Improved sludge dewaterability and hydrolysis performance after pretreatment with Fenton's reagent
Hongying Yuan, Yuping Yang, Jian Yuan, Yanning Wang, Yameng Song, Jingfang Lu and Jianyang Song

ABSTRACT

The dewaterability of excess sludge significantly improved upon pretreatment with Fenton’s reagent in this study. After 0.9 g/L of Fe²⁺ and 5.0 g/L of H₂O₂ were added to the sludge, and reacted for 2 h at pH = 4, the specific resistance to filtration (SRF) of the excess sludge decreased from an initial value of 29.74 x 10¹² m/kg to 6.49 x 10¹² m/kg. The factors that affected this improvement in sludge dewaterability as evaluated by SRF reduction showed the following order: H₂O₂ > pH > Fe²⁺ > reaction time. Furthermore, the hydrolysis performance of the sludge under the optimal reaction conditions was investigated. The results indicated that the concentration of soluble chemical oxygen demand in the supernatant increased almost 14 times compared to raw sludge, and the contents of soluble protein and soluble polysaccharide were more than 8 and 17 times higher, respectively, than for the untreated situation. However, the amounts of ammonia nitrogen (NH₄⁺-N) and phosphate (PO₄³⁻-P) released from the sludge showed different trends: NH₄⁺-N increased by 200%, while PO₄³⁻-P decreased by 82%. The production of volatile fatty acids (VFAs) from the treated sludge showed that total VFAs increased by 66%, and iso-butyric acid was the dominant product among the total VFAs.

Key words | dewaterability, excess sludge, Fenton's reagent, hydrolysis performance

INTRODUCTION

The activated sludge process is a widely used biological method for wastewater treatment (especially municipal wastewater); however, it has the serious drawback of producing large amounts of excess sludge (Kim et al. 2015). In 2016, according to the China Statistical Yearbook 2016 (2016), the amount of wastewater discharged in China was estimated to reach 41.03 billion tons, with about 39.73 million tons of sludge (moisture content 80%) produced per year, and increasing with a greater than 7% annual growth rate. Usually, the water concentration in the excess sludge is between 99% (before thickening) and 95% (after thickening) (Tony et al. 2008). The key to sludge treatment prior to disposal is the reduction in the sludge volume by solid–liquid separation. However, the presence of organic substances which contain most water, mainly extracellular polymeric substances (EPS) and bacterial cells, and super colloidal and colloidal particles in the excess sludge leads to difficulties in dewatering even at high pressures (Thapa et al. 2009). The main point of increasing the dewaterability of excess sludge is to destroy organic substances and release the water in it.

Various methods have been proposed to improve the dewaterability of excess sludge, such as physical conditioning, chemical conditioning and biological conditioning. Among these methods, chemical conditioning is thought to be an efficient and convenient tool for sludge dewatering. Many chemical treatments, such as ozonation and the addition of acids, surfactants, organic polymers and inorganic polymers, have been found to improve activated sludge dewaterability. Zhang et al. indicated that ozonation significantly reduced the production of excess sludge and increased the soluble chemical oxygen demand (SCOD) in the sludge (Zhang et al. 2016). Devlin et al. observed that the centrifugal dewatering efficiency was enhanced by a decrease in the sludge pH value, which was further improved if a surfactant was

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simultaneously applied (Devlin et al. 2011). The addition of polymers to flocculate the sludge particles was successful in decreasing the filter cake moisture content substantially (Luo et al. 2015). For decades, the Fenton process, an advanced oxidation process (AOP), has received much attention for sludge dewatering (Kaynak & Filibeli 2008; Erden & Filibeli 2010). The ferrous ions in Fenton’s reagent react with hydrogen peroxide, resulting in the generation of hydroxyl radicals with powerful oxidizing abilities that oxidize the sludge and destroy its floc structure, thus releasing water in the sludge (Neyens et al. 2005). Many factors affect the results of using Fenton’s reagent during this process, but the contents of Fe$^{2+}$ and H$_2$O$_2$ are two of the main factors affecting its efficiency. Lu et al. reported that when 6,000 mg/L of Fe$^{2+}$ and 3,000 mg/L of H$_2$O$_2$ were added to the sludge, the specific resistance to filtration (SRF) of the treated sludge was only 10% that of the original sludge (Lu et al. 2003). Tony et al. found the optimum conditions, determined by response surface methodology, of the Fenton reaction were Fe$^{2+}$ 21 mg/dry solids (DS) and H$_2$O$_2$ 105 mg/g DS, at which a cost reduction and efficiency improvement of 48 ± 3% could be achieved (Tony et al. 2008). Some researchers proposed that pH and reaction time could also influence the Fenton reaction. Yu et al. (2016) indicated that pH had a considerable effect on reducing SRF in the Fenton reaction and that, compared with an alkaline environment, acidification would enhance the process. Although there have been some previous studies investigating the use of Fenton’s reagent to improve sludge dewatering, there has been little research on the dissolution of substances such as organic matter, nitrogen, phosphate and volatile fatty acids (VFAs) from waste sludge after treatment by Fenton’s reagent. Meanwhile, the dissolution of substances such as SCOD, VFAs and soluble protein (SPN) from waste sludge has gained great interest due to the fact that they can improve both sludge reduction and utilization of recycled energy in wastewater treatment plants (Yan et al. 2010; Yuan et al. 2010), and further studies are necessary to assess whether Fenton’s reagent improves sludge hydrolysis.

In this study, the effects of four factors (the concentrations of Fe$^{2+}$ and H$_2$O$_2$, pH and reaction time) on sludge dewaterability will be investigated, and through a systematic analysis of the SRF reduction rate the optimal dewatering conditions will be established. Furthermore, the hydrolysis performance of treated sludge under the optimal reaction conditions is also discussed.

**MATERIALS AND METHODS**

**Sludge characteristics**

The sludge used in this study was collected from the secondary sedimentation tank of a municipal sewage treatment plant in Tianjin, China. After allowing particulate matter to settle by gravity for 24 h, the supernatant was removed and then stored in a refrigerator (4 °C) prior to use. The characteristics of the raw sludge are presented in **Table 1**. Hydrogen peroxide used in Fenton’s reagent was prepared from the liquid (30% by weight). Fe$^{2+}$ was obtained from a 0.5 mol/L FeSO$_4$ solution. HCl (0.6 mol/L) was used to adjust the pH of the sludge samples during conditioning.

**Experimental procedures**

Initially, sludge samples of 250 mL were transferred into a series of 500 mL beakers. The pH was adjusted to the required value using 0.6 mol/L HCl. Fe$^{2+}$ solution was added to the sludge and the Fenton reaction was initiated after adding H$_2$O$_2$. Following Fenton’s reagent addition the sludge was put into an oscillator and reacted at 25 °C, 150 rev/min to promote reaction and flocculation. The concentrations of Fe$^{2+}$ and H$_2$O$_2$, pH of the Fenton reaction and reaction time during mixing in the oscillator were controlled during each experimental run. The SRF value was used to test the sludge dewatering performance, and determine the optimal reaction conditions. Further analysis was conducted of the sludge hydrolysis characteristics through quantitative analysis of each index in the sludge supernatant under the optimal reaction conditions.

**Table 1 | Properties of the raw sludge**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific resistance to filtration</td>
<td>×10$^{12}$ m/kg</td>
<td>29.74 ± 1.25</td>
</tr>
<tr>
<td>Total solids (TS)</td>
<td>%</td>
<td>2.95 ± 0.67</td>
</tr>
<tr>
<td>Volatile solids (VS)</td>
<td>%</td>
<td>1.77 ± 0.33</td>
</tr>
<tr>
<td>Soluble oxygen demand</td>
<td>mg/g VS</td>
<td>5.08 ± 0.27</td>
</tr>
<tr>
<td>Soluble protein</td>
<td>mg/g VS</td>
<td>2.37 ± 0.91</td>
</tr>
<tr>
<td>Soluble polysaccharide</td>
<td>mg/g VS</td>
<td>0.67 ± 0.09</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>mg/g TS</td>
<td>1.87 ± 1.00</td>
</tr>
<tr>
<td>Phosphate</td>
<td>mg/g TS</td>
<td>2.47 ± 1.00</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>6.76 ± 0.12</td>
</tr>
</tbody>
</table>
Analytical methods

The dewaterability of the sludge was evaluated in terms of SRF, which was determined using the Buchner funnel method. Fifty milliliters of sludge were poured into a Buchner funnel fitted with a 0.45 μm pore size filter paper and filtered at a vacuum pressure of 0.071 MPa. The SRF was calculated using the following equation:

\[
SRF = \frac{2PA^2b}{\mu w} \times 10^{12}
\]

where SRF is the specific resistance to filtration (m/kg), \(P\) is the filtration pressure (N/m²), \(A\) is the filter area (m²), \(b\) is the slope of the filtrate discharge curve (s/m⁶), \(\mu\) is the viscosity of the filtrate (N·s/m²), and \(w\) is the weight of the cake solids per unit volume of filtrate (kg/m³). The moisture in the sludge before and after treatment was measured using a halogen rapid moisture analyzer (SFY-20A, Shenzhen, China).

The hydrolysis performance of the sludge was assessed according to the concentrations of SPN, soluble polysaccharide (SPS), SCOD, ammonia nitrogen (NH₄⁺-N), phosphate (PO₄³⁻/C0⁻-P) and VFAs in the sludge supernatant. SPN was determined by the Lowry Folin method (Lowry et al. 1951), and its absorbance was measured at 500 nm. SPS was measured by the anthrone method (David et al. 1993), and its absorbance was measured at 625 nm. VFAs were measured by gas chromatography (GC-500, Perkin Elmer, Norwalk, CT, USA). All other parameters were obtained according to the standard methods (SEPACE 2002) for the examination of water and wastewater.

RESULTS AND DISCUSSION

Effects of Fenton oxidation on sludge dewaterability

The Fenton reaction mechanism can be simplified to the following equations (Yoon et al. 2001):

\[
Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \tag{1}
\]

\[
Fe^{2+} + OH^- \rightarrow Fe^{3+} + OH^- \tag{2}
\]

In the Fenton treatment, the amount of hydroxyl radicals plays a key role in the oxidation and destruction of the floc structure of the sludge. Optimizing the factors that control the generation of hydroxyl radicals under the reaction conditions therefore improves the outcome of the Fenton process. Thus, we investigated the effects of four factors affecting Fenton's reagent (the concentrations of Fe²⁺ and H₂O₂, pH and reaction time) on sludge dewaterability.

Effects of pH on sludge dewaterability

To confirm the contribution of pH, experiments with pH adjusted to 2, 3, 4, 5 and 6 were conducted for comparison. The results show that the dewaterability of the excess sludge could be significantly improved by controlling the pH at 4. The SRF value was initially 29.74 × 10¹² m/kg but it decreased upon treatment with Fenton’s reagent (0.9 g/L Fe²⁺, 5.0 g/L H₂O₂) at pH 4 for 2 h (Figure 1) to 6.49 × 10¹² m/kg, which was approximately 0.24 times that of the untreated sludge (at pH 6.75). However, when the pH was increased beyond 4, the SRF value of the sludge increased quickly, indicating that Fenton’s reagent had detrimental effects on sludge dewatering under neutral conditions. These results may be attributed to the formation of Fe(OH)₃ from Fe³⁺, which has a low reactivity and will not react with hydrogen peroxide (Buyukkamaci 2004) at higher pH, thus decreasing the oxidation efficiency of Fenton’s reagent. In addition, when the pH is too low and thus the concentration of hydrogen ions is too high, this will cause the production rates of ferrous ions and hydroxyl radicals to decrease as well (Equation (2)). In other words, pH = 4 was the best reaction condition for sludge dewaterability.

Effects of Fe²⁺ concentration on sludge dewaterability

With the initial pH adjusted to 4, various concentrations of Fe²⁺ in the range of 0–1.2 g/L were investigated, keeping H₂O₂ at 5.0 g/L for 2 h. As shown in Figure 2, the
dewatering efficiency improved gradually with increases in the dosage of Fe$^{2+}$, then rebounded slightly. The optimal dosage for Fe$^{2+}$ addition that achieved the lowest SRF value ($7.24 \times 10^{12}$ m/kg) was 0.9 g/L, at which an SRF reduction of 76% was obtained. According to the Fenton reaction mechanism, the Fe$^{2+}$ initiates and catalyzes the decomposition of H$_2$O$_2$, resulting in the generation of hydroxyl radicals, which can oxidize and destroy the floc structure of the sludge (Yoon et al. 2003). In a certain concentration range, higher amounts of Fe$^{2+}$ added will result in more hydroxyl radicals being produced, thereby contributing to the oxidation of the sludge and improving sludge dewatering.

**Effects of H$_2$O$_2$ on sludge dewaterability**

The effects on sludge treated with different dosages of H$_2$O$_2$ at pH 4 and 0.9 g/L Fe$^{2+}$ for 2 h are illustrated in Figure 3. Clearly, at the beginning of the reaction, the SRF decreased dramatically with increasing H$_2$O$_2$ addition, and when the H$_2$O$_2$ concentration was held at 5.0 g/L, the SRF of the conditioned sludge decreased from $34.65 \times 10^{12}$ m/kg to $5.16 \times 10^{12}$ m/kg (85% SRF reduction), but there was no further significant change. Hydrogen peroxide as a redox mediator is the key in the Fenton reaction to producing hydroxyl radicals (Buyukkamaci 2004). Studies have shown that there is an optimum weight ratio of hydrogen peroxide molecules to ferrous ions during the Fenton reaction (De Julio et al. 2009; Lu et al. 2003). When the weight ratio of H$_2$O$_2$/Fe$^{2+}$ is higher than the optimum ratio, excessive H$_2$O$_2$ cannot be converted into hydroxyl radicals because of the lack of the Fe$^{2+}$ catalytic effect. Therefore, the sludge dewatering performance cannot be further improved and enhanced beyond this optimum weight ratio, which in this study was H$_2$O$_2$/Fe$^{2+} = 5.6$ by weight.

**Effects of reaction time on sludge dewaterability**

The Fenton reaction is harsh, rapid and influenced by reaction time (Lu et al. 2003). Therefore, this study also investigated the effect of the Fenton reaction time on sludge dewaterability. The reaction conditions were as follows: pH = 4, Fe$^{2+}$ and H$_2$O$_2$ concentrations 0.9 and 5 g/L, respectively, and the reaction propagates during mixing in the oscillator. The results in Figure 4 show clearly that the SRF dropped dramatically during the initial reaction period, while prolonging the reaction time led to insignificant further improvement in the SRF, with the lowest SRF at 2 h. This indicated that the Fenton reaction in the excess sludge is a rapid process.

In conclusion, the optimal reaction conditions for the best dewaterability were found to be pH = 4, 0.9 g/L Fe$^{2+}$, 5.0 g/L H$_2$O$_2$ and a reaction time of 2 h. Using the reduction
of SRF as the evaluation standard, a comprehensive analysis of the various factors that affect the sludge dewatering performance gave an order of \( \text{H}_2\text{O}_2 > \text{pH} > \text{Fe}^{2+} > \text{reaction time} \).

**Effects of Fenton’s reagent on sludge hydrolysis performance**

Changes in the sludge supernatant after pretreatment with Fenton’s reagent

In order to provide insights into the sludge hydrolysis performance after conditioning with Fenton’s reagent, measurements of the concentrations of SPN, SPS and SCOD in the sludge supernatant before and after Fenton conditioning under the optimal reaction conditions were carried out and the results are shown in **Figure 5**. The concentrations of SPN, SPS and SCOD in the sludge supernatant increased from 2.37, 0.67 and 5.08 mg/g volatile solids (VS) for the untreated sludge to 20.18, 9.78 and 76.61 mg/g VS, respectively, for the sludge conditioned at \( \text{pH} = 4, \text{Fe}^{2+} = 0.9 \text{ g/L}, \text{H}_2\text{O}_2 = 5 \text{ g/L} \) and a reaction time 2 h. This result indicates that Fenton’s reagent is conducive to the release of soluble organics.

Since the excess sludge mainly contains EPS and microbial cells, these components aid in the retention of water and significantly contribute to the water-binding capacity of the sludge floc (Shao et al. 2009), so that the excess sludge is often in a state in which dewatering is difficult. SCOD is one of the indexes used to evaluate organic matter and, as seen in **Figure 5**, the concentrations of SCOD in the sludge supernatant significantly increased, showing that Fenton’s reagent can disrupt the sludge and release organic matter from it. In general, proteins and polysaccharides are important components of sludge cells. They have associated amounts of bound water, so the amounts of protein and polysaccharide released into the aqueous phase indicate that bound water in the sludge cells may also be released into the aqueous phase.

**Changes in NH\(_4\)\textsuperscript{+} -N and PO\(_4\)\(_3\)\textsuperscript{3-} -P in the sludge supernatant after pretreatment with Fenton’s reagent**

The changes in NH\(_4\)\textsuperscript{+} -N and PO\(_4\)\(_3\)\textsuperscript{3-} -P concentrations in the sludge supernatant due to treatment with Fenton’s reagent were diverse. Fenton’s reagent improved the release of NH\(_4\)\textsuperscript{+} -N; as shown in **Figure 6**, the concentration of NH\(_4\)\textsuperscript{+} -N in the filtrate increased 2.14 times compared with the untreated sludge. However, the PO\(_4\)\(_3\)\textsuperscript{3-} -P concentration of the sludge supernatant decreased from 2.47 mg/g total solids (TS) to 0.44 mg/g TS after conditioning with Fenton’s reagent. The floc structure of the excess sludge was destroyed during the Fenton process (Neyens et al. 2003). According to previous research, nitrogenous substances such as proteins and amino acids in the sludge will dissolve and undergo further hydrolysis and ammonification. Therefore, the Fenton process not only contributes to the dissolution of organics but is also accompanied by the release of ammonia. However, in contrast, the Fenton process did not accelerate the release of PO\(_4\)\(_3\)\textsuperscript{3-} -P. The reason may be that the Fe\(^{2+}\) in Fenton’s reagent converted to Fe\(^{3+}\), which can flocculate the PO\(_4\)\(_3\)\textsuperscript{3-} -P in the water to
form FePO₄ (Ge et al. 2015); it has been reported that ferric iron salts have a good flocculation effect, and the optimum pH value of ferric salt coagulation is 3.5–5.0 (Lefebver & Legube 1990), Fytianos et al. also found that the removal rate of PO₄³⁻-P by Fe³⁺ was highest at pH of 4.0–5.5 (Fytianos et al. 1998).

**Changes in VFAs in the sludge supernatant after pretreatment with Fenton’s reagent**

The production of VFAs in the sludge filtrate was also investigated, and the results are shown in Figure 7. The fermentation of sludge usually has to go through a hydrolysis stage, which generally takes 6–7 days (Yuan et al. 2006). In this study, the sludge was treated for just 2 h with Fenton’s reagent at pH = 4, and a remarkable acceleration in VFAs production was found except for acetic acid and valeric acid. The production of propionic acid and iso-butylacetic acid increased from 13.19 mg COD/L and 37.34 mg COD/L to 21.05 mg COD/L and 109.38 mg COD/L, respectively, and iso-valeric acid was produced. The concentrations of total VFAs reached 215.71 mg COD/L, an increase of 66%. Clearly, Fenton’s reagent significantly accelerated the production of VFAs, and enhanced the sludge hydrolysis stage. In addition, the composition of the VFAs produced is important because it can provide useful information about the degree of hydrolysis and fermentation (Yan et al. 2010). In this study, the total VFAs mainly included acetic acid, propionic acid, iso-valeric acid, valeric acid and iso-butylacetic acid, and iso-butylacetic acid was the dominant product (approximately 51%), followed by valeric acid (about 28%).

**CONCLUSIONS**

The effects of Fenton’s reagent on sludge dewatering were analyzed according to the reaction conditions in this study. Four factors all influenced the sludge dewatering result. An acidic pH environment and high dosage of Fenton’s reagent enhanced sludge dewaterability, while a neutral environment did not improve sludge dewaterability. Treatment with Fe³⁺ 0.9 g/L, H₂O₂ 5.0 g/L, pH = 4 and a reaction time of 2 h was determined to be optimal for dewatering.

Increases in SCOD, SPN, SPS and NH₄⁺-N in the sludge supernatant after conditioning with Fenton’s reagent indicated that the floc structure of the sludge had been destroyed and bound water in the sludge cells may also have been released into the aqueous phase, which were determined to be the major reasons for the improvement in sludge dewaterability. In addition, the production of VFAs was significantly increased after conditioning for 2 h with Fenton’s reagent, and Fenton's reaction accelerated the sludge hydrolysis stage. The reason for the decrease of PO₄³⁻-P is likely to be the flocculation with Fe³⁺.

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