

Fenton and Fenton-like AOPs for alum sludge conditioning:

Effectiveness comparison with different Fe²⁺ and Fe³⁺ 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 (Fe²⁺/H₂O₂) and Fenton-like (Fe³⁺/H₂O₂) 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 FeCl₃ 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.

31

32 **Keywords:** Alum sludge, conditioning, Fenton's reagent, Fenton-like process, capillary suction
33 time (CST), specific resistance to filtration (SRF)

34

35 **1. Introduction**

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

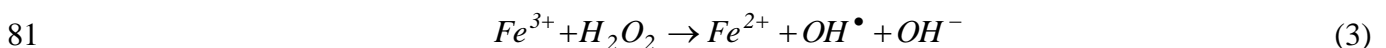
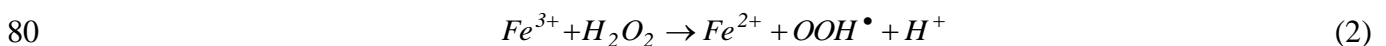
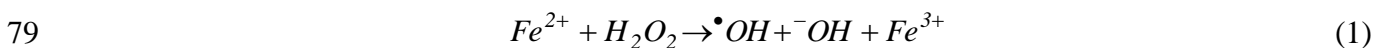
43 Although organic polymers are effective in alum sludge conditioning, an important concern is
44 raised specially in recent years regarding the potential toxicity of their basic units of acryl amide
45 and acrylate, which may release to the aquatic environment after a long-term degradation and cause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

53 Fenton's reagent, one of the components of AOPs has been applied in many areas including
54 wastewater treatment (Xiao et al., 2002; Sanz et al., 2003). However, until now there is no report of
55 such the process being applied in alum sludge conditioning in spite of few studies that applied it in

56 wastewater sludge conditioning (Mustranta and Viikari, 1993; Lu et al., 2001; Neyens, 2003). For
 57 example, Mustranta and Viikari (1993) applied Fenton's reagent for conditioning of different
 58 sludges from pulp and paper mill and the reduction of SRF (specific resistance to filtration) by 70 %
 59 was obtained. Lu et al., (2001) demonstrated that 80 % SRF reduction was achieved when the
 60 Fenton's reagent was applied in the conditioning of activated sludge. However, most literature
 61 focuses on applying the Fenton's reagent in wastewater sludge, rather than in the drinking water
 62 sludge.

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

71 The difference between Fenton and Fenton-like reagents is related to their mechanisms. In the
 72 case of Fenton's reagent the hydroxyl radicals are produced as shown in Eqs. (1) (James and
 73 Englehardt, 2006) and (2) (Neyens et al., 2003) and the main step in this Fenton's reagent
 74 mechanism is the hydrogen peroxide O-O lysis to promote the essential reaction (James and
 75 Englehardt, 2006). However, the mechanism differs slightly in the case of the Fenton-like reagent in
 76 which Fe^{3+} forms intermediates and Fe^{2+} instead of O-O bond breaking takes place (Eq. (3)). Then,
 77 Fe^{2+} slowly reduces the H_2O_2 compared to Fenton's reagent as a second step (Eq. (1)) (Ensing et al.,
 78 2003; James and Englehardt, 2006).



82 From the reaction mechanisms of the Fenton's and Fenton-like reagents, it is obvious that
83 Fenton reaction is friendly to the environment as its products are hydroxyl radicals and oxygen
84 (Cravotto et al., 2008). However, the Fenton's reagent sludge after the treatment process contains
85 the iron salt in the final discharge (Peres et al., 2004; Hsueh et al., 2005; James and Englehardt,
86 2006; Muthuvel et al., 2007), which may draw attention for additional treatment.

87 In our previous study, the investigation of the alum sludge conditioning with Fenton's reagent
88 ($\text{FeCl}_2/\text{H}_2\text{O}_2$) was conducted and the process parameters were optimized (Tony et al., 2008). In
89 addition, different transition metal salts (Cu^{2+} , Zn^{2+} , Co^{2+} and Mn^{2+}) used jointly with H_2O_2 as
90 Fenton-like process have also been tested for alum sludge conditioning (Tony et al., 2009). The aim
91 of the present work is to exploit the effectiveness of different Fe^{2+} and Fe^{3+} salts adopted jointly
92 with H_2O_2 as Fenton and Fenton-like reagents for an alum sludge conditioning. Focuses were placed
93 on the comparison of conditioning efficiencies of the two systems with different Fe^{2+} and Fe^{3+} salts
94 and the effect of parameters, such as pH and temperature on the efficiency of alum sludge
95 dewaterability, which was evaluated using capillary suction time method (CST) and specific
96 resistance of filtration.

97

98 **2. Experimental**

99 **2.1 Materials**

100 The alum sludge samples used during this study were taken from a water treatment plant as
101 described in detail in Tony et al., (2008). Principle properties of the alum sludge are given in Table
102 1. Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) reagents, as the conditioners, are prepared by
103 making solutions from different Fe^{2+} and Fe^{3+} salts. Hence, three Fe^{2+} salts, namely $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$,
104 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and two Fe^{3+} salts, namely $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ were used.
105 Commercial H_2O_2 (30 % by wt) was used. Sulfuric acid is used for adjusting the pH of the sludge
106 samples.

107 **2.2 Methods**

108 Initially iron solution (Fe^{2+} or Fe^{3+}) was added to a 250 ml sludge samples, Fenton or Fenton-like
109 reagent reaction was then initiated after adding hydrogen peroxide. Thereafter, the sludge was
110 subjected to rapid mixing (for 30 second) and slow mixing (for 30 second) to generate reaction.
111 This conditioning procedure, especially the reaction time, has been investigated previously for the
112 time of reaction from 1 min to 4 hrs (Tony et al., 2008). The optimum doses of hydrogen peroxide
113 and Fe^{2+} salt were also optimized previously on the response surface methodology (RSM), which is
114 a collection of mathematical and statistical techniques for optimising purpose (Montgomery, 1991).
115 According the previous study (Tony et al., 2008), the dosage of Fe^{2+} or Fe^{3+} of 20 mg/g DS and the
116 dosage of H_2O_2 of 125 mg/g DS are applied in this study.

117 In order to evaluate the effect of the operating parameters on the conditioning processes, the
118 effect of the initial pH on the Fenton and Fenton-like reagents was tested. The initial pH was
119 adjusted (using H_2SO_4) at the desired values before the reagent was added to the sludge. In addition,
120 the initial temperature of the Fenton's reagent process was also tested. Temperatures in the range of
121 20 to 60 °C were used with hot plate magnetic stirrer equipped with stirrer and heater control.

122

123 **2.3 Analytical methods**

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

$$128 \quad SRF = \frac{2A^2 P b}{\mu w} \quad (4)$$

129

130 where P is the filtration pressure (N/m^2); A the filter area (m^2); μ the viscosity of the filtrate (N
131 s/m^2); w the weight of the cake solids per unit volume of filtrate (kg/m^3); b the slope of filtrate

132 discharge curve (s/m^6), i.e. the gradient of linear plot of filtrate (V) against the time over filtrate
133 (t/V).

134 Three samples were taken to measure CST and SRF and the average value was used.
135 Dewaterability of the sludge under Fenton and Fenton-like conditioning is evaluated by the
136 percentage reduction of CST and SRF via the following equation:

$$137 \quad E(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (5)$$

138 where C_0 and C are, respectively, the CST or SRF of alum sludge before and after conditioning.

139

140 **3. Results**

141 **3.1 Fenton's reagent conditioning**

142 *3.1.1 Effectiveness of different Fe^{2+} salts*

143 Fe^{2+}/H_2O_2 solutions of different iron salts (sulphate, oxalate and chloride) were added to the sludge
144 in order to determine the most effective Fe^{2+} salt in the Fenton's reagent conditioning. The pH of
145 the sludge without adjustment (5.7-6.0) and with adjustment (to 3.0) was also tested using the
146 different salts. However, the blank pH adjustment for the alum sludge revealed an enhancement in
147 the dewaterability due to the release of metal such as Fe and Al as mentioned in our previous study
148 (Tony et al., 2008). The concentrations of Fe^{2+} and H_2O_2 were 20 and 125 mg/g DS, respectively.
149 Conditioning of the sludge under Fenton process without H_2O_2 was also conducted. The results are
150 illustrated in Fig. 1. Examination of Fig. 1 (a, b, c), shows that both the chloride and sulphate salts
151 in Fenton reaction have good effectiveness on alum sludge conditioning with chloride salt being
152 slightly better than sulphate salt. A maximum reduction of SRF and CST of 74 % and 47 %, respectively,
153 was obtained when the chloride salt was adopted, while the minimum values of CST
154 and SRF reduction were obtained when the oxalate salt was used. This result indicates that the
155 Fenton's process is dependent upon the type of the iron compound used. The reason may be
156 attributed to the solubility of different iron compounds in water in different amounts.

157 By comparing the results in Fig. 1(a) and (b) it is clear that the pH affects the Fenton reagent
158 conditioning, depending on the type of iron salt employed. Under the two pH values (3.0 with pH
159 adjustment and 6.0 for the original sludge) tested in this study, the three iron salts exhibited
160 different responses to the pH. In the case of oxalate salt the reaction occurred to a limited extent
161 without pH adjustment, while in the case of chloride and sulphate salts the CST and SRF reductions
162 were high at pH 6.0, rather than pH 3.0, which has been recommended as the optimal pH for Fenton
163 reactions in other studies (Xiao et al., 2002; Lu et al., 2001; Zhang et al., 2005) although higher pH
164 was also recommended (Kang et al., 2000).

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

169

170 *3.1.2 Effect of temperature*

171 The results of alum sludge conditioning with Fenton reagent (using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at a dose of 20 mg/
172 g DS and H_2O_2 at a dose of 125 mg/g DS) at different temperatures in the range of 20 to 60 °C are
173 shown in Fig. 2. The trends in Fig. 2 indicate the minor effect of increasing temperature in Fenton
174 process during alum sludge conditioning since a CST reduction of 50 % and SRF reduction of 77 %
175 at the temperature of 60 °C are achieved compared with the values of 47 % and 74 % for CST and
176 SRF, respectively, at room temperature (20 °C). Thus, the main effect of the alum sludge
177 conditioning is derived from the Fenton's reagent, rather than the thermal effect.

178

179

180 **3.2 Fenton-like reagent conditioning**

181 Two types of ferric salts, sulphate and chloride, were tested to explore the Ferric effect as a Fenton-
182 like process on alum sludge conditioning process. Each salt was added along with hydrogen

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

191

192 **4. Discussion**

193 The present study aims to evaluate different Fenton processes in an alum sludge conditioning.
194 Coagulation method using FeCl_3 alone was also tested with comparison of the Fenton and Fenton-
195 like processes to evaluate its effectiveness on the sludge dewaterability.

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

200 The evaluated order under a comparable study showed that Fenton's reagent > FeCl_3 > Fenton-
201 like. These results are in accordance with that conducted by Lu et al., (2001) and Krzemieniewski et
202 al., (2003) in conditioning digested sludge. Furthermore, Xu (2001) and Wang (2008) also found
203 the same trend in treating different wastewater effluents using Fenton and Fenton-like reagents. The
204 mechanism in each process is different, leading to different CST/SRF reduction rates for the
205 conditioning process. The mechanism of Fenton reaction in the alum sludge conditioning may be
206 complicated and the exact mechanism may remain unclear in this stage. However, as an attempt to
207 partially try to understand the process, it is reasonable to believe that the $\cdot\text{OH}$ attack of the cells of

208 some particles/materials in the alum sludge, leads to the destruction of the original cells and
209 forming new intermediates. The evidence on this lies in the investigation of the measurement of the
210 molecular size distribution before and after Fenton reagent conditioning in our preliminary work
211 (Tony et al., 2008). Thus, both the bound water and the interstitial water were released, and
212 accordingly the filterability and dewaterability of the sludge would increase. Moreover, iron salt in
213 the sludge has its action of coagulating the sludge. Different iron salts (chloride, sulphate and
214 oxalate) in the Fenton processes exhibiting different CST/SRF reduction rates may be attributed to
215 the difference in their solubility of the salts in water, which consequently leads to different amounts
216 of $\cdot\text{OH}$ produced. In case of applying Fenton-like reagent process production of $\cdot\text{OH}$ radicals is
217 shown slower than that in Fenton's reaction because when ferric ions were used the species of
218 hydroxyl radical were formed only in the second stage of the reaction. Obviously, application of
219 hydrogen peroxide in Fenton-like process is insensitive to improve sludge dewaterability compared
220 with FeCl_3 alone (see Fig. 3). The reason remains unclear and further investigation may be required.

221 Fig. 4 provides visible description of sludge appearances after conditioning with Fenton,
222 Fenton-like and FeCl_3 , respectively. In spite of the rough and qualitative description, it can be seen
223 from Fig. 4 that the flocs (if any) formed in Fenton's reagent process (Fig. 4b) are relatively larger
224 than those formed with Fenton-like (Fig. 4c) and FeCl_3 (Fig. 4d). This is to be compared with the
225 untreated alum sludge (Fig. 4a) where no flocs were observed.

226 In our previous investigation (Tony et al., 2008), blanks for the pH adjustment alone were
227 conducted on the alum sludge and the maximum CST reduction (%) was obtained in the range of
228 pH 4-5. This phenomenon was explained by the role of the acidic medium in the release of the
229 metal from the sludge which promotes flocculation. Application of Fenton's reagent (using ferrous
230 chloride salt), the acidic medium is preferred, however, the basic environment exhibited the
231 formation of the hydroxyl radicals (Tony et al., 2008). In case of Fenton-like process, it is
232 interesting to see from Fig. 3 that the adjustment of pH did not exhibit any significant change of

233 CST/SRF reduction rate. Although the pH value used in the reaction controls the type of hydroxyl
234 radicals produced which are responsible for the progress of the reaction (Lu et al., 2001; Neyens et
235 al., 2003; Zhang et al., 2005), it is fair to say that the Fenton process seems to be more dependent
236 on pH than that of Fenton-like process.

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

241

242

243 **5. Conclusions**

244 Fenton and Fenton-like reagent have been tested along with coagulant method of FeCl_3 addition to
245 seek an alternative alum sludge conditioning options, as an initiative action, to replace widely used
246 organic polymers, which are believed to have a potential negative impact to the environment
247 regarding the release of polymer's residual in long term point of view. Focused on the comparison,
248 experimental results have shown that the $\text{Fe} + \text{H}_2\text{O}_2$ conditioning processes (for different Fenton's
249 and Fenton-like reagents) and FeCl_3 appear to have considerable effectiveness on alum sludge
250 conditioning. The order of the effectiveness falls into the followings: Fenton's
251 reagent > FeCl_3 > Fenton-like reagent. The maximum reduction (%) of SRF and CST of 74 % and 47
252 %, respectively, can be obtained for Fenton's reagent. Such reduction of 64 % for SRF and 38 % for
253 CST can be achieved when Fenton-like reagents were applied. The ferrous chloride is
254 recommended salt for Fenton process. The less efficiency of Fenton-like method may be attributed
255 to its reaction feature of producing less reactive hydroxyl radical. Fenton process seems to be more
256 dependent on pH than that of Fenton-like process. In addition, temperature had a minor effect on
257 alum sludge conditioning with Fenton's reagent.

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358 **List of Figures**

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387 **Table caption**

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Table 1 Characteristics of alum sludge used in this study

Parameter	TSS (mg/L)	SS (mg/L)	Al (mg Al/g sludge)	pH	SRF (m/kg)	CST (s)
Value	3,021	2,350-2,850	194	5.7-6.0	6.32×10^{11}	59.0-67.5

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418 **Figure caption**

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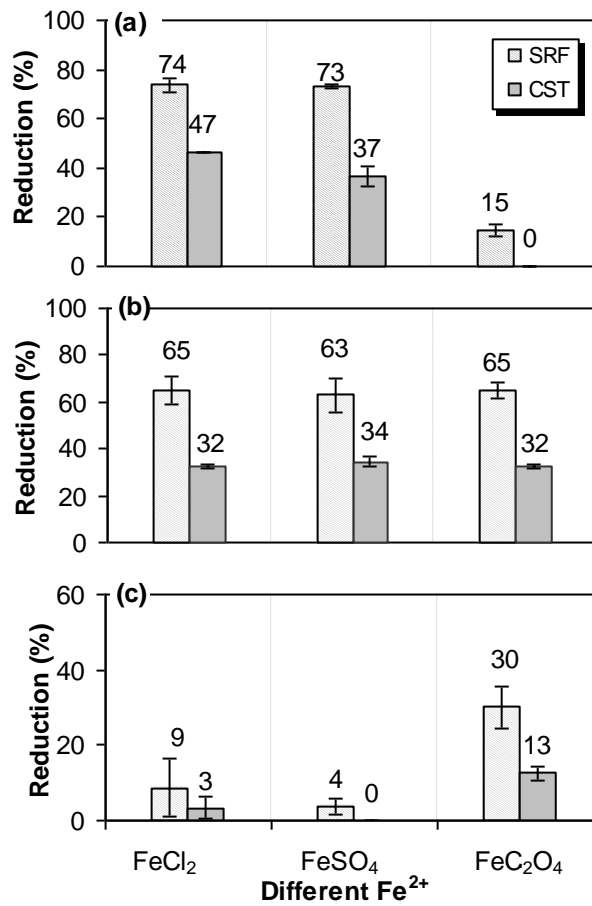
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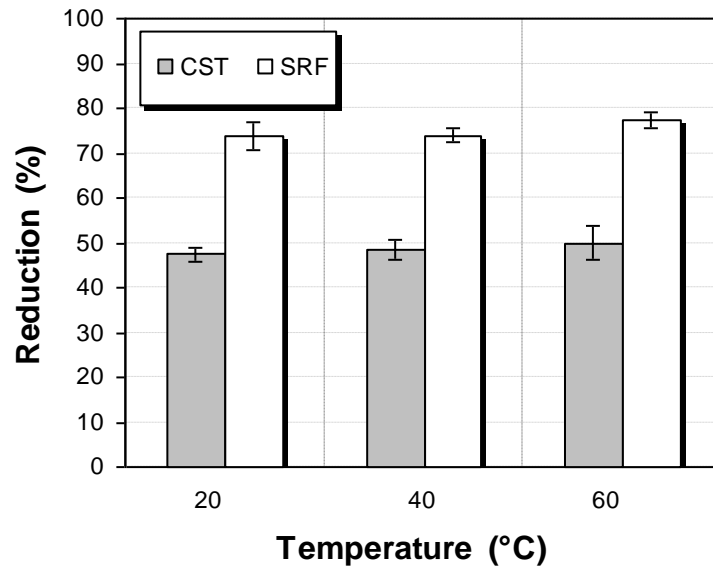
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Fig. 1 Effect of Fenton's reagent on alum sludge conditioning: (a) with hydrogen peroxide, without pH adjustment; (b) with hydrogen peroxide, at pH 3.0; (c) without hydrogen peroxide, without pH adjustment

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449 Fig. 2 Effect of temperature on Fenton's reagent process using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ at dose of 20 mg/g DS

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and H_2O_2 at dose of 125 mg/g DS

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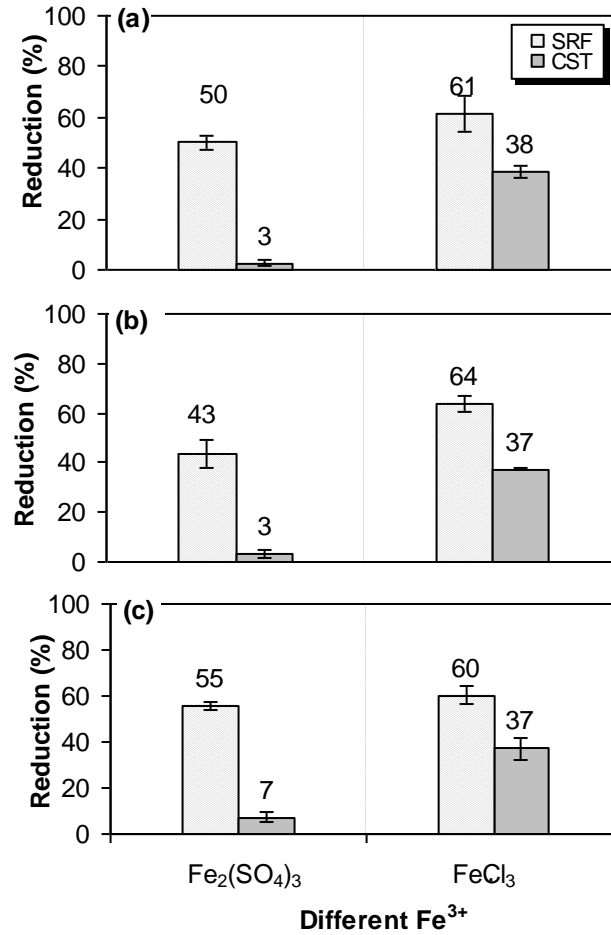


Fig. 3 Effect of Fenton-like reagent on alum sludge conditioning: (a) with hydrogen peroxide, without pH adjustment; (b) with hydrogen peroxide, at pH 3.0; (c) without hydrogen peroxide, without pH adjustment

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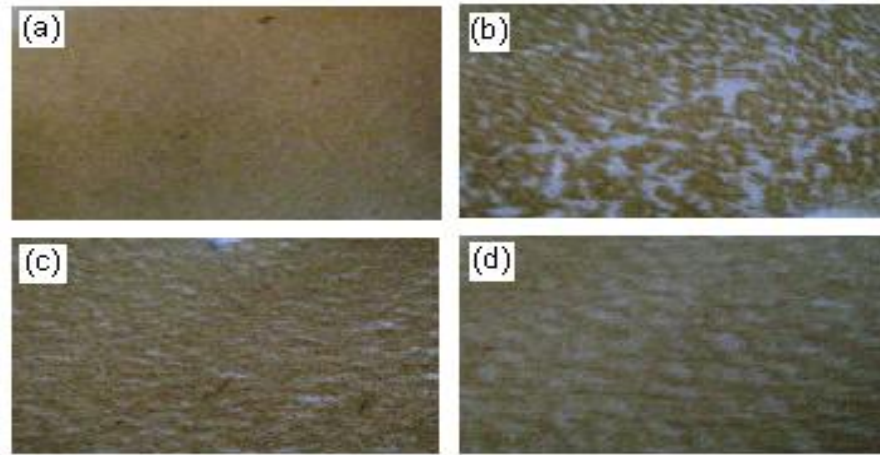
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Fig. 4 Photographs of effectiveness of different conditioners on alum sludge conditioning: (a) raw alum sludge, (b) after Fenton's process using FeCl_2 at pH 6.0, (c) after Fenton-like process using $\text{Fe}_2(\text{SO}_4)_3$ at pH 6.0 and (d) after FeCl_3 conditioning process at pH 6.0