



24 achieved, this agreed with that predicted by an established polynomial model in this  
25 study.

26

27 *Keywords:* Fenton reaction; Aluminium-based water treatment sludge; Conditioning,  
28 Optimization; Response surface methodology; Box-Behnken design

29

### 30 **1. Introduction**

31 Aluminium sulphate is probably the most widely used coagulant in the treatment  
32 of raw waters for the production of drinking water. The resultant aluminium-based  
33 water treatment sludge is a two-phase mixture of solids and water and its water  
34 content is generally in the level between 99% (before thickening) and 95% (after  
35 thickening). Such sludges are often regarded as ‘difficult to dewater’ (Zhao and  
36 Bache, 2002). The conditioning of the sludge lies in the improvement of its  
37 dewaterability in subsequent mechanical dewatering operation.

38 Organic polymers among many other chemicals, such as ferric salts and lime etc.  
39 are most widely employed conditioners in water and wastewater industry. However,  
40 the use, especially the improper use, such as overdosing, of polymers may cause a  
41 problem in the supernatant water generated during sludge dewatering. Such  
42 supernatant water is usually discharged into a nearby stream or a sanitary sewer. In  
43 addition, residual polymers in dewatered sludge cakes may pose a long-term risk to  
44 surround environment when the cakes are subject to landfill as the final disposal. As is  
45 known the polymers are mainly made of acryl amide and acrylate, they can be one of  
46 possible toxic chemicals to aquatic animals and human bodies at certain concentration  
47 even though they are sometimes biodegradable (Bolto and Gregory, 2007).

48 It is noted from the literature that a considerable number of studies have been  
49 carried out to explore Fenton reagent (hydrogen peroxide and ferrous sulphate) as an  
50 alternative chemical conditioner for different sludges (Mustranta and Viikari, 1993;  
51 Lu et al. 2003; Neyens et al. 2003, Neyens et al. 2004; Buyukkamaci, 2004; Kwon et  
52 al. 2004; Dewil et al. 2005). It should be pointed out that, for waste activated sludge,  
53 the effect of Fenton reaction may lie in the degradation of extracellular polymeric  
54 substances, which represent up to 80% of the mass of activated sludge (Frolund et al.  
55 1996). In such case, the addition of organic polymer remains necessary after the  
56 Fenton reaction as pre-treatment and in some cases the optimal polymer dosage even  
57 increases (Neyens et al. 2004). Regarding water treatment sludge, Kwon et al. (2004)  
58 reported that the enhanced sludge dewaterability and filterability after  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$   
59 treatment were comparable to polymer conditioning. Obviously, more work is needed  
60 to explore the effectiveness and impact of water treatment sludge conditioning under  
61 Fenton reaction.

62 Factors to control the Fenton reaction process are the amounts of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ,  
63 or the ratio of  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ . Optimising such amounts plays a key role towards the  
64 success of the Fenton process. A statistical-based technique commonly known as  
65 RSM (response surface methodology) (Montgomery, 1991) as a powerful  
66 experimental design tool has been increasingly applied in many fields including  
67 wastewater treatment and sludge pretreatment to study the optimization of the  
68 treatment process (SAS, 1990; Torrades et al. 2003; Benatti et al. 2006). However, it  
69 has not been well exploited to optimize water treatment sludge conditioning using  
70 Fenton reagent according to the literature survey.

71 In this study, Fenton reagent was employed to condition an aluminium-based  
72 drinking water treatment sludge collected from a local water treatment plant.

73 Emphases are placed on: (1) the effectiveness of Fenton reaction in improving sludge  
74 dewaterability, which was evaluated by CST (capillary suction time), and (2) the  
75 optimization of Fenton reaction conditions ( $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$  and pH) using RSM to achieve  
76 the maximum CST reduction of the sludge.

77

## 78 **2. Materials and Methods**

### 79 *2.1. Experimental Materials*

80 The aluminium-based sludge used in this study was collected directly from the  
81 underflow channel of the sedimentation tank of a local water treatment plant in  
82 southwest Dublin. The plant employs aluminium sulphate as the coagulant for  
83 flocculating reservoir water (with turbidity and colour at range of 0.3-3.0 NTU and  
84 40-120 Hazen, respectively) at a typical dose of 42-60 mg L<sup>-1</sup>. It is expected that the  
85 Fenton's reagent may be explored as a preliminary alternative conditioner, followed  
86 by conventional polymer conditioning with reduced dosage for an environmentally  
87 safe manner in alum sludge conditioning process. Therefore, the sludge from the  
88 original discharge stream was collected although it was obvious low in concentration  
89 in this study. Properties of the alum sludge are listed in Table 1.  $\text{Fe}^{2+}$  in Fenton's  
90 reagent is prepared by making a solution from  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . Hydrogen peroxide was  
91 obtained in liquid (30% by wt) from a commercial supplier. Sulfuric acid and sodium  
92 hydroxide are used for adjusting the pH of the sludge samples during conditioning.

93

### 94 *2.2. Experimental Methods*

95 Initially, sludge samples of 250 mL were carefully transferred to a number of 500  
96 mL breakers. Their pHs were then adjusted to the desired values using  $\text{H}_2\text{SO}_4$  or  
97  $\text{NaOH}$ .  $\text{Fe}^{2+}$  solution was added to the sludge and Fenton reaction was then initiated

98 after adding H<sub>2</sub>O<sub>2</sub>. Following Fenton reagent addition the sludge was subjected to 30 s  
99 of rapid mixing followed by a slow mixing in a jar test apparatus to promote reaction  
100 and flocculation during the reaction time.

101

### 102 2.3. Analytical Methods

103 The pH was measured by using a digital pH-meter (model PHM62).  
104 Dewaterability of the sludge after conditioning was evaluated using a CST apparatus  
105 (Triton-WPRL, Type 130 CST). The CST reduction efficiency (*E*) is calculated by  
106 Eq. (1):

107

$$108 \quad E(\%) = \frac{CST_0 - CST}{CST_0} \times 100 \quad \text{Eq. (1)}$$

109

110 where CST<sub>0</sub> and CST are respectively the CST of the aluminium-based water sludge  
111 before and after conditioning.

112

### 113 2.4. RSM

114 A Box-Behnken experimental design (Montgomery, 1991) was chosen to evaluate  
115 the combined effects of the three independent variables, i.e. Fe<sup>2+</sup> dosing, H<sub>2</sub>O<sub>2</sub> dosing  
116 and initial pH as *X*<sub>1</sub>, *X*<sub>2</sub> and *X*<sub>3</sub> respectively, during the Fenton reagent conditioning.  
117 The range of the experimental variables investigated were chosen according to  
118 preliminary tests. These ranges and levels are presented in Table 2. Fifteen runs were  
119 required for a complete set of the experimental design and are shown in Table 3.

120 The first step in the RSM is to find a suitable approximation for the true functional  
121 relationship between the response (*E*) and the set of the independent variables. An

122 empirical second-order polynomial model for three factors was in the following form  
123 (Montgomery, 1991):

124

$$125 \quad E = \beta_o + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j \quad \text{Eq. (2)}$$

126

127 where  $E$  is the predicted response (CST reduction efficiency, %);  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$   
128 ( $i = 1, 2, 3$  and  $j = 1, 2, 3$ ) are the model regression coefficients;  $X_i$  and  $X_j$  ( $i = 1, 2, 3$   
129 and  $j = 1, 2, 3$ ) are the coded independent variables (see Table 2). The coefficient  
130 parameters are estimated by multiple linear regression analysis using the software of  
131 Statistical Analysis System (SAS, 1990).

132

### 133 **3. Results and discussion**

#### 134 *3.1. Conditioning of aluminium-based sludge with Fenton reagent*

135 Figure 1 jointly illustrates the effectiveness of Fenton's reagent, together with the  
136 separated addition of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  to provide comparative data, for conditioning of  
137 the alum sludge. Different sets of experiments at various concentrations in the range  
138 of 3.5 to 350  $\text{mg g}^{-1} \text{DS}^{-1}$  for both  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  were conducted. The data revealed  
139 that  $\text{H}_2\text{O}_2$  addition could even result in an increased CST, indicating that  $\text{H}_2\text{O}_2$  alone  
140 has no function to improve sludge dewaterability. This agreed with the finding  
141 reported by Kwon et al. (2004) who claimed that  $\text{H}_2\text{O}_2$  alone was not effective due to  
142 low reaction rate. The optimal dose for  $\text{Fe}^{2+}$  alone addition to achieve highest CST  
143 reduction was 350  $\text{mg g}^{-1} \text{DS}^{-1}$ , at which only 16% of CST reduction efficiency was  
144 obtained. However, combined use of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ , i.e. Fenton reagent, at the dosage  
145 of 14 and 140  $\text{mg g}^{-1} \text{DS}^{-1}$  for  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ , respectively, could achieve a CST

146 reduction of 45%. This reflects the effectiveness of Fenton's reagent as an alternative  
147 conditioner in alum sludge conditioning.

148 The effects of Fenton reaction time on alum sludge conditioning were investigated  
149 at  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  dosage of 14/17.5  $\text{mg g}^{-1} \text{DS}^{-1}$  and 14/140  $\text{mg g}^{-1} \text{DS}^{-1}$ , respectively,  
150 while the pH of the sludge was kept its original without any adjustment. The results,  
151 as illustrated in Fig. 2, show clearly that the highest CST reduction occurred in the  
152 initial period of reaction time for both cases, while prolonged reaction time could lead  
153 to insignificant improvement of sludge dewaterability. The reason remains unclear in  
154 the current study without further investigation. The maximum CST reduction  
155 efficiency (%) was obtained at 1 min reaction for both the trends although lower  
156 dosage corresponded to a relative low CST reduction efficiency. In spite of the fact  
157 that such rapid reaction makes it questionable to implement this technology in  
158 practice, it reflects the feature of Fenton reaction.

159 In order to provide the insight into such the characteristics, measurements of  
160 chemical oxygen demand (COD) via Hach DR-2400 spectrometer (CAMLAB Ltd,  
161 UK) and molecular size distribution (MSD) of dissolved organic substances using a  
162 high-pressure size exclusion chromatography (HPSEC) for the sludge samples before  
163 and after Fenton conditioning at different reaction times were carried out and the  
164 results are shown in Table 4 and Fig. 3. Results of COD measurements in Table 4  
165 reveal that the Fenton reaction immediately oxidizes the organics in the sludge  
166 regardless of the reaction time. Figure 3 provides the evidence that the MSD of  
167 dissolved organic substances at reaction time of 1 min and 30 min exhibits very  
168 similar trends, indicating the unnecessary in prolonging Fenton reaction time in  
169 conditioning of the alum sludge. Compared with the MSD of raw sludge, it is clear  
170 that the Fenton reaction degraded/broke the organics from large molecular sizes into

171 smaller ones via highly reactive hydroxyl radicals (Neyens et al. 2004). Therefore, it  
172 is reasonable to address that the improvement of sludge dewaterability by the Fenton  
173 reaction lies in the release of both interstitial water trapped between organics and  
174 adsorbed or chemically bound water by the degradation of organics. It is noted that  
175 Kwon et al. (2004) conducted a quite similar investigation with reaction time varied  
176 from 2-60 min. However, there was no detailed description of the effects of reaction  
177 time on conditioning efficiency.

178 Effects of initial pH in the range of 2 to 8 of the Fenton reaction at dosage of  
179  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 14/140 \text{ mg g}^{-1} \text{ DS}^{-1}$  and reaction time of 1 min were examined. In  
180 particular, the blanks for the pH adjustment alone were conducted while the  
181 measurement of CST at the time of 10 min after pH adjustment was applied. The  
182 results are jointly presented in Table 5. The purpose of adjusting pH alone lies in the  
183 reflection of the effectiveness of pure Fenton reaction in the sludge conditioning  
184 studied. It can be seen from Table 5 that the pH adjustment alone has significant  
185 effect on alum sludge dewaterability. The acidic environment can clearly improve  
186 sludge dewaterability with pH of 4-5 being the best. This may be attributed to the  
187 release of metal ions, such as Al and Fe from the sludge to promote the flocculation,  
188 as demonstrated by Kwon et al. (2004). The basic environment, however, exhibited  
189 negative effect on the sludge dewaterability, as increased CST (negative CST  
190 reduction) was obtained. The reason remains unclear. However, it is known that high  
191 pH can decrease the amount of hydroxyl radicals, which is believed to be the driving  
192 force towards the improvement of sludge dewaterability. By considering such the  
193 influence of pH, the CST reduction efficiency at the pH of 6 in this study is the best  
194 regarding the highest net CST reduction efficiency being obtained, as shown in Table  
195 5. It is noted, however, that Lu et al. (2001) claimed the similar level of dewaterability

196 of an activated sludge when it was subjected to conditioning with Fenton reagent at  
197 pH in the range of 2 to 7. Obviously, more work is desirable to explore such effect.

198 Figure 4 illustrates various ratios of  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  in a wide range of  $\text{Fe}^{2+}$  (3.5-2100  
199  $\text{mg g}^{-1} \text{DS}^{-1}$ ) and  $\text{H}_2\text{O}_2$  (3.5-3510  $\text{mg g}^{-1} \text{DS}^{-1}$ ) in alum sludge conditioning. It is seen  
200 that the CST reduction efficiency increases with increased  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  dosage until a  
201 certain ratio at which the reversible results were obtained. Although the enhancement  
202 of sludge dewaterability occurred at a broad range of  $\text{Fe}^{2+}$  addition,  $\text{H}_2\text{O}_2$  can only  
203 beneficially affect the sludge dewaterability in a relative small range of less than 280  
204  $\text{mg g}^{-1} \text{DS}^{-1}$  except for the case of  $\text{Fe}^{2+}$  addition of 2100  $\text{mg g}^{-1} \text{DS}^{-1}$ , at which the  
205  $\text{H}_2\text{O}_2$  addition of up to 1750  $\text{mg g}^{-1} \text{DS}^{-1}$  can still bring about the improved sludge  
206 dewaterability. However, considering the lower amount of reagent addition, the best  
207 dosage in current study seems at  $\text{Fe}^{2+}$  less than 28  $\text{mg g}^{-1} \text{DS}^{-1}$  and  $\text{H}_2\text{O}_2$  less than 280  
208  $\text{mg g}^{-1} \text{DS}^{-1}$ , as shown in Fig. 4. Nevertheless, it appears that the  $\text{H}_2\text{O}_2$  concentration  
209 plays an important role in Fenton reaction since excess addition of  $\text{H}_2\text{O}_2$  may lead to  
210 the negative impact on sludge dewaterability. The reason may be attributed to the  
211 amount of hydroxyl radicals. When  $\text{H}_2\text{O}_2$  concentration increases until a critical  
212 concentration, a so-called scavenging effect occurred. Several references are available  
213 with concern of the hydroxyl radical production on the effect of Fenton reaction (Lin  
214 and Gurol, 1998; Torrades et al. 2003; Zhang et al. 2005).

215

### 216 3.2. Optimization of Fenton's reagent operating variables using RSM

217 The results of the three-level experiments based on a Box-Behnken design are  
218 presented in Table 3. The following second-order fitting polynomial equation was  
219 then obtained after the data fitting.

220

$$E(\%) = 42.0 + 9.375X_1 - 1.625X_2 + 3.5X_3 - 11.5X_1^2 - 0.5X_1X_2 + 1.75X_1X_3 + 5.5X_2^2 - 1.25X_2X_3 - 3.25X_3^2 \quad \text{Eq. (3)}$$

The predicted CST reduction efficiencies (%) via Eq. (3) are jointly shown in Table 3. A good agreement of the data between the experimental and the predicted can be obtained with regression coefficient  $R^2$  value of 0.925 (plotting not shown). Thus, it is reasonable to believe that the polynomial model (Eq. 3) is a reliable model to describe the Fenton reaction behaviour in the alum sludge conditioning.

The three-dimensional surface and the contour plot of the response ( $E$ , i.e. CST reduction efficiency, %), generated by MATLAB 7.0, is an informative and visible illustration to facilitate the relations between two interacting factors with the response, while third factor was kept constant at its zero level. Figure 5 illustrates the response under the coded variables of  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$  and pH. It can be seen from Fig. 5(a) that a significant enhancement of CST reduction efficiency is observed when the  $\text{H}_2\text{O}_2$  concentration was increased. However, at higher concentrations of  $\text{H}_2\text{O}_2$  the reduction rate was negatively affected. Thus, an excess of  $\text{H}_2\text{O}_2$  does not mean a continuous increase in CST reduction of the conditioned sludge. Similarly, the CST reduction in percentage increased with increasing the  $\text{Fe}^{2+}$  concentration to a certain limit. Obviously, there is an optimal dosage for both  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations. In the similar way, the 3D surface and the corresponding contour plotted in Fig. 5(b) show that the combination of  $\text{Fe}^{2+}$  concentration and pH has a significant effects on CST reduction. Figure 5(c) demonstrates that the increase in pH with the increase in  $\text{H}_2\text{O}_2$  concentration enhances the efficiency of CST reduction in a certain region, beyond that region the less reduction of CST is observed. Hence, the optimisation of the  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  concentrations as well as pH was conducted to achieve the highest CST reduction from the statistical point of view.

245 Mathematical software (V 5.2., Wolfram research Inc.) and response surface  
246 analysis were used to determine optimum conditions of the operating variables in the  
247 Fenton reaction. The maximum CST reduction efficiency ( $E$ ) is 53%, whereas  
248 maximum values of the process variables in coded values given as follows:  $X_1 = 0.66$ ,  
249  $X_2 = -1$  and  $X_3 = 0.99$ . Accordingly,  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$  and pH are  $21 \text{ mg g}^{-1} \text{ DS}^{-1}$ ,  $105 \text{ mg g}^{-1}$   
250  $\text{DS}^{-1}$  and 6, respectively.

251 Three additional experiments using the above optimum operation conditions were  
252 conducted to validate the model. The replicate experiments yielded a CST reduction  
253 efficiency of  $48 \pm 3\%$ . This clearly demonstrated the effectiveness of the model to  
254 optimise the Fenton reaction in alum sludge conditioning.

255

## 256 **Conclusions**

257 Application of Fenton reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) in conditioning of an aluminium-based  
258 water treatment sludge has demonstrated the effectiveness of such kind of its use.  
259 Effects of Fenton reagent in a wide range of concentrations on alum sludge  
260 dewaterability were tested. Considerable improvement of such sludge dewaterability  
261 was obtained. Experimental investigation confirmed that the Fenton reaction rapidly  
262 degrades organics in the sludge from large molecular sizes into smaller sizes and  
263 oxidises them in a short time. The optimum condition, determined by RSM, of Fenton  
264 process is at  $\text{Fe}^{2+}$   $21 \text{ mg g}^{-1} \text{ DS}^{-1}$  and  $\text{H}_2\text{O}_2$   $105 \text{ mg g}^{-1} \text{ DS}^{-1}$  while the optimum pH is  
265 6, at which the CST reduction efficiency of 53 % can be achieved. By using RSM, a  
266 multi-variable polynomial equation has been developed to describe the behaviour of  
267 Fenton reaction regarding the response of CST reduction efficiency. The replicate  
268 experiments at optimal conditions yielded an average CST reduction efficiency of

269 48±3%, which shows high agreement of predicted level using the established  
270 polynomial equation.

271

## 272 **Acknowledgements**

273 The first author would like to thank the ministry of higher education, missions  
274 department, Egypt for the financial support granted through Channel Scheme. Mr P.  
275 Kearney and Mr W.C. Li are thanked for their invaluable technical assistance during  
276 the study. The authors wish to sincerely acknowledge the stimulating questions and  
277 remarks of the anonymous reviewers and the editor to improve the quality of the  
278 paper.

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## 281 **References**

282 Benatti, C.T., Tavares, C.R.G., Guedes, T.A., 2006. Optimization of Fenton's  
283 oxidation of chemical laboratory wastewaters using the response surface  
284 methodology. *J. Environ. Manage.* 80, 66–74.

285 Bolto, B., Gregory, J., 2007. Organic polyelectrolytes in water treatment. *Water Res.*  
286 41, 2301-2324.

287 Buyukkamaci, N., 2004. Biological sludge conditioning by Fenton's reagent. *Process*  
288 *Biochem.* 39, 1503–1506.

289 Dewil, R., Baeyens, J., Neyens, E., 2005. Fenton peroxidation improves the drying  
290 performance of waste activated sludge. *J. Hazard. Mater.* 117, 161–170.

291 Forlund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of  
292 extracellular polymers from activated sludge using a cation exchange resin. *Water*  
293 *Res.* 30, 1749-1758.

294 Kwon, J.H., Park, K.Y., Park, J.H., Lee, S.H., Ahn, K.H., 2004. Acidic and hydrogen  
295 peroxide treatment of polyaluminum chloride (PACL) sludge from water treatment.  
296 Water Sci. Technol. 50(9), 99–105.

297 Lin, S., Gurol, M., 1998. Catalytic decomposition of hydrogen peroxide on iron  
298 oxide: kinetics, mechanisms and implications. Environ. Sci. Technol. 32, 1417- 1423.

299 Lu, M.C., Lin, C.J., Liao, C. H., Huang, R.Y., Ting, W.P., 2003. Dewatering of  
300 activated sludge by Fenton's reagent. Adv. Environ. Res. 7, 667– 670.

301 Lu, M.C., Lin, C.J., Liao, C.H., Ting, W.P., Huang, R.Y., 2001. Influence of pH on  
302 the dewatering of activated sludge by Fenton's reagent. Water Sci. Technol. 44(10),  
303 327–332.

304 Montgomery, D.C., 1991. Design and Analysis of Experiments. John Wiley, New  
305 York.

306 Mustranta, A., Viikari, L., 1993. Dewatering of activated sludge by an oxidative  
307 treatment. Water Sci. Technol. 28(1), 213–221.

308 Neyens, E., Baeyens, J., Dewil, R., Deheyder, B., 2004. Advanced sludge treatment  
309 affects extracellular polymeric substances to improve activated sludge dewatering. J.  
310 Hazard. Mater. 106(2-3), 83–92.

311 Neyens, E., Baeyens, J., Weemaes, M., Deheyder, B., 2003. Pilot-scale peroxidation  
312 ( $H_2O_2$ ) of sewage sludge. J. Hazard. Mater. 98(1-3), 91–106.

313 SAS, 1990. SAS /STAT User's Guide. SAS Institute, Inc., Cary, NC.

314 Torrades, F., Perez, M., Mansilla, H.D., Peral, J., 2003. Experimental design of  
315 Fenton and photo-Fenton reactions for the treatment of cellulose bleaching effluents.  
316 Chemosphere 53, 1211-1220.

317 Zhang, H., Choi, H.J., Huang, C., 2005. Optimization of Fenton process for the  
318 treatment of landfill leachate. J. Hazard. Mater. 125(1-3), 166–174.

319 Zhao, Y.Q., Bache, D.H., 2002. Integrated effects of applied pressure, time, and  
320 polymer doses on alum sludge dewatering behaviour. Waste Manage. 22, 813-819.

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322

### 323 **Figure Captions**

324 Fig. 1 Effects of  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  on CST reduction efficiency (%) of alum  
325 sludge (Operating parameters:  $\text{H}_2\text{O}_2 = 3.5 \text{ mg g}^{-1} \text{ DS}^{-1}$ ;  $\text{Fe}^{2+} = 350 \text{ mg g}^{-1} \text{ DS}^{-1}$ ;  
326 Fenton's reagent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) = 14/140  $\text{mg g}^{-1} \text{ DS}^{-1}$ ; pH = 6.0, reaction time = 1  
327 min)

328 Fig. 2 Effects of the Fenton reaction time on conditioning of the alum sludge with  
329 two concentrations of Fenton reagent

330 Fig. 3 Response of raw and Fenton's reagent conditioned alum sludge under HPSEC  
331 (HPSEC consists of a Waters 1515 isocratic pump; a Waters 2487 UV dual  $\lambda$   
332 detector operated at 254 nm; A PL Aquagel-OH 40 (300 $\times$ 7.5 mm) column.  
333 Molecular weight standards were composed of sodium polystyrenesulfonates  
334 (35, 18, 8, 5.4, and 1.8K) and acetone).

335 Fig. 4 CST reduction efficiency at various Fenton's reagent dosages (Operating  
336 parameters: pH = 6.0; reaction time = 1 min)

337 Fig. 5 Optimising Fenton reaction in alum sludge conditioning: (a) surface and  
338 contour of coded  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  vs. predicted CST reduction efficiency; (b)  
339 surface and contour of coded  $\text{Fe}^{2+}$  and pH vs. predicted CST reduction  
340 efficiency; (c) surface and contour of coded  $\text{H}_2\text{O}_2$  and pH vs. predicted CST  
341 reduction efficiency.

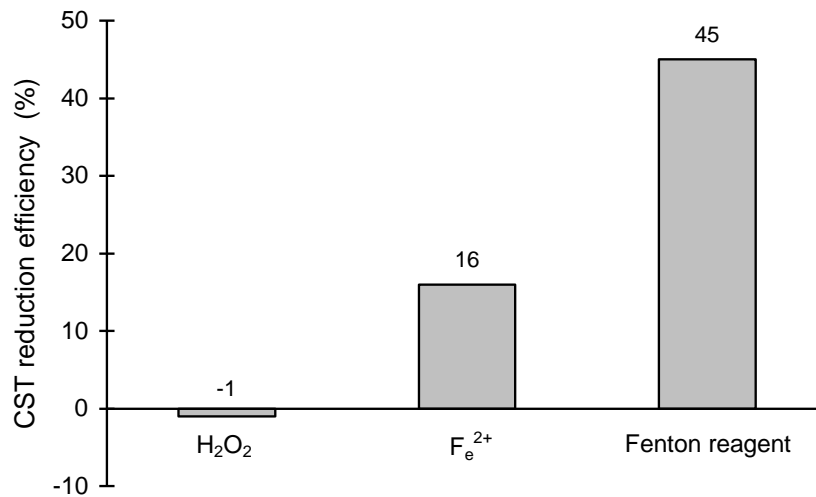
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344 **Figures**

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348 Fig. 1 Effects of H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup> and Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> on CST reduction efficiency (%) of alum

349 sludge (Operating parameters: H<sub>2</sub>O<sub>2</sub> = 3.5 mg g<sup>-1</sup> DS<sup>-1</sup>; Fe<sup>2+</sup> = 350 mg g<sup>-1</sup> DS<sup>-1</sup>;

350 Fenton's reagent (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) = 14/140 mg g<sup>-1</sup> DS<sup>-1</sup>; pH = 6.0, reaction time = 1 min)

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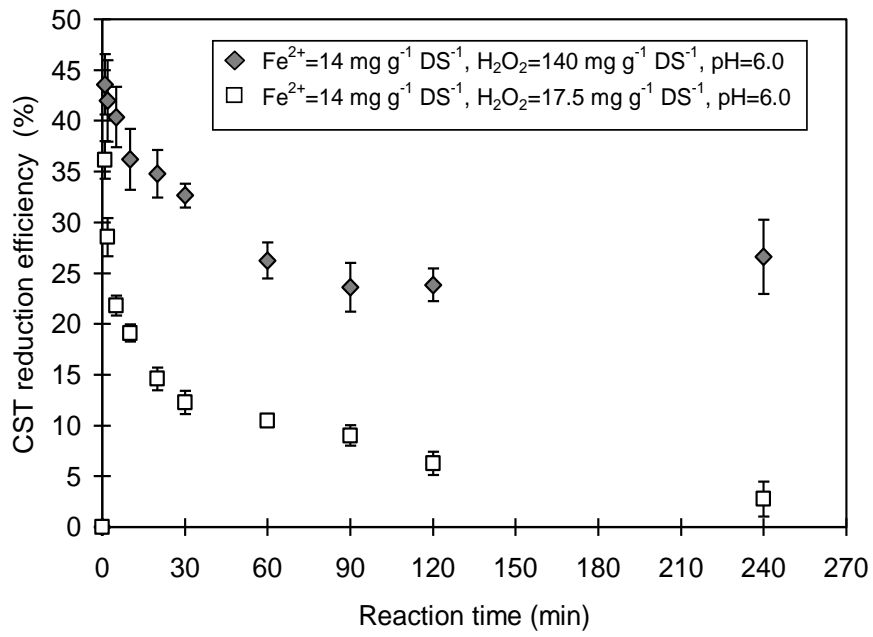
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364 Fig. 2 Effects of the Fenton reaction time on conditioning of the alum sludge with  
365 two concentrations of Fenton reagent

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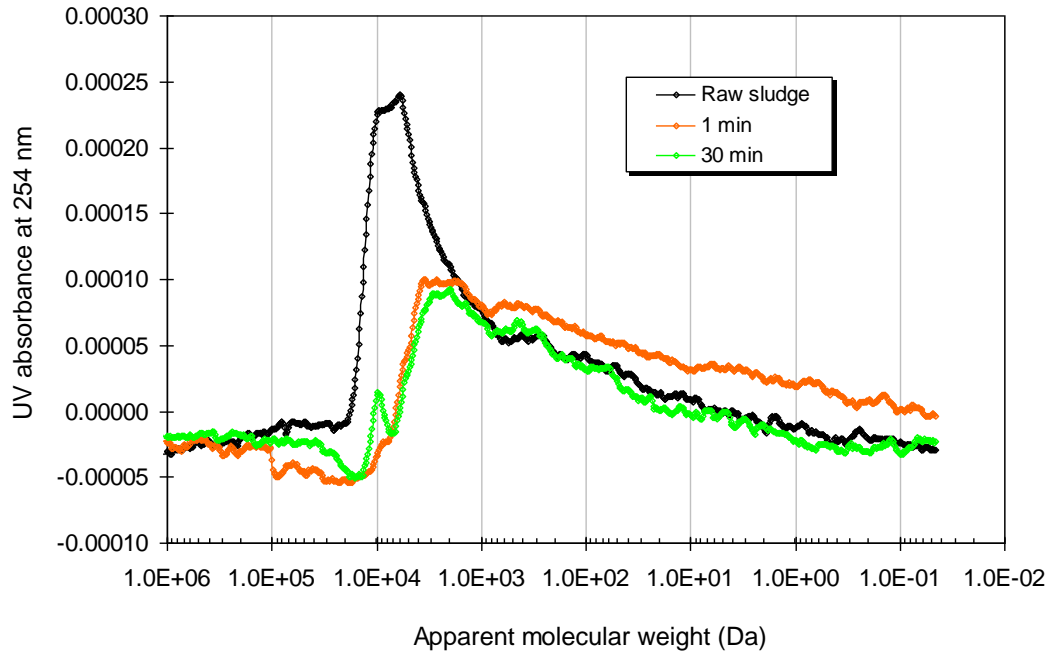
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380 Fig. 3 Response of raw and Fenton's reagent conditioned alum sludge under HPSEC

381 (HPSEC consists of a Waters 1515 isocratic pump; a Waters 2487 UV dual  $\lambda$

382 detector operated at 254 nm; A PL Aquagel-OH 40 (300×7.5 mm) column.

383 Molecular weight standards were composed of sodium polystyrenesulfonates (35,

384 18, 8, 5.4, and 1.8K) and acetone).

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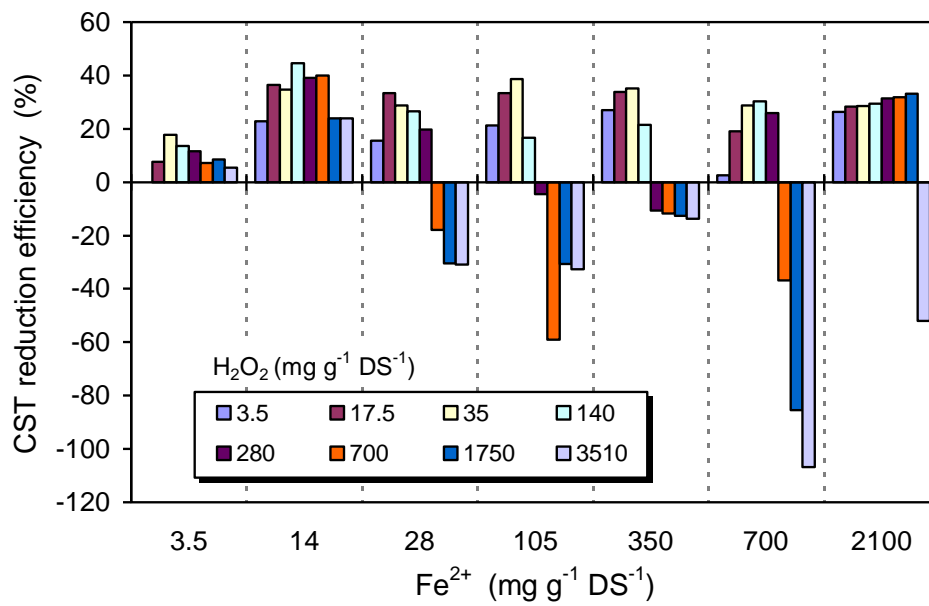
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396 Fig. 4 CST reduction efficiency at various Fenton's reagent dosages (Operating  
 397 parameters: pH = 6.0; reaction time = 1 min)

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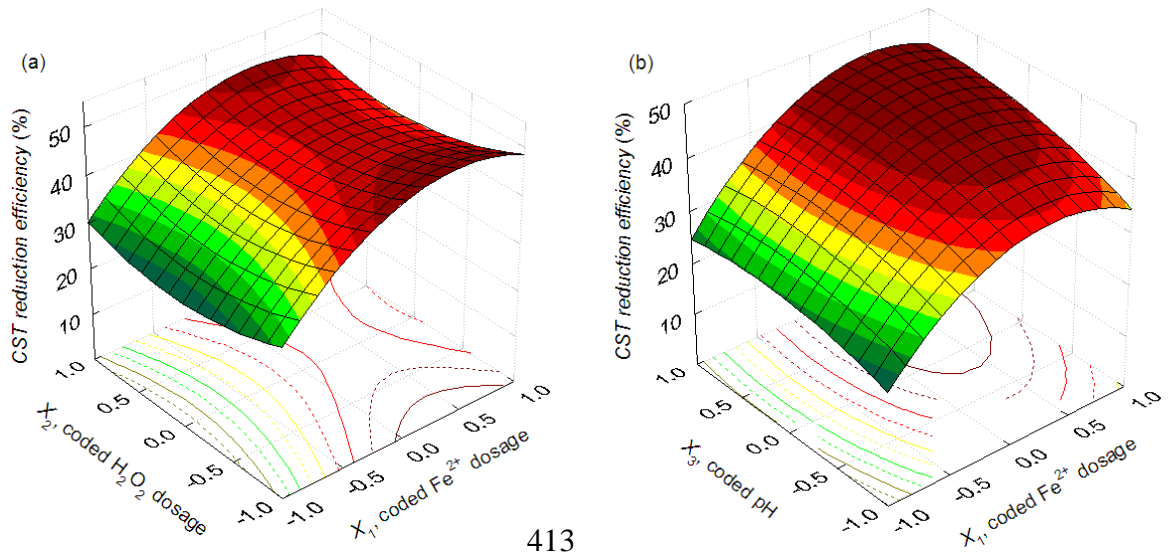
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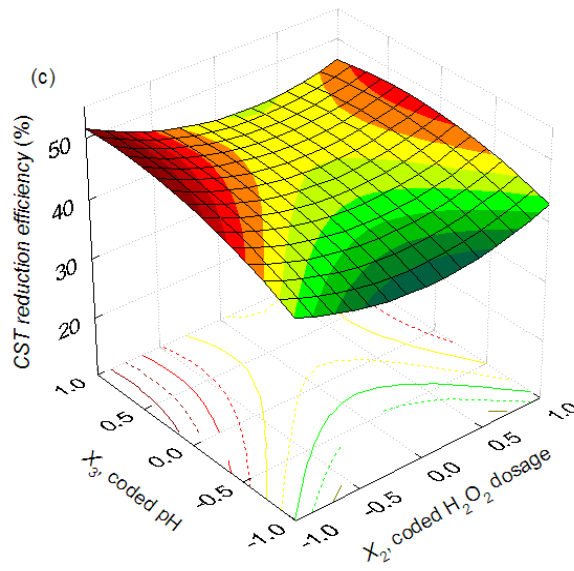
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416 Fig. 5 Optimising Fenton reaction in alum sludge conditioning: (a) surface and  
 417 contour of coded  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  vs. predicted CST reduction efficiency; (b) surface  
 418 and contour of coded  $\text{Fe}^{2+}$  and pH vs. predicted CST reduction efficiency; (c) surface  
 419 and contour of coded  $\text{H}_2\text{O}_2$  and pH vs. predicted CST reduction efficiency.

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424 **Table Captions**

425 Table 1 Properties of aluminium-based sludge used in this study

426 Table 2 Range and levels of natural and corresponded coded variables for RSM of  
427 Fenton's reagent to condition alum-based water treatment sludge

428 Table 3 RSM for the three experimental variables in coded units and its experimental  
429 and predicted response of Fenton's reagent to condition alum-based water  
430 treatment sludge

431 Table 4 COD measurements of sludge filtrate before and after Fenton conditioning at  
432 different reaction time (Mean  $\pm$ SD)\*

433 Table 5 Effects of pH (2 ~ 8) on conditioning of alum sludge with Fenton's reagent  
434 (reaction time of 1 min) at dosage of  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 14/140$  ( $\text{mg g}^{-1} \text{DS}^{-1}$ )

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Table 1 Properties of aluminium-based sludge used in this study

Parameters	Unit	Value
Suspend solids	mg L <sup>-1</sup>	2,850
pH		5.7-6.0
SRF	m kg <sup>-1</sup>	6.32×10 <sup>11</sup>
CST	s	67.5

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Table 2 Range and levels of natural and corresponded coded variables for RSM of Fenton's reagent to condition alum-based water treatment sludge

Variable	Symbols		Range and levels		
	Natural	Coded*	-1	0	1
Fe <sup>2+</sup> (mg g <sup>-1</sup> DS <sup>-1</sup> )	$\xi_1$	$X_1$	3.5	14	24.5
H <sub>2</sub> O <sub>2</sub> (mg g <sup>-1</sup> DS <sup>-1</sup> )	$\xi_2$	$X_2$	105	140	175
pH	$\xi_3$	$X_3$	2.0	4.0	6.0

472 \*  $X_1 = (\xi_1 - 14)/10.5$ ,  $X_2 = (\xi_2 - 140)/35$ ,  $X_3 = (\xi_3 - 4)/2$

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Table 3 RSM for the three experimental variables in coded units and its experimental and predicted response of Fenton's reagent to condition alum-based water treatment sludge

Run no.	Coded factors			Response ( <i>E</i> , %)	
	$X_1$	$X_2$	$X_3$	Experimental	Predicted
1	-1	-1	0	29	28
2	-1	1	0	26	26
3	1	-1	0	47	48
4	1	1	0	42	43
5	0	-1	-1	37	41
6	0	-1	1	54	51
7	0	1	-1	37	40
8	0	1	1	49	45
9	-1	0	-1	19	16
10	1	0	-1	36	31
11	-1	0	1	15	20
12	1	0	1	39	42
13	0	0	0	41	42
14	0	0	0	42	42
15	0	0	0	43	42

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Table 4 COD measurements of sludge filtrate before and after Fenton conditioning at different reaction time (Mean  $\pm$ SD)\*

Reaction time (min)	After Fenton conditioning	
	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> =3.5/17.5 (mg g <sup>-1</sup> DS <sup>-1</sup> ), pH = 6.0	Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> =3.5/140 (mg g <sup>-1</sup> DS <sup>-1</sup> ), pH = 6.0
1	39 $\pm$ 1	30 $\pm$ 2
30	40 $\pm$ 1	35 $\pm$ 1
90	39 $\pm$ 5	40 $\pm$ 2

509 \* All sludge samples were filtered using Whatman No. 1 qualitative filter paper. Raw  
510 sludge COD = 221  $\pm$ 5  
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530 Table 5 Effects of pH (2 ~ 8) on conditioning of alum sludge with Fenton's reagent  
 531 (reaction time of 1 min) at dosage of  $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 14/140$  ( $\text{mg g}^{-1} \text{DS}^{-1}$ )

CST reduction efficiency (mean $\pm$ SD, %)	pH of alum sludge						
	2	3	4	5	6	7	8
Fenton reaction	37 $\pm$ 0.2	43 $\pm$ 0.2	44 $\pm$ 0.3	43 $\pm$ 0.4	43 $\pm$ 0.2	-10 $\pm$ 0.5	-121 $\pm$ 6.3
Blank (pH adjustment alone)	0.7 $\pm$ 0.9	4 $\pm$ 3.0	14 $\pm$ 3.2	13 $\pm$ 2.4	0	-7 $\pm$ 5.3	-52 $\pm$ 6.1

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