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. maha.tony@ucdconnect.ie
2. Basic Science of Engineering Department, Faculty of Engineering, Menofya University, Menofya, Egypt
3. Chemical Engineering Department, Faculty of Engineering, Minia University, Minia, Egypt

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

Abstract: The use of Fenton’s reagent (Fe^{2+}/H_2O_2) 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 in this study. 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 Fe^{2+}/H_2O_2 = 20/125 mg/gDS (Dry Solids) and pH = 6.0. The observation of floc-like particles after Fenton’s reagent conditioning of alum sludge suggests that the mechanism of Fenton’s reagent conditioning was different with that of polymer conditioning. In spite of the less efficiency in CST reduction of Fenton’s reagent in alum sludge conditioning compared with that of polymer conditioning, is less than that of polymer conditioning. 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

* Corresponding author. E-mail: yaqian.zhao@ucd.ie
1 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 was characterized as rather difficult to dewater. The 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 associated with the conventional polymer conditioning of the sludge. In particular, it is unclear on 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 (Majam and Thompson, 2006; Bolto and Gregory, 2007). The use of Fenton's reagent (Fe^{2+}/H_{2}O_{2}) 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 H_{2}SO_{4} plus H_{2}O_{2} 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 was preliminarily investigated (Tony et al., 2008). The addition of Fe^{2+}/H_{2}O_{2} 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 a comparative 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 the reference the traditional polymer conditioning of such sludge was also provided. Comparisons were conducted 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 was analysed.
2 Materials and methods

2.1 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 a SS (Suspended Solids) concentration of 2,850 mg/L. The CST, specific resistance to filtration (SRF), pH, and Al content of the alum sludge were 67.5 s, 6.3×10^{11} m/kg, 5.7--6.0 and 194 mgAl /g sludge, respectively. Five dibasic salts (FeCl₂·4H₂O, ZnCl₂, CuSO₄·5H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O) were used individually to make different dibasic metal solution in Fenton and Fenton-like reagents. Hydrogen peroxide in liquid form (30% by 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.

![Table 1](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ionic character</th>
<th>Molecular weight</th>
<th>Conc. (%)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnafloc LT-25</td>
<td>Anionic</td>
<td>(10--15)×10^6</td>
<td>0.01</td>
<td>CIBA Speciality Chemicals Ltd., UK</td>
</tr>
<tr>
<td>FO-4140 PWG</td>
<td>Cationic</td>
<td>5×10^6</td>
<td>0.01</td>
<td>SNF SAC ZAC de Milieux, France</td>
</tr>
</tbody>
</table>

2.2 Experimental methods

For the conditioning experiments, several 250 ml of the sludge samples contained in 500 ml beakers were used. Magnetic stirring was employed during the conditioning process as shown in Fig. 1. 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/gDS 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 behaviour. The height of the floc/liquid interface was then recorded with the settling time.
2.3 Analytical methods

Sludge dewaterability was evaluated by CST which was measured using a standard CST apparatus (Triton-WPRL, Type 130 CST). 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. pH was measured using a digital pH-meter (PHM62, Company, Nation).

\[
CST = (1 - \frac{CST}{CST_0}) \times 100\% \tag{1}
\]

where, \(CST_0\) and \(CST\) are the capillary suction time of the alum sludge before and after conditioning, respectively.

3 Results and discussion
3.1 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), many 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 H\(_2\)O\(_2\) were named as “Fenton-like reagents”. Extensive experiments on the alum sludge conditioning with Fenton and Fenton-like reagents used in this study at two pH levels (3.0 and 6.0) were conducted. The results are illustrated in Fig. 2. The values of the CST reduction efficiency (%) show that the ferrous salt is the most efficient source in the sludge conditioning compared to the other transition metal salts tested. The Cu, Co, and Mn salts can only bring about a quite similar CST reduction rate in a range of 11% to 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 examined, 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, pH shows an obvious effect on CST reduction efficiency when Fe$^{2+}$/H$_2$O$_2$ is used at pH 6.0.

Fig. 2 Effectiveness of different transition metals on Fenton and Fenton-like reagents conditioning of alum sludge (metal ions 20 mg/gDS, H$_2$O$_2$ 125 mg/gDS, reaction time 1 min)

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, due 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 in order to enhance its filtration properties. However, for the iron ions, the produced hydroxyl radicals are much more sufficient than for the other transition metals. More significantly, our previous investigation (Tony et al., 2008) 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.

3.2 Polymer conditioning

The results of the polymer conditioning of the alum sludge ranged from 1.8 to 21.0 mg/gDS 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 dose exceeded 12.5 mg/gDS. The optimal dose of polymer LT-25 was 3.5 mg/gDS and this gave a maximum CST reduction efficiency of 67%. However, for the cationic polymer (FO-4140), a maximum CST reduction efficiency of 82% was obtained at a dose of 7.0 mg/gDS, which represents the optimal dose. 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 due 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).

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Fig. 3 CST reduction efficiency of the sludge as a function of the polyelectrolyte dose for both a cationic and an anionic polymer.

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

3.3.1 Conditioning/treatment efficiency and characteristics

For the purpose of comparison, the values of the CST reduction efficiency at the optimal dose of the different conditioners were compared, and also their settling behaviour and the turbidity of the supernatant. As shown in Fig. 4 the CST reduction efficiency for the cationic polymer gave the highest value of 82%, followed by the anionic polymer (67%) and then the Fenton’s (Fe$^{2+}$/H$_2$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 less 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 radicals) that may attack the cells of the sludge organic particles. This leads to 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. By observing Fig. 4, the values of the supernatant turbidity are quite similar, regardless of the conditioner 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 of up to 90 min. It suggests that the settling characteristics for the sludge conditioned with Fenton’s reagent are quite 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 behaviour 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).

Figure 6 provides a qualitative description of the effectiveness of the different conditioners on the sludge conditioning as compared with that of the raw sludge. The obvious and largest flocs are observed when the polymers were added. However, Fenton’s reagent does not show particle bridging in contrast to the synthetic polyelectrolytes. Consequently, small floc-like appearance would be expected.

Fig. 4 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/gDS; cationic polymer FO-4140, 7.0 mg/gDS; Fenton’s reagent Fe$^{2+}$/H$_2$O$_2$, 20/125 mg/gDS, pH 6.0).

Fig. 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/gDS; cationic polymer FO-4140, 7.0 mg/gDS; Fenton’s reagent Fe$^{2+}$/H$_2$O$_2$, 20/125 mg/gDS pH 6.0).

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

3.3.2 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 the cost analysis is based on the assumptions. (1) The cost (Euro, €) 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 being considered. (3) The prices used for the calculation are listed in Table 2. The energy consumption was only from the magnetic stirrer (625 W).

Table 2 Prices used for cost estimation

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost (€*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$ (30 %, wt) (L)</td>
<td>70</td>
</tr>
<tr>
<td>FeCl$_2$·4H$_2$O (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**</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).

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’. Although some increase of cost in Fenton reagent may be added by considering its dual-reagent addition related to cost increase of equipment installation, operation, and control process, it should be noted that by placing emphasis on the apparent cost of the Fenton’s reagent conditioning process, its potential advantage, which is eliminating the perceived long term risk associated with polymer residual in the environment, may be overshadowed.

Table 3 Cost estimate for the various conditioning processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Optimal dose (mg/gDS)</th>
<th>CST reduction (%)</th>
<th>Chemicals costs (€)</th>
<th>Energy demand (kWh)</th>
<th>Energy cost (€)</th>
<th>Total costs (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton’s reagent (Fe$^{2+}$/H$_2$O$_2$)</td>
<td>20/125</td>
<td>47</td>
<td>0.35</td>
<td>3.65</td>
<td>0.47</td>
<td>0.82</td>
</tr>
<tr>
<td>Polymer FO-4140</td>
<td>7.0</td>
<td>82</td>
<td>0.032</td>
<td>5.48</td>
<td>0.71</td>
<td>0.74</td>
</tr>
<tr>
<td>Polymer LT-25</td>
<td>3.5</td>
<td>67</td>
<td>0.015</td>
<td>5.48</td>
<td>0.71</td>
<td>0.73</td>
</tr>
</tbody>
</table>
4 Conclusions

The results from the present study have demonstrated that the Fenton and Fenton-like reagents peroxidation processes positively influence the sludge dewatering characteristics. Ions, copper, cobalt, zinc, and manganese were tested as substitutes for ferrous ion. Ferrous ion had the highest influence on the alum sludge dewaterability, with CST reduction efficiency of 47% to be achieved under test conditions of Fe$^{2+}$/H$_2$O$_2$ 20/125 mg/gDS 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 with 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 specific promise to eliminate the perceived long term risk of polymer residual to the environment.

Acknowledgment

The first author wishes 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


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Figure 3: CST reduction efficiency of the sludge as a function of the polyelectrolyte dose for both a cationic and an anionic polymer

Figure 4: Effects of the different conditioners on the sludge CST reduction efficiency (%) and turbidity of the supernatant of the alum sludge (dose of anionic polymer, LT-25, 3.5 mg g-DS⁻¹; cationic polymer, FO-4140, 7.0 mg g-DS⁻¹; Fenton’s reagent, Fe²⁺/H₂O₂=20/125 mg g-DS⁻¹ and pH, 6.0)

Figure 5: Interface position of sludge/supernatant as a function of the settling time for raw alum sludge and conditioned slurges using three different conditioners (dose of anionic polymer, LT-25, 3.5 mg g-DS⁻¹; cationic polymer, FO-4140, 7.0 mg g-DS⁻¹; Fenton’s reagent, Fe²⁺/H₂O₂=20/125 mg g-DS⁻¹ and pH, 6.0)

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