Exploitation of Fenton and Fenton-like reagents as alternative conditioners for alum sludge conditioning

Maha A. Tony¹,², Y. Q. Zhao¹,⁺, Aghareed M. Tayeb³

¹. Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Newstead, Belfield, Dublin 4, Ireland. E-mail: maha.tony@ucdconnect.ie
². Basic Science of Engineering Department, Faculty of Engineering, Minoufiya University, Minoufiya 32511, Egypt
³. Chemical Engineering Department, Faculty of Engineering, Minia University, Minia 61111, Egypt

Received 17 January 2008; revised 06 March 2008; accepted 09 April 2008

Abstract

The use of Fenton’s reagent (Fe²⁺/H₂O₂) and Fenton-like reagents containing transition metals of Cu(II), Zn(II), Co(II), and Mn(II) for an alum sludge conditioning to improve its dewaterability was investigated. The results obtained were compared with those obtained from conditioning the same alum sludge using cationic and anionic polymers. Experimental results show that Fenton’s reagent was the best among the Fenton and Fenton-like reagents for the alum sludge conditioning. A considerable effectiveness of capillary suction time (CST) reduction efficiency of 47% can be achieved under test conditions of Fe²⁺/H₂O₂ = 20/125 mg/g DS (dry solid) and pH 6.0. The observation of floc-like particles after Fenton’s reagent conditioning of alum sludge suggested that the mechanism of Fenton’s reagent conditioning was different from that of polymer conditioning. In spite of the lower efficiency in the CST reduction of Fenton’s reagent in alum sludge conditioning compared to that of polymer conditioning, Fenton’s reagent offers a more environmentally safe option. This study provided an example of proactive treatment engineering, which is aimed at seeking a safe alternative to the use of polymers in sludge conditioning towards achieving a more sustainable sludge management strategy.

Key words: alum sludge; conditioning; Fenton and Fenton-like reagents; organic polymers; cost estimate

Introduction

Alum sludge conditioning involves chemical and/or physical treatment to enhance the removal of water in the ensuing mechanical dewatering process. Generated in large quantities from drinking water treatment plants that use aluminium sulphate as a primary coagulant, alum sludge is characterized as being difficult to dewater. Organic polymers (polyelectrolytes) have been used mostly in practice for conditioning the sludge prior to the dewatering operation (Zhao and Bache, 2001; Ma et al., 2007). In recent years, advanced oxidation processes (AOPs) for sludge conditioning have been gaining increased global attention. This is due to the recognized potential of such processes and the perceived long term risks of polymer residual to the aquatic/surrounding environment which is associated with the conventional polymer conditioning of the sludge. In particular, the fate of the polymer residual when the dewatered sludge cakes (which contain the residues of the polymer used) are landfilled as a final disposal option is still unclear (Majam and Thompson, 2006; Bolto and Gregory, 2007). Fenton’s reagent (Fe²⁺/H₂O₂), as one of the AOPs (Chiron et al., 2000; Neyens and Baeyens, 2002; Perez et al., 2002; Will et al., 2004), has been used as an alternative conditioner particularly in wastewater sludge conditioning (Mustranta and Viikari, 1993; Vosteen and Weiuenberg, 2000; Lu et al., 2003; Neyens et al., 2003; Buyukkamaci, 2004; Dewil et al., 2005). On the contrary, there is very little information found in the literature on the use of the Fenton’s reagent for water treatment sludge conditioning. Kwon et al. (2004) reported that alum sludge dewaterability and filterability were enhanced upon treatment with H₂SO₄ plus H₂O₂, and strikingly, the improved sludge dewaterability was comparable to polymer conditioning.

In our previous study, the effectiveness and optimization of Fenton’s reagent for an alum sludge conditioning were preliminarily investigated (Tony et al., 2008). The addition of Fe²⁺/H₂O₂ led to a considerable improvement in the alum sludge dewaterability as evaluated by the capillary suction time (CST). The aim of this study is to provide for comparison profile among the use of Fenton’s reagent and Fenton-like reagents containing four transition metals for conditioning of an aluminium-based drinking water treatment sludge. As reference, the traditional polymer conditioning of such sludge was also provided. Comparisons were made on the basis of their treatment efficiency for the sludge conditioning process. In addition, cost-effectiveness of Fenton reagent and polymer for alum sludge conditioning...
conditioning was analyzed.

1 Materials and methods

1.1 Experimental materials

The experimental alum sludge was collected from the underflow of the sedimentation tank of a local waterworks in southwest Dublin, Ireland, which treats reservoir water using aluminium sulphate as a primary coagulant. The sludge had an SS (suspended solids) concentration of 2 850 mg/L. The CST, specific resistance to filtration (SRF), pH, and Al content of the sludge were 67.5 s, 6.3 × 10^{11} m/kg, in the range of 5.7–6.0, and 194 mg Al/g sludge, respectively. Five dibasic salts (FeCl₂·4H₂O, ZnCl₂, CuSO₄·5H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O) were used individually to make different dibasic metal solutions in Fenton and Fenton-like reagents. Hydrogen peroxide in liquid form (30 wt.%) was obtained from a commercial supplier. Sulfuric acid was used for adjusting the pH of the sludge samples during conditioning. Two organic polymers, namely, Magnafloc LT-25 and FO-4140 PWG were also used for the sludge conditioning tests. The properties of the polymers are listed in Table 1.

1.2 Experimental methods

For the conditioning experiments, several sludge samples of 250 mL contained in 500 mL beakers were used. Magnetic stirring was employed during the conditioning process. During the Fenton and Fenton-like reagents conditioning, different types of dibasic metal solutions were separately added to the sludge and the reaction was then initiated after adding H₂O₂. The adopted dosage of metal ion (such as Fe^{2+}) and H₂O₂ was 20 and 125 mg/g DS, respectively, according to a previous study (Tony et al., 2008). After the Fenton and/or Fenton-like reagent addition, the sludge was subjected to 30 s of rapid mixing followed by 30 s of slow mixing in a common jar test apparatus. However, when organic polymers were added as conditioners, the sludge was subjected to 30 s of rapid mixing followed by 60 s of a slow mixing to promote flocculation. The experimental setup is shown schematically in Fig. 1. Different samples of the treated and raw sludges were poured into 100 mL graduated cylinders for observing their settling behavior. The height of the floc/liquid interface was then recorded with the settling time.

1.3 Analytical methods

Sludge dewaterability was evaluated by CST, which was measured using a standard CST apparatus (Triton-WPRL, Type 130 CST, Triton Electronics Limited, England). Changes of sludge’s CST before and after the conditioning were termed as CST reduction efficiency and expressed in percentage (Eq. (1)). The CST reduction efficiency was used to evaluate the effectiveness of the conditioner. Turbidity of the supernatant of the sludge was also measured using a HACH 2100N IS Turbidimeter (USA) for the conditioned sludge. The result was compared with the supernatant of the raw sludge. The pH was measured using a digital pH-meter (PHM62, Radiometer, Copenhagen, Denmark).

\[
\text{CST} = \left( 1 - \frac{\text{CST}}{\text{CST}_0} \right) \times 100\%
\]  

where, CST₀ and CST are the capillary suction time of the alum sludge before and after conditioning, respectively.

2 Results and discussion

2.1 Fenton and Fenton-like reagents conditioning

As is well known, Fe(II) serves as a catalyst for the formation of the highly reactive hydroxyl radical via Fenton reaction. In addition to Fe(II), several transition metal ions including Cu(II) and Co(II) were found to have oxidative features of the Fenton reagent. Thus, the mixtures of these metal compounds with H₂O₂ were named as “Fenton-like reagents”. Extensive experiments were conducted on the alum sludge conditioning with Fenton and Fenton-like reagents at two pH levels (3.0 and 6.0). The results are illustrated in Fig. 2. The values of the CST reduction efficiency (%) show that the ferrous salt is the most effective source in the sludge conditioning compared to the other transition metal salts. The Cu, Co, and Mn salts can bring a similar CST reduction rate in a range of 11%–6% when they are used as Fenton-like reagents. However, the CST reduction rate obtained using Zn salt was 0.8%, indicating its ineffectiveness. In addition, for all the transition metals, except for the iron ion, there was no significant effect on the CST reduction efficiency at pH 6.0 and 3.0. This may suggest that pH has no significant effect on the CST reduction efficiency when either Fe, Zn, Co, or Mn salt is used as a sludge conditioner. However, in contrast, the pH

![Fig. 1 Schematic diagram of the experimental setup.](image-url)
shows an obvious effect on CST reduction efficiency when Fe\(^{2+}/\text{H}_2\text{O}_2\) is used at pH 6.0.

The difference in the abilities of the various transition metal salts in Fenton and Fenton-like reagents conditioning of alum sludge may be related to the different abilities of transition metals to react with oxygen in a variety of ways, owing to the unpaired oxygen electrons (Mustranta and Viikari, 1993). The hydroxyl radicals formed is not enough to attack the sludge particles to form the new intermediates, which is able to treat the sludge for enhancing its filtration properties. However, for the iron ions, the hydroxyl radicals produced are considerably more sufficient than for the other transition metals. More significantly, our previous investigation has demonstrated (by the molecular size distribution measurement of sludge samples before and after Fenton reagent conditioning) that the Fenton reaction degraded/broke the organics from large molecular sizes into smaller ones via highly reactive hydroxyl radicals, thus improving sludge dewaterability through the release of both interstitial waters, which were trapped among organics, and adsorbed and chemically bound water by the degradation of organics (Tony et al., 2008).

2.2 Polymer conditioning

The results of the polymer conditioning of the alum sludge ranging from 1.8 to 21.0 mg/g DS are shown in Fig. 3. For the two polymers used, the result of the CST reduction efficiency shows that the sludge dewaterability was enhanced in both cases for definite polymer doses. It is also noted from Fig. 3 that for the anionic polymer (LT-25), a reverse effect on sludge dewaterability was observed when the dosage exceeded 12.5 mg/g DS. The optimal dosage of polymer LT-25 was 3.5 mg/g DS and this provided a maximum CST reduction efficiency of 67%. However, for the cationic polymer (FO-4140), a maximum CST reduction efficiency of 82% was obtained at 7.0 mg/g DS, which represents the optimal dosage. The effectiveness of the conditioning in the case of the cationic polymer is higher than that of the anionic polymer. This is believed to be owing to the differences in the nature and the ionic charge of the polymers, which control the coagulation and flocculation (Wu et al., 1997; Zhao and Bache, 2002).

2.3 Comparison between Fenton’s reagent and organic polymer for alum sludge conditioning

2.3.1 Conditioning/treatment efficiency and characteristics

For the purpose of comparison, the values of the CST reduction efficiency at the optimal dosage of the different conditioners were compared as well as their settling behavior and the turbidity of the supernatant. As seen in Fig. 4, the CST reduction efficiency for the cationic polymer provided the highest value of 82%, followed by the anionic polymer (67%) and then the Fenton’s (Fe\(^{2+}/\text{H}_2\text{O}_2\)) reagent (47%). Although the Fenton’s reagent cannot achieve the same level of CST reduction as that achieved by the polymers, the application of the Fenton reagent for alum sludge conditioning as alternative conditioner lies in its advantage over polymer on environmental safety. The lower CST reduction efficiency of Fenton reagent over polymer conditioning may be attributed to the different mechanisms of the polymer and Fenton reaction during sludge conditioning. In the case of the Fenton’s reagent, the improvement of sludge dewaterability lies in the active intermediates (OH) that may attack the cells of the sludge organic particles. This leads to an increase in hydrophobicity and the release of interstitial water, which was trapped inside the organic particles of the sludge (Kwon et al., 2004; Yang et al., 2006; Tony et al., 2008). In addition, during the Fenton reaction, ferric ions can be produced. This plays a role of flocculating the sludge particles into aggregate. In the case of polymer conditioning, the mechanism of the reaction is different as the polymers may serve the function of charge neutralization and inter particle or primary flocs bridging (Bache and Gregory, 2007). The difference between the two types of polymers is related to their ionic charges, which may affect their adsorption capacity onto the sludge particles. It can be observed from Fig. 4 that the values of the supernatant turbidity are quite similar, regardless of the conditioner.
Effects of the different conditioners on the sludge CST reduction efficiency and turbidity of the supernatant of the alum sludge (anionic polymer LT-25, 3.5 mg/g DS; cationic polymer FO-4140, 7.0 mg/g DS; Fenton’s reagent Fe$^{2+}$/H$_2$O$_2$, 20/125 mg/g DS, pH 6.0).

Figure 5 Interface position of sludge/supernatant as a function of the settling time for raw alum sludge and conditioned sludge using three different conditioners (anionic polymer LT-25, 3.5 mg/g DS; cationic polymer FO-4140, 7.0 mg/g DS; Fenton’s reagent Fe$^{2+}$/H$_2$O$_2$, 20/125 mg/g DS pH 6.0).

Figure 6 Images of the alum sludge. (a) raw sludge; (b) after Fenton process at Fe$^{2+}$/H$_2$O$_2$ 20/125 mg/g DS, pH 6.0; (c) after polymer LT-25 conditioning at 3.5 mg/g DS; (d) after polymer FO-4140 conditioning at 7.0 mg/g DS.

used. These values notably have a remarkable difference with that of the raw sludge. The comparison of the settling characteristics is shown in Fig. 5, which illustrates the position of the sludge/supernatant interface as a function of the settling time up to 90 min. It suggests that the settling characteristics for the sludge conditioned with Fenton’s reagent are similar to that of the raw sludge. This may be explained by the insignificant change of particle size of the sludge conditioned by Fenton reaction (Kwon et al., 2004). However, considerable differences in the settling behavior can be observed between the sludge conditioned with the polymers and those conditioned with the Fenton’s reagent. This may be explained by the polymer particle size-bridging mechanism, which significantly increases the size of sludge particles (Zhao, 2004; Ma et al., 2007).

2.3.2 Cost estimates

A cost-effective analysis of Fenton reagent as conditioner was conducted. The same analysis for polymers used in this study was also conducted for the purpose of providing reference. Such a cost analysis is based on the following assumptions. (1) The cost of conditioning of 1 kg sludge (dry solids) is considered; (2) only the chemicals and the energy costs are calculated, no investment costs for apparatus and buildings are considered. The prices used for the calculation are listed in Table 2. The energy consumption was only from the magnetic stirrer (625 W).

The results of the cost estimates for the three conditioners at different dosages are shown in Table 3. It can be
seen that compared with polymer conditioning, the cost of Fenton’s reagent is in the same level of polymers. It should be noted that there may be some increase of cost associated with the Fenton’s reagent due to its dual-reagent addition. Such costs may be related to cost increase of equipment installation, operation, and control process. However, notwithstanding the cost increases, Fenton’s reagent has a potential advantage of eliminating the perceived long term risk associated with polymer residual in the environment.

3 Conclusions

The results demonstrated that the Fenton and Fenton-like reagents peroxidation processes positively influence the sludge dewatering characteristics. Ions of Cu²⁺, Co²⁺, Zn²⁺, and Mn²⁺ were tested as substitutes for Fe²⁺, Fe³⁺ had the highest influence on the alum sludge dewaterability, with CST reduction efficiency of 47% achieved under the test conditions of Fe²⁺/H₂O₂ 20/125 mg/g DS at pH 6.0, while other dibasic salts tested exhibited a limited improvement on alum sludge dewaterability. The floc-like particles have been identified after Fenton’s reagent conditioning of alum sludge. The mechanism of Fenton’s reagent conditioning is believed to be different from that of polymer conditioning. Although the conditioning efficiency (in terms of CST reduction) of Fenton’s reagent is less than that of polymer conditioning, Fenton’s reagent offers a potential advantage of eliminating the perceived long term risk of polymer residual to the environment.

Acknowledgments

The first author would like to appreciate Ministry of Higher Education, Missions Department, Egypt for the financial support granted through Channel Scheme Mission. The authors also thank Mr P. Kearney for his technical assistance during this study.

References


Table 2: Prices used for cost estimation

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost (€/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O₂ (30 wt.%) (L)</td>
<td>70</td>
</tr>
<tr>
<td>FeCl₂·4H₂O (kg)</td>
<td>100</td>
</tr>
<tr>
<td>Magnafloc LT-25 (kg)</td>
<td>106</td>
</tr>
<tr>
<td>FO-4140 PWG (kg)</td>
<td>113.6</td>
</tr>
<tr>
<td>Electrical energy (kWh)</td>
<td>0.13^b</td>
</tr>
</tbody>
</table>

^ The price refers to 25 kg (L) bag for industrial uses. ^ The average industrial tariff for the large electricity user in Ireland (at time of study, October 2007).

Table 3: Cost estimate for the various conditioning processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Fenton’s reagent (Fe²⁺/H₂O₂)</th>
<th>Polymer FO-4140</th>
<th>Polymer LT-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal dosage (mg/g DS)</td>
<td>20/125</td>
<td>7.0</td>
<td>3.5</td>
</tr>
<tr>
<td>CST reduction efficiency (%)</td>
<td>47</td>
<td>82</td>
<td>67</td>
</tr>
<tr>
<td>Chemicals cost (€)</td>
<td>0.35</td>
<td>0.032</td>
<td>0.015</td>
</tr>
<tr>
<td>Energy demand (kWh)</td>
<td>3.65</td>
<td>5.48</td>
<td>5.48</td>
</tr>
<tr>
<td>Energy cost (€)</td>
<td>0.47</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>Total cost (€)</td>
<td>0.82</td>
<td>0.74</td>
<td>0.73</td>
</tr>
</tbody>
</table>