Technical Note

Conditioning of sewage sludge by Fenton’s reagent combined with skeleton builders

Huan Liu, Jiakuan Yang, Yafei Shi, Ye Li, Shu He, Changzhu Yang, Hong Yao

ABSTRACT

Physical conditioners, often known as skeleton builders, are commonly used to improve the dewaterability of sewage sludge. This study evaluated a novel joint usage of Fenton’s reagent and skeleton builders, referred to as the F–S inorganic composite conditioner, focusing on their efficacies and the optimization of the major operational parameters. The results demonstrate that the F–S composite conditioner for conditioning sewage sludge is a viable alternative to conventional organic polymers, especially when ordinary Portland cement (OPC) and lime are used as the skeleton builders. Experimental investigations confirmed that Fenton reaction required sufficient time (80 min in this study) to degrade organics in the sludge. The optimal condition of this process was at pH = 5, Fe2+ = 40 mg g−1 (dry solids), H2O2 = 32 mg g−1, OPC = 300 mg g−1 and lime = 400 mg g−1, in which the specific resistance to filtration reduction efficiency of 95% was achieved.

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1. Introduction

Increasing global attention has been given to the reduction of sewage sludge volume before its disposal or reuse (Tokumura et al., 2007). Organic polymers (polyelectrolytes) are widely used to condition sludge prior to dewatering (Zhao and Bache, 2001; Ma et al., 2007). Despite its popularity, the use of organic polymers has limitations. First, centrifuge or belt press dewatering can only achieve a water content level of 75–80% (Neyens et al., 2003), which fails to meet the requirements of incineration or landfill disposal. Second, polymer residual left in the dewatered sludge can pose long-term environmental risks (Baeyens and Van Puyvelde, 2004). These shortcomings arouse urgent needs for alternative advanced sludge treatment (AST) methods by using environment-friendly conditioners to alter the sludge structure such as rupturing bacteria cells to release cell content (Neyens et al., 2003).

Fenton peroxidation (Fe2+/H2O2) alone or combined with other conditioning methods has been proven to be a promising AST (Dewil et al., 2005; Beauchesne et al., 2007). The Fenton reaction produces hydroxyl radicals in acidic solutions by iron-catalyzed decomposition of H2O2 (Kitis et al., 1999; Neyens and Baeyens, 2003; Pham et al., 2010).

The OH is the main reactant in the oxidation process capable of decomposing a number of organic substances via strong oxidation. Others (Lu et al., 2003; Tony et al., 2008, 2009) reported the increases in filtration and dewatering efficiency due to Fenton reaction. With 6000 mg L−1 of Fe2+ and 3000 mg L−1 of H2O2, the specific resistance to filtration (SRF) of the treated sludge was sharply reduced to only 10% of that of the original sludge. Buyukkamaci (2004) investigated the effects of various Fe2+ and H2O2 doses on SRF and capillary suction time (CST) of biological sludge. As low as 6.1 × 109 m kg−1 in SRF and 15.7 s in CST were achieved at a dose of 5000 mg L−1 Fe2+ and 6000 mg L−1 H2O2. Adding Fenton’s reagent apparently yields a high dewatering efficiency. However, the high cost of Fenton’s reagent prohibits its practical use of these levels.

Sewage sludge produces highly compressible filter cakes that are difficult to be dewatered by pressure filtration because its particles will deform under pressure during the compression phase of filtration with the cake growing (Zall et al., 1987). This action causes cake Void closure, which impedes deep dewatering (Zall et al., 1987; Zhao, 2002). Physical conditioners, often known as skeleton builders, are commonly used to enhance the rate and extent of sewage sludge dewatering (Lee et al., 2001; Chen et al., 2010; Ruiz et al., 2010) because they form a permeable and rigid lattice structure in sludge cakes (Benitez et al., 1994). Zall et al. (1987) opted for hydrated lime and fly ash as skeleton builders and successfully produced sludge cakes with a more rigid and incompressible structure, capable of maintaining high porosity during high pressure filtration. Albertson and Kopper (1983) found that with the addition of coal fines to the waste activated sludge and optimization of the process and machine parameters, cake solids of 25% to 37% total solids were achieved with 0.1 to 0.3 kg coal kg−1 sludge solids. Others (Thapa et al., 2009, 2011; Qi et al., 2011)......
demonstrated the benefit of using lignite as the skeleton builder for dewatering of digested sewage sludge. Chen et al. (2010) studied the improvement of sludge dewaterability with coal fly ash modified by sulfuric acid (MCFA). Under a MCFA dosage of 273%, the SRF of the sludge decreased from $1.9 \times 10^{13}$ to $4.2 \times 10^{11}$ kg $^{-1}$, and the filter cake moisture decreased from 87% to 57%. However, according to these researches, large dosages of skeleton builders will lead to expanded sludge cake volume, which exerts a significant negative influence on the subsequent sludge disposal, e.g. landfill, or incineration.

Fenton peroxidation and skeleton builders have been separately examined to determine their ability to boost the dewatering performance of sludge. The separate application of either conditioner has been largely limited due to the weaknesses mentioned above. The interactions of these two types of conditioners have not been investigated previously. This study was to use combined Fenton’s reagent and skeleton builders, referred to as the F–S inorganic composite conditioner, for sludge dewatering to determine if there are synergistic effects between them. The objective of this study was to unravel the interactions between Fenton’s reagent and skeleton builders for sludge dewatering.

2. Materials and methods

2.1. Experimental materials

2.1.1. Sludge

Raw sludge (RS) used in this study was a mixture of sludges from the primary and secondary sedimentation tanks of Longwangzui Wastewater Treatment Plant, Wuhan, China. Samples were collected in polypropylene bottles and stored at 4 °C. Since the characteristic of the sludge is volatile, three batches of fresh sludge were used and the experiments based on each batch were completed in 2 d. The main characteristics of the RS in three batches are shown in Table 1.

2.1.2. Fenton’s reagent

Sulfuric acid (analytical grade, Xinyang Chemical, China) was used to adjust pH of the sludge samples. Fe$^{2+}$ in Fenton’s reagent is prepared by mixing a solution of FeSO$_4/7$H$_2$O (analytical grade, Sinopharm Chemical Reagent, China) and H$_2$O$_2$ (30 wt.%).

2.1.3. Skeleton builders

Quick lime, ordinary Portland cement (OPC), fly ash, phosphogypsum (PG), red mud and magnesia were used as skeleton builders in sludge dewatering. All the samples were milled and sieved to less than 0.5 mm in particle size. The chemical compositions of these skeleton builders are presented in Table 2.

2.2. Conditioning procedure

Initially, 200 mL of sludge samples were carefully transferred to 500 mL beakers and then conditioned in accordance with the following procedure: adjusting pH → 30 s of rapid mixing at 300 rpm → adding Fe$^{2+}$ solution → 30 s of rapid mixing at 300 rpm → adding H$_2$O$_2$ to initiate Fenton reaction → 30 s of rapid mixing at 300 rpm → 1–120 min of slow mixing at 100 rpm → adding skeleton builder I → 1–3 min of slow mixing at 100 rpm → adding skeleton builder II → 1–3 min of slow mixing at 100 rpm.

2.3. Conditioning performance

Table 3 Types of skeleton builders used in the experiments.

<table>
<thead>
<tr>
<th>Sequence number</th>
<th>Fenton’s reagent (F)</th>
<th>Skeleton builders (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$^{2+}$/H$_2$O$_2$</td>
<td>S-I S-II</td>
</tr>
<tr>
<td>1 (control)</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>Fe$^{2+}$/H$_2$O$_2$</td>
<td>Fly ash Lime</td>
</tr>
<tr>
<td>3</td>
<td>Fe$^{2+}$/H$_2$O$_2$</td>
<td>OPC Lime</td>
</tr>
<tr>
<td>4</td>
<td>Fe$^{2+}$/H$_2$O$_2$</td>
<td>PG Lime</td>
</tr>
<tr>
<td>5</td>
<td>Fe$^{2+}$/H$_2$O$_2$</td>
<td>Red mud Lime</td>
</tr>
<tr>
<td>6</td>
<td>Fe$^{2+}$/H$_2$O$_2$</td>
<td>Magnesia Lime</td>
</tr>
</tbody>
</table>

Fig. 1. Effects of different types of skeleton builders combined with Fenton’s reagent on sludge conditioning (operating parameters: RS = batch 1; pH = 6; Fe$^{2+}$ = 20 mg g$^{-1}$; H$_2$O$_2$ = 125 mg g$^{-1}$; S-I = 335.2 mg g$^{-1}$; S-II = 223.5 mg g$^{-1}$; Fenton reaction time = 30 min).

Table 1 Characteristics of the raw sludge.

<table>
<thead>
<tr>
<th>Batch</th>
<th>pH</th>
<th>Water content (%)</th>
<th>COD (mg L$^{-1}$)</th>
<th>VSS/TSS (%)</th>
<th>SRF (10$^{12}$ mk g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.5</td>
<td>95.9</td>
<td>35,400</td>
<td>42</td>
<td>16.6</td>
</tr>
<tr>
<td>2</td>
<td>6.5</td>
<td>96.4</td>
<td>18,100</td>
<td>36</td>
<td>10.5</td>
</tr>
<tr>
<td>3</td>
<td>6.5</td>
<td>96.8</td>
<td>19,900</td>
<td>37</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 2 Chemical compositions of the skeleton builders.

<table>
<thead>
<tr>
<th>Skeleton builders</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Al$_2$O$_3$</th>
<th>Cl</th>
<th>MgO</th>
<th>Na$_2$O + K$_2$O</th>
<th>Fe$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime</td>
<td>6.7</td>
<td>60.1</td>
<td>–</td>
<td>–</td>
<td>1.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>22.6</td>
</tr>
<tr>
<td>OPC</td>
<td>20.6</td>
<td>58.8</td>
<td>5.4</td>
<td>0.0</td>
<td>3.3</td>
<td>0.6</td>
<td>2.9</td>
<td>–</td>
<td>–</td>
<td>4.0</td>
</tr>
<tr>
<td>Fly ash</td>
<td>52.5</td>
<td>5.7</td>
<td>26.3</td>
<td>3.6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.5</td>
</tr>
<tr>
<td>PG</td>
<td>71.1</td>
<td>28.6</td>
<td>2.9</td>
<td>0.4</td>
<td>0.6</td>
<td>2.4</td>
<td>0.1</td>
<td>0.3</td>
<td>39.5</td>
<td>19.1</td>
</tr>
<tr>
<td>Red mud</td>
<td>21.0</td>
<td>6.2</td>
<td>22.0</td>
<td>–</td>
<td>1.3</td>
<td>10.5</td>
<td>0.3</td>
<td>2.3</td>
<td>0.6</td>
<td>10.0</td>
</tr>
<tr>
<td>Magnesia</td>
<td>5.5</td>
<td>1.1</td>
<td>0.3</td>
<td>0.0</td>
<td>74.4</td>
<td>0.0</td>
<td>0.3</td>
<td>–</td>
<td>0.1</td>
<td>18.1</td>
</tr>
</tbody>
</table>

* LOI = loss of ignition.
SRF test was performed by using self-designed multi-coupled measuring device of sludge SRF.

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

where SRF (m kg⁻¹), \(P\) is the filtration pressure (N m⁻²), \(A\) is the filter area (m²), \(\mu\) is the viscosity of the filtrate (N s m⁻²), \(w\) is the weight of the cake solids per unit volume of filtrate (kg m⁻³), and \(b\) is the slope of filtrate discharge curve (s m⁻⁶).

Five sets of different types of physical conditioners were used in combination with quick lime as the skeleton builders to enhance Fenton’s reagent conditioning effect as shown in Table 3. Then a series of single-factor experiments were conducted to optimize the major operation parameters. Each sample was tested for four times and corresponding standard deviation was calculated.

3. Results and discussion

3.1. Selection of skeleton builders

SRF values of sludge conditioned combinedly with Fenton’s reagent and skeleton builders were lower than that of sludge conditioned with Fenton peroxidation alone (Fig. 1). It is reasonable to reckon that skeleton builders can further increase dewatering effici-

![Figure 2](image-url)
ciency. The combining conditioners are ranked by the enhancement of sludge dewaterability from the largest to the lowest as follows: OPC and Lime, Fly ash and Lime, PG and Lime, Red mud and Lime, Magnesia and Lime. In addition, the lowest SRF of 1.1 \times 10^{12} \text{m kg}^{-1} and highest SRF reduction efficiency of 93\% were obtained when OPC was used as one of the conditioner components.

3.2. Optimization of F–S composite conditioner

To evaluate the effect of each component of the F–S inorganic composite conditioner on sludge dewatering capacity, a series of single-factor experiments were conducted. Factors under evaluation included reaction time, skeleton builder dosages, pH and Fenton’s reagent dosages.

3.2.1. Factor 1: reaction time

The effects of Fenton reaction time on sludge conditioning were investigated at Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} dosage of 20/125 mg g\textsuperscript{-1} (all data are based on dry solids) using RS from batch 2 and pH was adjusted to 6. After Fenton peroxidation, OPC and lime were added in succession. The results, as illustrated in Fig. 2a, show clearly that the highest SRF reduction efficiency occurred when reaction time was 80 min and that prolonged reaction time failed to significantly improve sludge dewaterability. The results also stress the necessity of sufficient time for Fenton’s reagent in degrading organics via highly reactive hydroxyl radicals, which facilitate the releasing of both interstitial water trapped among organics and adsorbed or bound water. And without sufficient time for Fenton reaction, acid–base neutralization would occur when alkaline skeleton builders were added, and sequentially resulted in a poor performance. In contrast, for Fenton peroxidation only, Tony et al. (2008) illustrated that a high CST reduction occurred initially.

3.2.2. Factor 2: skeleton builder dosages

Fig. 2b displays a significant enhancement in SRF reduction efficiency (89\% → 94\%) when the OPC dosage increased from 0 to 300 mg g\textsuperscript{-1} and using RS from batch 2. However, at higher dosages of OPC, the reduction rate was negatively affected slightly. The effect of lime dosages is similar to that of OPC, and the lowest SRF was achieved at the lime dosage of 400 mg g\textsuperscript{-1}, as shown in Fig. 2c. This may be attributed to the generation of a permeable and rigid lattice structure when skeleton builders were added into sludge. Just as Deneux-Mustin and Lartiges (2001) reported that clumps of crystalloids developed on the external surfaces of flocs after the application of Fe\textsuperscript{3+} and lime. The precipitates create a rigid structure around the flocs which, upon mechanical dewatering, transmit the stresses to the inner parts of the flocs. The porous structure of the precipitates may also participate in the withdrawal of water as a draining media. However, strong alkaline may inhibit further dewatering and the reinforcement is not obvious when there are sufficient hard spots.

3.2.3. Factor 3: pH

Based on the optimal results shown above, the addition of conditioners was set at Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2}/OPC/lime = 20/125/300/400 mg g\textsuperscript{-1} using RS from batch 3 in the subsequent tests for pH optimization. The effects of initial pH in the range of 2–8 were examined. Fig. 2d reveals that the acidic environment could clearly improve sludge dewaterability and reached a peak SRF reduction efficiency of 94\% at pH of 5. There has not been a convincing conclusion of the optimal pH for Fenton peroxidation in previous studies. Lu et al. (2001) claimed the similar level of dewaterability of an activated sludge when it was subjected to conditioning with Fenton’s reagent at pH in the range of 2–7. This is inconsistent with the results of Tony et al. (2008, 2009) and Buyukkamaci (2004), which is pH = 6 and pH \leq 3.5 respectively.

3.2.4. Factor 4: Fenton’s reagent dosages

To probe into the contribution of Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} on the filterability of sludge, experiments of adding various ratios of Fenton’s reagent for a broad range of Fe\textsuperscript{2+} (5–320 mg g\textsuperscript{-1}) and H\textsubscript{2}O\textsubscript{2} (4–2048 mg g\textsuperscript{-1}) were conducted for comparison. The RS in this experiment came from batch 3. SRF decreases with increasing Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} dosage until a specific ratio, beyond which the opposite results were obtained. Although the enhancement of sludge dewaterability occurred at a broad range of Fe\textsuperscript{2+}/H\textsubscript{2}O\textsubscript{2} addition, they could only positively affect the sludge dewaterability under an appropriate ratio due to the strong synergistic effect between them. Moreover, low concentrations of Fe\textsuperscript{2+} are not sufficient to catalyze a complete decomposition of high concentrations of H\textsubscript{2}O\textsubscript{2} into \textit{OH}. As shown in Fig. 2e and f, sludge dewaterability was stably improved when Fe\textsuperscript{2+} addition varied in the range from 20 to 160 mg g\textsuperscript{-1} and H\textsubscript{2}O\textsubscript{2} concentration from 32 to 512 mg g\textsuperscript{-1}. The reason why excessive addition of H\textsubscript{2}O\textsubscript{2} caused a negative impact on sludge dewaterability might be connected with the amount of hydroxyl radicals. When H\textsubscript{2}O\textsubscript{2} concentration increases to a critical level, a so-called scavenging effect will occur. Several references are available with regard to the effect of hydroxyl radical production on the efficacy of Fenton reaction (Lin and Gurol, 1998; Torrades et al., 2003; Zhang et al., 2005). The optimal dosages in current study were found to be at 40 mg g\textsuperscript{-1} Fe\textsuperscript{2+} and 32 mg g\textsuperscript{-1} H\textsubscript{2}O\textsubscript{2} in which the SRF reduction efficiency reached 95\%.

4. Conclusions

Joint application of Fenton’s reagent and skeleton builders in conditioning of sewage sludge for subsequent dewatering has been successfully demonstrated to be effective, especially when OPC and lime were used as skeleton builders. Experimental results confirm that Fenton reaction needs sufficient reaction time, specifically 80 min in this study, to degrade organics in the sludge. Based on a series of single-factor experiments, a SRF reduction efficiency of 95\% was achieved in the optimal condition of this process (pH = 5, Fe\textsuperscript{2+} = 40 mg g\textsuperscript{-1}, H\textsubscript{2}O\textsubscript{2} = 32 mg g\textsuperscript{-1}, OPC = 300 mg g\textsuperscript{-1} and lime = 400 mg g\textsuperscript{-1}).

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