and PS concentrations were 300 mg/L and 1.2 mmol/g VSS respectively, the SCOD increased from 79 mg/L to 710 mg/L. This is likely due to the fact that nZVI/HA-PS conditioning processes destroyed the cell membrane structure, thus leading to cell lysis and the release of bound water.

**Economic analysis**

To analyze the economic potential of the nZVI/HA-PS conditioning method, a desktop scale-up study was performed based on a WWTP with a 100,000 population equivalent (Table S1, available with the online version of this paper). Table 3 presents a comparison of treatment efficiency and total cost of enhancing sludge dewaterability. The total costs of sludge conditioning by nZVI/HA-PS, the Fenton process and CPAM are US$159,600, US$187,950 and US$21,600 per year, respectively. By comparison with CPAM conditioning (Zhu et al. 2018), nZVI/HA-PS conditioning had higher costs because of the conditioner, but nZVI/
HA-PS oxidation can achieve a much higher SRF reduction efficiency and a lower Wc of dewatered sludge cake than CPAM. Lu et al. 2003 reported the SRF reduction and Wc of treated sludge cake as being 90.0% and 75.20% in the Fenton process, which was similar to our results (86.47% and 78.57%). We ignored the labor cost of synthesizing nanocomposite, so the total cost of nZVI/HA-PS is close to that of the Fenton process. However, the Fenton reaction normally works in acidic conditions, whereas the nZVI/HA-PS conditioning process has excellent performance on sludge dewaterability in neutral conditions, saving an other extra cost.

**CONCLUSIONS**

In this study, nZVI/HA nanocomposite was synthesized to activate PS for improving municipal sludge dewaterability performance. Compared with raw sludge, 86.47% reduction of SRF was achieved with 300 mg/L of nZVI/HA and 1.2 mmol/gVSS of PS in neutral conditions. The nZVI/HA-PS conditioning method might destroy the cell membrane and enhance the sludge dewaterability. A preliminary economic analysis indicated that it is a promising method.

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**Table 3** Comparison of different conditioning methods for sludge dewaterability

<table>
<thead>
<tr>
<th>Treatment methods</th>
<th>TSS (g/L)</th>
<th>pH</th>
<th>SRF reduction (%)</th>
<th>Water content (%)</th>
<th>Amount of sludge before and after conditioning (dry tonne/year)</th>
<th>Total cost (US$/year)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>nZVI/HA-PS</td>
<td>11.75</td>
<td>6.9</td>
<td>86.47</td>
<td>78.57</td>
<td>750</td>
<td>159,600</td>
<td>This study</td>
</tr>
<tr>
<td>Fenton process</td>
<td>8.3</td>
<td>3.0</td>
<td>90.0</td>
<td>75.20</td>
<td>750</td>
<td>187,950</td>
<td>Lu et al. 2003</td>
</tr>
<tr>
<td>CPAM</td>
<td>–</td>
<td>7.7</td>
<td>53.2</td>
<td>85.20</td>
<td>750</td>
<td>21,600</td>
<td>Zhu et al. 2008</td>
</tr>
</tbody>
</table>


Yan, J., Han, L., Gao, W., Xue, S. & Chen, M. 2015 Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. Bioresour. Technol. 175, 269–274.


