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Fenton and Fenton-like AOPs for alum sludge conditioning:

Effectiveness comparison with different Fe$^{2+}$ and Fe$^{3+}$ salts

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Abstract

Currently, organic polymers are adopted in alum sludge (aluminium-coagulated drinking water treatment sludge) conditioning. However, there are important concerns regarding the use of these polymers because of the unknown and long-term effects of the potential release of excess polymer to the surrounding environment when the sludge is landfilled. Therefore, as an initiative action, this study aimed at investigating alternative chemical conditioning methods and focused mainly on exploiting Fenton (Fe$^{2+}$/H$_2$O$_2$) and Fenton-like (Fe$^{3+}$/H$_2$O$_2$) reagents as the conditioner. Experiments have been conducted to test the effectiveness of Fenton’s reagent (containing the ferrous salts of chloride, sulphate or oxalate), Fenton-like reagent (containing ferric salts of chloride and sulphate) and the coagulation method using FeCl$_3$ for an alum sludge conditioning at a constant hydrogen peroxide and iron salt concentrations of 125 and 20 mg/g DS (dry solids), respectively. The effectiveness on dewaterability of the alum sludge demonstrated that the maximum reduction (%) of SRF (specific resistance to filtration) and CST (capillary suction time) of 74 % and 47 %, respectively, can be obtained when Fenton’s reagent was adopted for sludge conditioning. Such reduction of 64% for SRF and 38% for CST can be achieved when Fenton-like reagents were applied.
Keywords: Alum sludge, conditioning, Fenton’s reagent, Fenton-like process, capillary suction time (CST), specific resistance to filtration (SRF)

1. Introduction

Aluminium sulphate is most widely used as a primary coagulant in the treatment of raw waters. The sludge resulting from the treatment is thus termed as alum sludge. Alum sludge is generated in large amounts and its characteristics make it difficult to dewater. Historically, chemical conditioning is widely applied to improve its dewaterability prior to mechanical dewatering (Lee and Liu, 2000; Wu et al., 2003; Bache and Gregory, 2007; Saveyna et al., 2008; Yu et al., 2009). This includes the use of various organic polymers (Zhao and Bache, 2002; Zhao, 2002; Ma et al., 2007) and surfactants (Huang et al., 2002).

Although organic polymers are effective in alum sludge conditioning, an important concern is raised specially in recent years regarding the potential toxicity of their basic units of acryl amide and acrylate, which may release to the aquatic environment after a long-term degradation and cause an unknown damage of surface water quality (Xiao et al., 2002; Majam and Thom, 2006; Bolto and Gregory, 2007). For instance, the use of polyelectrolytes in Japan and Switzerland are not permitted in the drinking water treatment, while Germany and France located a strict limit for such use (Bolto and Gregory, 2007). As a result of this a stringent limits for the polymer use to prevent the environmental damage has been proposed (Majam and Thom, 2006). Accordingly, more research is necessary, as an initiative action, to seek an alternative method for alum sludge conditioning in more environmental safe manners, such as the application of advanced oxidation processes (AOPs).

Fenton’s reagent, one of the components of AOPs has been applied in many areas including wastewater treatment (Xiao et al., 2002; Sanz et al., 2003). However, until now there is no report of such the process being applied in alum sludge conditioning in spite of few studies that applied it in
wastewater sludge conditioning (Mustranta and Viikari, 1993; Lu et al., 2001; Neyens, 2003). For example, Mustranta and Viikari (1993) applied Fenton’s reagent for conditioning of different sludges from pulp and paper mill and the reduction of SRF (specific resistance to filtration) by 70 % was obtained. Lu et al., (2001) demonstrated that 80 % SRF reduction was achieved when the Fenton’s reagent was applied in the conditioning of activated sludge. However, most literature focuses on applying the Fenton’s reagent in wastewater sludge, rather than in the drinking water sludge.

Fenton-like process that uses ferric salts as a source of iron salt was also applied in treating wastewaters (Xu, 2001; Wang et al., 2008). Interestingly, a few papers were published in using it in sewage sludge conditioning. For example, Lu et al., (2003) studied the effect of Fenton-like process on the conditioning of activated sludge and the comparison of the Fenton-like process with the Fenton reagent process. It was reported that, although the same trend for both Fenton and Fenton-like processes on SRF reduction (%) was obtained, the Fenton’s reagent had higher efficiency on improving sludge dewaterability than that of Fenton-like reaction. Again, there is no such kind of study on alum sludge conditioning.

The difference between Fenton and Fenton-like reagents is related to their mechanisms. In the case of Fenton’s reagent the hydroxyl radicals are produced as shown in Eqs. (1) (James and Englehardt, 2006) and (2) (Neyens et al., 2003) and the main step in this Fenton’s reagent mechanism is the hydrogen peroxide O-O lysis to promote the essential reaction (James and Englehardt, 2006). However, the mechanism differs slightly in the case of the Fenton-like reagent in which Fe$^{3+}$ forms intermediates and Fe$^{2+}$ instead of O-O bond breaking takes place (Eq. (3)). Then, Fe$^{2+}$ slowly reduces the H$_2$O$_2$ compared to Fenton’s reagent as a second step (Eq. (1)) (Ensing et al., 2003; James and Englehardt, 2006).

\begin{align*}
Fe^{2+} + H_2O_2 & \rightarrow \cdot OH + OH + Fe^{3+} \\
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + OOH \cdot + H^+ \\
Fe^{3+} + H_2O_2 & \rightarrow Fe^{2+} + OH \cdot + OH^-
\end{align*}

(1) (2) (3)
From the reaction mechanisms of the Fenton’s and Fenton-like reagents, it is obvious that Fenton reaction is friendly to the environment as its products are hydroxyl radicals and oxygen (Cravotto et al., 2008). However, the Fenton’s reagent sludge after the treatment process contains the iron salt in the final discharge (Peres et al., 2004; Hsueh et al., 2005; James and Englehardt, 2006; Muthuvel et al., 2007), which may draw attention for additional treatment.

In our previous study, the investigation of the alum sludge conditioning with Fenton’s reagent (FeCl₂/H₂O₂) was conducted and the process parameters were optimized (Tony et al., 2008). In addition, different transition metal salts (Cu²⁺, Zn²⁺, Co²⁺ and Mn²⁺) used jointly with H₂O₂ as Fenton-like process have also been tested for alum sludge conditioning (Tony et al., 2009). The aim of the present work is to exploit the effectiveness of different Fe²⁺ and Fe³⁺ salts adopted jointly with H₂O₂ as Fenton and Fenton-like reagents for an alum sludge conditioning. Focuses were placed on the comparison of conditioning efficiencies of the two systems with different Fe²⁺ and Fe³⁺ salts and the effect of parameters, such as pH and temperature on the efficiency of alum sludge dewaterability, which was evaluated using capillary suction time method (CST) and specific resistance of filtration.

2. Experimental

2.1 Materials

The alum sludge samples used during this study were taken from a water treatment plant as described in detail in Tony et al., (2008). Principle properties of the alum sludge are given in Table 1. Fenton (Fe²⁺/H₂O₂) and Fenton-like (Fe³⁺/H₂O₂) reagents, as the conditioners, are prepared by making solutions from different Fe²⁺ and Fe³⁺ salts. Hence, three Fe²⁺ salts, namely FeCl₂·4H₂O, FeSO₄·7H₂O and FeC₂O₄·2H₂O, and two Fe³⁺ salts, namely FeCl₃·6H₂O and Fe₂(SO₄)₃ were used. Commercial H₂O₂ (30 % by wt) was used. Sulfuric acid is used for adjusting the pH of the sludge samples.
2.2 Methods

Initially iron solution (Fe$^{2+}$ or Fe$^{3+}$) was added to a 250 ml sludge samples, Fenton or Fenton-like reagent reaction was then initiated after adding hydrogen peroxide. Thereafter, the sludge was subjected to rapid mixing (for 30 second) and slow mixing (for 30 second) to generate reaction. This conditioning procedure, especially the reaction time, has been investigated previously for the time of reaction from 1 min to 4 hrs (Tony et al., 2008). The optimum doses of hydrogen peroxide and Fe$^{2+}$ salt were also optimized previously on the response surface methodology (RSM), which is a collection of mathematical and statistical techniques for optimising purpose (Montgomery, 1991). According the previous study (Tony et al., 2008), the dosage of Fe$^{2+}$ or Fe$^{3+}$ of 20 mg/g DS and the dosage of H$_2$O$_2$ of 125 mg/g DS are applied in this study.

In order to evaluate the effect of the operating parameters on the conditioning processes, the effect of the initial pH on the Fenton and Fenton-like reagents was tested. The initial pH was adjusted (using H$_2$SO$_4$) at the desired values before the reagent was added to the sludge. In addition, the initial temperature of the Fenton’s reagent process was also tested. Temperatures in the range of 20 to 60 °C were used with hot plate magnetic stirrer equipped with stirrer and heater control.

2.3 Analytical methods

The dewatering capacity of the sludge samples was evaluated jointly by CST apparatus (Trition-WPRL, Type 130 CST, Triton Electronics Limited, England) and standard SRF test (Coackley and Jones, 1956), which was performed using a Buchner Funnel with a Whatman no.1 filter paper applying 0.5 atm suction. SRF was calculated using the following equation:

$$SRF = \frac{2A^2 P b}{\mu w}$$

where $P$ is the filtration pressure (N/m$^2$); $A$ the filter area (m$^2$); $\mu$ the viscosity of the filtrate (N s/m$^2$); $w$ the weight of the cake solids per unit volume of filtrate (kg/m$^3$); $b$ the slope of filtrate
Three samples were taken to measure CST and SRF and the average value was used. Dewaterability of the sludge under Fenton and Fenton-like conditioning is evaluated by the percentage reduction of CST and SRF via the following equation:

\[ E(\%) = \frac{C_0 - C}{C_0} \times 100 \]  

(5) where \( C_0 \) and \( C \) are, respectively, the CST or SRF of alum sludge before and after conditioning.

3. Results

3.1 Fenton’s reagent conditioning

3.1.1 Effectiveness of different Fe\(^{2+} \) salts

Fe\(^{2+}/\text{H}_2\text{O}_2 \) solutions of different iron salts (sulphate, oxalate and chloride) were added to the sludge in order to determine the most effective Fe\(^{2+} \) salt in the Fenton’s reagent conditioning. The pH of the sludge without adjustment (5.7-6.0) and with adjustment (to 3.0) was also tested using the different salts. However, the blank pH adjustment for the alum sludge revealed an enhancement in the dewaterability due to the release of metal such as Fe and Al as mentioned in our previous study (Tony et al., 2008). The concentrations of Fe\(^{2+} \) and H\(_2\)O\(_2 \) were 20 and 125 mg/g DS, respectively.

Conditioning of the sludge under Fenton process without H\(_2\)O\(_2 \) was also conducted. The results are illustrated in Fig. 1. Examination of Fig. 1 (a, b, c), shows that both the chloride and sulphate salts in Fenton reaction have good effectiveness on alum sludge conditioning with chloride salt being slightly better than sulphate salt. A maximum reduction of SRF and CST of 74 % and 47 %, respectively, was obtained when the chloride salt was adopted, while the minimum values of CST and SRF reduction were obtained when the oxalate salt was used. This result indicates that the Fenton’s process is dependent upon the type of the iron compound used. The reason may be attributed to the solubility of different iron compounds in water in different amounts.
By comparing the results in Fig. 1(a) and (b) it is clear that the pH affects the Fenton reagent conditioning, depending on the type of iron salt employed. Under the two pH values (3.0 with pH adjustment and 6.0 for the original sludge) tested in this study, the three iron salts exhibited different responses to the pH. In the case of oxalate salt the reaction occurred to a limited extent without pH adjustment, while in the case of chloride and sulphate salts the CST and SRF reductions were high at pH 6.0, rather than pH 3.0, which has been recommended as the optimal pH for Fenton reactions in other studies (Xiao et al., 2002; Lu et al., 2001; Zhang et al., 2005) although higher pH was also recommended (Kang et al., 2000).

Other series of experiments were conducted without using hydrogen peroxide in order to ensure the significant role of presence of hydrogen peroxide with Fe$^{2+}$ salt in Fenton’s reagent conditioning. It is obvious from Fig. 1(c) that insignificant reaction for sludge regarding CST and SRF reductions was observed in the absence of hydrogen peroxide.

### 3.1.2 Effect of temperature

The results of alum sludge conditioning with Fenton reagent (using FeCl$_2$·4H$_2$O at a dose of 20 mg/g DS and H$_2$O$_2$ at a dose of 125 mg/g DS) at different temperatures in the range of 20 to 60 °C are shown in Fig. 2. The trends in Fig. 2 indicate the minor effect of increasing temperature in Fenton process during alum sludge conditioning since a CST reduction of 50 % and SRF reduction of 77 % at the temperature of 60 °C are achieved compared with the values of 47 % and 74 % for CST and SRF, respectively, at room temperature (20 °C). Thus, the main effect of the alum sludge conditioning is derived from the Fenton’s reagent, rather than the thermal effect.

### 3.2 Fenton-like reagent conditioning

Two types of ferric salts, sulphate and chloride, were tested to explore the Ferric effect as a Fenton-like process on alum sludge conditioning process. Each salt was added along with hydrogen
peroxide with and without pH adjustment (at 3.0) to investigate the response of CST and SRF reduction. Furthermore, ferric salts alone were also tested to explore its role in alum sludge conditioning to see its effect on alum sludge conditioning. As shown in Fig. 3 (a, b, c) the results have revealed that the reduction on the CST and SRF is obviously high when the ferric chloride salt was used rather than that when using the ferric sulphate. However, in all the cases of testing conditions the efficiencies regarding CST and SRF reduction are close to each other for the two salts used. In particular, it seems that the Fenton-like process tested has similar efficiency with that when the ferric salts alone were used.

4. Discussion

The present study aims to evaluate different Fenton processes in an alum sludge conditioning. Coagulation method using FeCl₃ alone was also tested with comparison of the Fenton and Fenton-like processes to evaluate its effectiveness on the sludge dewaterability.

The results demonstrated that for both Fenton and Fenton-like reagents tested, the Cl-containing iron salts are more efficient than other salts. This might be due to the fact that the Cl-containing iron salts may produce more reactive radical species besides the scavenging effect of the hydroxyl radicals (Laat et al., 2004; Orozco et al., 2008).

The evaluated order under a comparable study showed that Fenton’s reagent>FeCl₃>Fenton-like. These results are in accordance with that conducted by Lu et al., (2001) and Krzemieniewski et al., (2003) in conditioning digested sludge. Furthermore, Xu (2001) and Wang (2008) also found the same trend in treating different wastewater effluents using Fenton and Fenton-like reagents. The mechanism in each process is different, leading to different CST/SRF reduction rates for the conditioning process. The mechanism of Fenton reaction in the alum sludge conditioning may be complicated and the exact mechanism may remain unclear in this stage. However, as an attempt to partially try to understand the process, it is reasonable to believe that the ∙OH attack of the cells of
some particles/materials in the alum sludge, leads to the destruction of the original cells and forming new intermediates. The evidence on this lies in the investigation of the measurement of the molecular size distribution before and after Fenton reagent conditioning in our preliminary work (Tony et al., 2008). Thus, both the bound water and the interstitial water were released, and accordingly the filterability and dewaterability of the sludge would increase. Moreover, iron salt in the sludge has its action of coagulating the sludge. Different iron salts (chloride, sulphate and oxalate) in the Fenton processes exhibiting different CST/SRF reduction rates may be attributed to the difference in their solubility of the salts in water, which consequently leads to different amounts of ∙OH produced. In case of applying Fenton-like reagent process production of ∙OH radicals is shown slower than that in Fenton’s reaction because when ferric ions were used the species of hydroxyl radical were formed only in the second stage of the reaction. Obviously, application of hydrogen peroxide in Fenton-like process is insensitive to improve sludge dewaterability compared with FeCl$_3$ alone (see Fig. 3). The reason remains unclear and further investigation may be required.

Fig. 4 provides visible description of sludge appearances after conditioning with Fenton, Fenton-like and FeCl$_3$, respectively. In spite of the rough and qualitative description, it can be seen from Fig. 4 that the flocs (if any) formed in Fenton’s reagent process (Fig. 4b) are relatively larger than those formed with Fenton-like (Fig. 4c) and FeCl$_3$ (Fig. 4d). This is to be compared with the untreated alum sludge (Fig. 4a) where no flocs were observed.

In our previous investigation (Tony et al., 2008), blanks for the pH adjustment alone were conducted on the alum sludge and the maximum CST reduction (%) was obtained in the range of pH 4-5. This phenomenon was explained by the role of the acidic medium in the release of the metal from the sludge which promotes flocculation. Application of Fenton’s reagent (using ferrous chloride salt), the acidic medium is preferred, however, the basic environment exhibited the formation of the hydroxyl radicals (Tony et al., 2008). In case of Fenton-like process, it is interesting to see from Fig. 3 that the adjustment of pH did not exhibit any significant change of
CST/SRF reduction rate. Although the pH value used in the reaction controls the type of hydroxyl radicals produced which are responsible for the progress of the reaction (Lu et al., 2001; Neyens et al., 2003; Zhang et al., 2005), it is fair to say that the Fenton process seems to be more dependent on pH than that of Fenton-like process.

Temperature should have a positive effect in the reaction rate as previously formulated in the literature (Hammer, 1996). However, the temperature tested in this study seems to have minor effect on alum sludge conditioning with Fenton’s reagent as shown in Fig. 2. This may be related to the very rapid reaction of Fenton process, which hinders the temperature effect.

5. Conclusions

Fenton and Fenton-like reagent have been tested along with coagulant method of FeCl₃ addition to seek an alternative alum sludge conditioning options, as an initiative action, to replace widely used organic polymers, which are believed to have a potential negative impact to the environment regarding the release of polymer’s residual in long term point of view. Focused on the comparison, experimental results have shown that the Fe + H₂O₂ conditioning processes (for different Fenton’s and Fenton-like reagents) and FeCl₃ appear to have considerable effectiveness on alum sludge conditioning. The order of the effectiveness falls into the followings: Fenton’s reagent>FeCl₃>Fenton-like reagent. The maximum reduction (%) of SRF and CST of 74 % and 47 %, respectively, can be obtained for Fenton’s reagent. Such reduction of 64 % for SRF and 38 % for CST can be achieved when Fenton-like reagents were applied. The ferrous chloride is recommended salt for Fenton process. The less efficiency of Fenton-like method may be attributed to its reaction feature of producing less reactive hydroxyl radical. Fenton process seems to be more dependent on pH than that of Fenton-like process. In addition, temperature had a minor effect on alum sludge conditioning with Fenton’s reagent.
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Fig. 3 Effect of Fenton-like reagent on alum sludge conditioning: (a) with hydrogen peroxide, without pH adjustment; (b) with hydrogen peroxide, at pH 3.0; (c) without hydrogen peroxide, without pH adjustment.

Fig. 4 Photographs of effectiveness of different conditioners on alum sludge conditioning: (a) raw alum sludge; (b) after Fenton’s process using FeCl$_2$ at pH 6.0; (c) after Fenton-like process using Fe$_2$(SO$_4$)$_3$ at pH 6.0 and (d) after FeCl$_3$ conditioning process at pH 6.0.
Table 1 Characteristics of alum sludge used in this study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>TSS (mg/L)</th>
<th>SS (mg/L)</th>
<th>Al (mg Al/g sludge)</th>
<th>pH</th>
<th>SRF (m/kg)</th>
<th>CST (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>3,021</td>
<td>2,350-2,850</td>
<td>194</td>
<td>5.7-6.0</td>
<td>6.32×10^{11}</td>
<td>59.0-67.5</td>
</tr>
</tbody>
</table>
Figure caption

Fig. 1 Effect of Fenton’s reagent on alum sludge conditioning: (a) with hydrogen peroxide, without pH adjustment; (b) with hydrogen peroxide, at pH 3.0; (c) without hydrogen peroxide, without pH adjustment
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