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Conditioning of aluminium-based water treatment sludge with Fenton's reagent: Effectiveness and optimising study to improve dewaterability

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Abstract

Alternative conditioning of aluminium-based drinking water treatment sludge using Fenton reagent (Fe^{2+}/H_2O_2) was examined in this study. Focuses were placed on effectiveness and factors to affect such novel application of Fenton process. Experiments have demonstrated that considerable improvement of alum sludge dewaterability evaluated by capillary suction time (CST) can be obtained at the relative low concentrations of Fenton reagent. A Box-Behnken experimental design based on the response surface methodology was applied to evaluate the optimum of the influencing variables, i.e. iron concentration, hydrogen peroxide concentration and pH. The optimal values for Fe^{2+}, H_2O_2, and pH are 21 mg g^{-1} DS^{-1}(dry solids), 105 mg g^{-1} DS^{-1} and 6, respectively, at which the CST reduction efficiency of 48 ± 3 % can be achieved, this agreed with that predicted by an established polynomial model in this study.

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

1. Introduction

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

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

It is noted from the literature that a considerable number of studies have been carried out to explore Fenton reagent (hydrogen peroxide and ferrous sulphate) as an alternative chemical conditioner for different sludges (Mustranta and Viikari, 1993; Lu et al. 2003; Neyens et al. 2003, Neyens et al. 2004; Buyukkamaci, 2004; Kwon et al. 2004; Dewil et al. 2005). It should be pointed out that, for waste activated sludge, the effect of Fenton reaction may lie in the degradation of extracellular polymeric substances, which represent up to 80% of the mass of activated sludge (Frolund et al. 1996). In such case, the addition of organic polymer remains necessary after the Fenton reaction as pre-treatment and in some cases the optimal polymer dosage even increases (Neyens et al. 2004). Regarding water treatment sludge, Kwon et al. (2004) reported that the enhanced sludge dewaterability and filterability after H_2SO_4/H_2O_2 treatment were comparable to polymer conditioning. Obviously, more work is needed to explore the effectiveness and impact of water treatment sludge conditioning under Fenton reaction.

Factors to control the Fenton reaction process are the amounts of Fe^{2+} and H_2O_2, or the ratio of Fe^{2+}/H_2O_2. Optimising such amounts plays a key role towards the success of the Fenton process. A statistical-based technique commonly known as RSM (response surface methodology) (Montgomery, 1991) as a powerful experimental design tool has been increasingly applied in many fields including wastewater treatment and sludge pretreatment to study the optimization of the treatment process (SAS, 1990; Torrades et al. 2003; Benatti et al. 2006). However, it has not been well exploited to optimize water treatment sludge conditioning using Fenton reagent according to the literature survey.

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

Emphases are placed on: (1) the effectiveness of Fenton reaction in improving sludge dewaterability, which was evaluated by CST (capillary suction time), and (2) the optimization of Fenton reaction conditions (Fe^{2+}, H_2O_2 and pH) using RSM to achieve the maximum CST reduction of the sludge.

2. Materials and Methods

2.1. Experimental Materials

The aluminium-based sludge used in this study was collected directly from the underflow channel of the sedimentation tank of a local water treatment plant in southwest Dublin. The plant employs aluminium sulphate as the coagulant for flocculating reservoir water (with turbidity and colour at range of 0.3-3.0 NTU and 40-120 Hazen, respectively) at a typical dose of 42-60 mg L^{-1}. It is expected that the Fenton's reagent may be explored as a preliminary alternative conditioner, followed by conventional polymer conditioning with reduced dosage for an environmentally safe manner in alum sludge conditioning process. Therefore, the sludge from the original discharge stream was collected although it was obvious low in concentration in this study. Properties of the alum sludge are listed in Table 1. Fe^{2+} in Fenton's reagent is prepared by making a solution from $FeCl_2 \cdot 4H_2O$. Hydrogen peroxide was obtained in liquid (30% by wt) from a commercial supplier. Sulfuric acid and sodium hydroxide are used for adjusting the pH of the sludge samples during conditioning.

2.2. Experimental Methods

Initially, sludge samples of 250 mL were carefully transferred to a number of 500 mL breakers. Their pHs were then adjusted to the desired values using H_2SO_4 or NaOH. Fe^{2+} solution was added to the sludge and Fenton reaction was then initiated after adding H_2O_2. Following Fenton reagent addition the sludge was subjected to 30 s of rapid mixing followed by a slow mixing in a jar test apparatus to promote reaction and flocculation during the reaction time.

2.3. Analytical Methods

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

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

where CST_0 and CST are respectively the CST of the aluminium-based water sludge before and after conditioning.

2.4. RSM

A Box-Behnken experimental design (Montgomery, 1991) was chosen to evaluate the combined effects of the three independent variables, i.e. Fe^{2+} dosing, H_2O_2 dosing and initial pH as X_1, X_2 and X_3 respectively, during the Fenton reagent conditioning. The range of the experimental variables investigated were chosen according to preliminary tests. These ranges and levels are presented in Table 2. Fifteen runs were required for a complete set of the experimental design and are shown in Table 3.

The first step in the RSM is to find a suitable approximation for the true functional relationship between the response (*E*) and the set of the independent variables. An empirical second-order polynomial model for three factors was in the following form (Montgomery, 1991):

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

where E is the predicted response (CST reduction efficiency, %); β_0, β_i, β_{ii} and β_{ij} (i = 1, 2, 3 and j = 1, 2, 3) are the model regression coefficients; X_i and X_j (i = 1, 2, 3 and j = 1, 2, 3) are the coded independent variables (see Table 2). The coefficient parameters are estimated by multiple linear regression analysis using the software of Statistical Analysis System (SAS, 1990).

3. Results and discussion

3.1. Conditioning of aluminium-based sludge with Fenton reagent

Figure 1 jointly illustrates the effectiveness of Fenton's reagent, together with the separated addition of H_2O_2 and Fe^{2+} to provide comparative data, for conditioning of the alum sludge. Different sets of experiments at various concentrations in the range of 3.5 to 350 mg g^{-1} DS^{-1} for both Fe^{2+} and H_2O_2 were conducted. The data revealed that H_2O_2 addition could even result in an increased CST, indicating that H_2O_2 alone has no function to improve sludge dewaterability. This agreed with the finding reported by Kwon et al. (2004) who claimed that H_2O_2 alone was not effective due to low reaction rate. The optimal dose for Fe^{2+} alone addition to achieve highest CST reduction was 350 mg g^{-1} DS^{-1}, at which only 16% of CST reduction efficiency was obtained. However, combined use of H_2O_2 and Fe^{2+}, i.e. Fenton reagent, at the dosage of 14 and 140 mg g^{-1} DS^{-1} for Fe^{2+} and H_2O_2, respectively, could achieve a CST reduction of 45%. This reflects the effectiveness of Fenton's reagent as an alternative conditioner in alum sludge conditioning.

The effects of Fenton reaction time on alum sludge conditioning were investigated at Fe^{2+}/H_2O_2 dosage of 14/17.5 mg g^{-1} DS^{-1} and 14/140 mg g^{-1} DS^{-1}, respectively, while the pH of the sludge was kept its original without any adjustment. The results, as illustrated in Fig. 2, show clearly that the highest CST reduction occurred in the initial period of reaction time for both cases, while prolonged reaction time could lead to insignificant improvement of sludge dewaterability. The reason remains unclear in the current study without further investigation. The maximum CST reduction efficiency (%) was obtained at 1 min reaction for both the trends although lower dosage corresponded to a relative low CST reduction efficiency. In spite of the fact that such rapid reaction makes it questionable to implement this technology in practice, it reflects the feature of Fenton reaction.

In order to provide the insight into such the characteristics, measurements of chemical oxygen demand (COD) via Hach DR-2400 spectrometer (CAMLAB Ltd, UK) and molecular size distribution (MSD) of dissolved organic substances using a high-pressure size exclusion chromatography (HPSEC) for the sludge samples before and after Fenton conditioning at different reaction times were carried out and the results are shown in Table 4 and Fig. 3. Results of COD measurements in Table 4 reveal that the Fenton reaction immediately oxidizes the organics in the sludge regardless of the reaction time. Figure 3 provides the evidence that the MSD of dissolved organic substances at reaction time of 1 min and 30 min exhibits very similar trends, indicating the unnecessary in prolonging Fenton reaction time in conditioning of the alum sludge. Compared with the MSD of raw sludge, it is clear that the Fenton reaction degraded/broke the organics from large molecular sizes into smaller ones via highly reactive hydroxyl radicals (Neyens et al. 2004). Therefore, it is reasonable to address that the improvement of sludge dewaterability by the Fenton reaction lies in the release of both interstitial water trapped between organics and adsorbed or chemically bound water by the degradation of organics. It is noted that Kwon et al. (2004) conducted a quite similar investigation with reaction time varied from 2-60 min. However, there was no detailed description of the effects of reaction time on conditioning efficiency.

Effects of initial pH in the range of 2 to 8 of the Fenton reaction at dosage of Fe^{2+}/H_2O_2 = 14/140 mg g^{-1} DS^{-1} and reaction time of 1 min were examined. In particular, the blanks for the pH adjustment alone were conducted while the measurement of CST at the time of 10 min after pH adjustment was applied. The results are jointly presented in Table 5. The purpose of adjusting pH alone lies in the reflection of the effectiveness of pure Fenton reaction in the sludge conditioning studied. It can be seen from Table 5 that the pH adjustment alone has significant effect on alum sludge dewaterability. The acidic environment can clearly improve sludge dewaterability with pH of 4-5 being the best. This may be attributed to the release of metal ions, such as Al and Fe from the sludge to promote the flocculation, as demonstrated by Kwon et al. (2004). The basic environment, however, exhibited negative effect on the sludge dewaterability, as increased CST (negative CST reduction) was obtained. The reason remains unclear. However, it is known that high pH can decrease the amount of hydroxyl radicals, which is believed to be the driving force towards the improvement of sludge dewaterability. By considering such the influence of pH, the CST reduction efficiency at the pH of 6 in this study is the best regarding the highest net CST reduction efficiency being obtained, as shown in Table 5. It is noted, however, that Lu et al. (2001) claimed the similar level of dewaterability of an activated sludge when it was subjected to conditioning with Fenton reagent at pH in the range of 2 to 7. Obviously, more work is desirable to explore such effect.

Figure 4 illustrates various ratios of Fe^{2+}/H_2O_2 in a wide range of Fe^{2+} (3.5-2100 mg g^{-1} DS^{-1}) and H_2O_2 (3.5-3510 mg g^{-1} DS^{-1}) in alum sludge conditioning. It is seen that the CST reduction efficiency increases with increased Fe^{2+}/H_2O_2 dosage until a certain ratio at which the reversible results were obtained. Although the enhancement of sludge dewaterability occurred at a broad range of Fe^{2+} addition, H_2O_2 can only beneficially affect the sludge dewaterability in a relative small range of less than 280 mg g^{-1} DS^{-1} except for the case of Fe^{2+} addition of 2100 mg g^{-1} DS^{-1}, at which the H_2O_2 addition of up to 1750 mg g^{-1} DS^{-1} can still bring about the improved sludge dewaterability. However, considering the lower amount of reagent addition, the best dosage in current study seems at Fe^{2+} less than 28 mg g^{-1} DS^{-1} and H_2O_2 less than 280 mg g^{-1} DS^{-1}, as shown in Fig. 4. Nevertheless, it appears that the H_2O_2 concentration plays an important role in Fenton reaction since excess addition of H_2O_2 may lead to the negative impact on sludge dewaterability. The reason may be attributed to the amount of hydroxyl radicals. When H_2O_2 concentration increases until a critical concentration, a so-called scavenging effect occurred. Several references are available with concern of the hydroxyl radical production on the effect of Fenton reaction (Lin and Gurol, 1998; Torrades et al. 2003; Zhang et al. 2005).

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

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

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

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 Fe^{2+}, H_2O_2 and pH. It can be seen from Fig. 5(a) that a significant enhancement of CST reduction efficiency is observed when the H_2O_2 concentration was increased. However, at higher concentrations of H_2O_2 the reduction rate was negatively affected. Thus, an excess of H_2O_2 does not mean a continuous increase in CST reduction of the conditioned sludge. Similarly, the CST reduction in percentage increased with increasing the Fe^{2+} concentration to a certain limit. Obviously, there is an optimal dosage for both Fe^{2+} and H_2O_2 concentrations. In the similar way, the 3D surface and the corresponding contour plotted in Fig. 5(b) show that the combination of 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 H_2O_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 Fe^{2+} and H_2O_2 concentrations as well as pH was conducted to achieve the highest CST reduction from the statistical point of view.

Mathematical software (V 5.2., Wolfram research Inc.) and response surface analysis were used to determine optimum conditions of the operating variables in the Fenton reaction. The maximum CST reduction efficiency (*E*) is 53%, whereas maximum values of the process variables in coded values given as follows: $X_1 = 0.66$, $X_2 = -1$ and $X_3 = 0.99$. Accordingly, Fe^{2+}, H_2O_2 and pH are 21 mg g^{-1} DS^{-1}, 105 mg g^{-1} DS^{-1} and 6, respectively.

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

Conclusions

Application of Fenton reagent (Fe^{2+}/H_2O_2) in conditioning of an aluminium-based water treatment sludge has demonstrated the effectiveness of such kind of its use. Effects of Fenton reagent in a wide range of concentrations on alum sludge dewaterability were tested. Considerable improvement of such sludge dewaterability was obtained. Experimental investigation confirmed that the Fenton reaction rapidly degrades organics in the sludge from large molecular sizes into smaller sizes and oxidises them in a short time. The optimum condition, determined by RSM, of Fenton process is at Fe^{2+} 21 mg g^{-1} DS^{-1} and H_2O_2 105 mg g^{-1} DS^{-1} while the optimum pH is 6, at which the CST reduction efficiency of 53 % can be achieved. By using RSM, a multi-variable polynomial equation has been developed to describe the behaviour of Fenton reaction regarding the response of CST reduction efficiency. The replicate experiments at optimal conditions yielded an average CST reduction efficiency of

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

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Figure Captions

Fig. 1 Effects of H_2O_2, Fe^{2+} and Fe^{2+}/H_2O_2 on CST reduction efficiency (%) of alum sludge (Operating parameters: H_2O_2 = 3.5 mg g^{-1} DS^{-1}; Fe^{2+} = 350 mg g^{-1} DS^{-1}; Fenton's reagent (Fe^{2+}/H_2O_2) = 14/140 mg g^{-1} DS^{-1}; pH = 6.0, reaction time = 1 min)

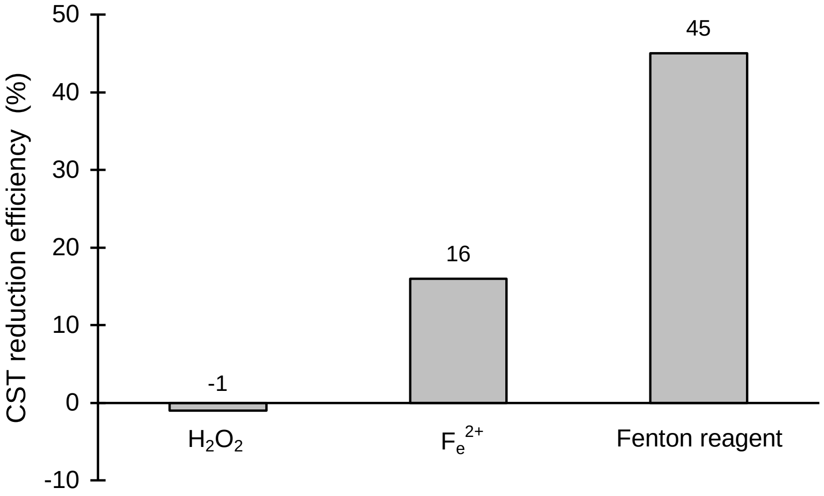
Fig. 2 Effects of the Fenton reaction time on conditioning of the alum sludge with two concentrations of Fenton reagent

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

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

Fig. 5 Optimising Fenton reaction in alum sludge conditioning: (a) surface and contour of coded Fe^{2+} and H_2O_2 vs. predicted CST reduction efficiency; (b) surface and contour of coded $Fe^{2+}$and pH vs. predicted CST reduction efficiency; (c) surface and contour of coded H_2O_2 and pH vs. predicted CST reduction efficiency.

Figures



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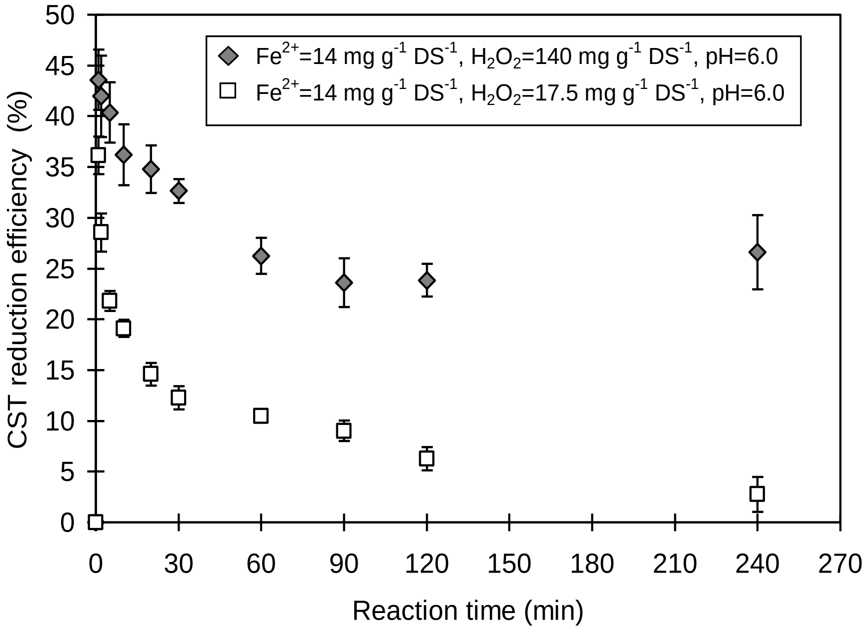

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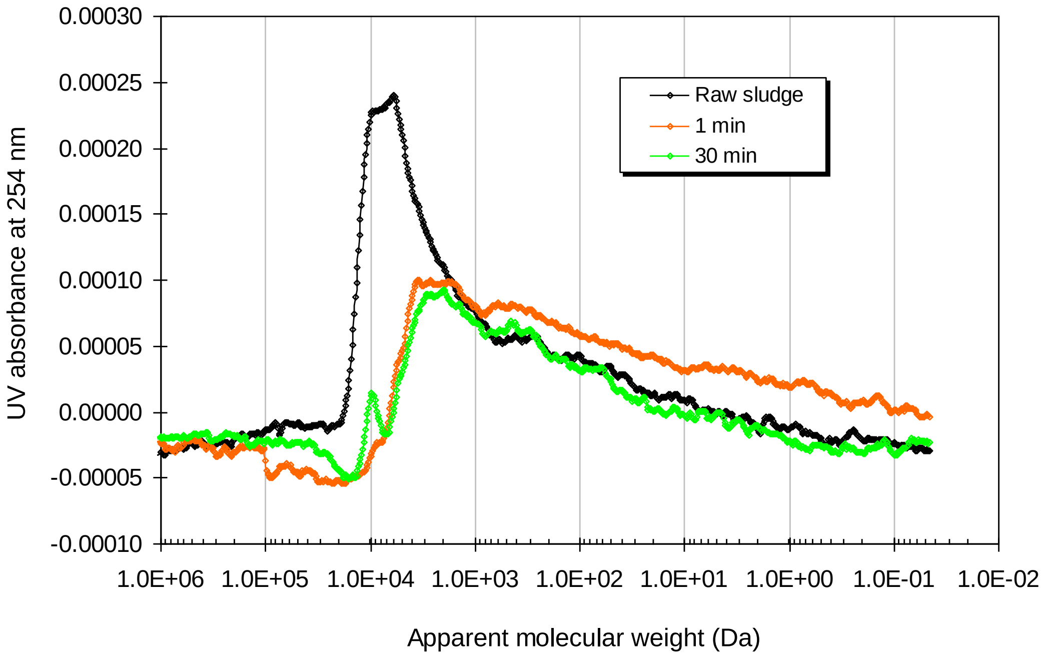

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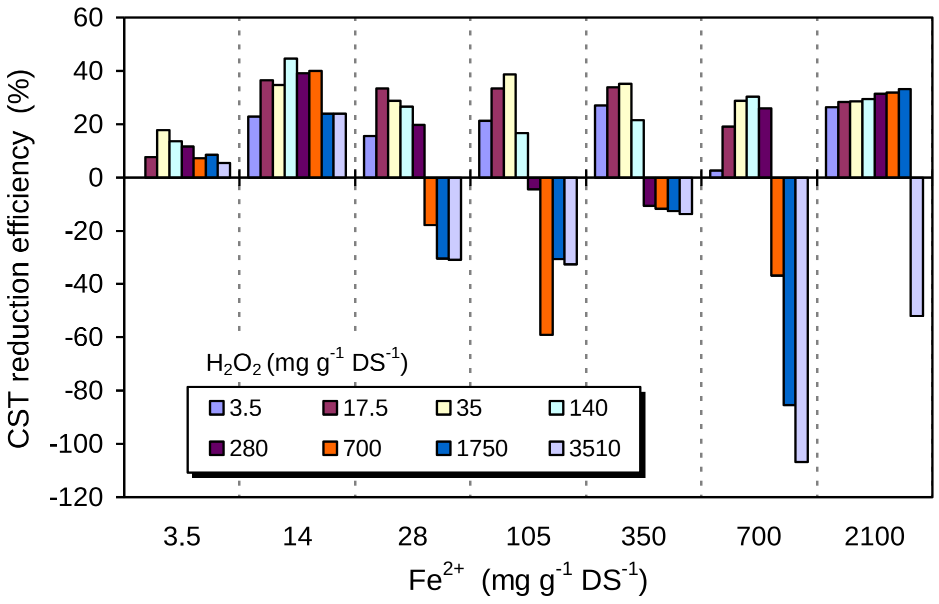

Fig. 4 CST reduction efficiency at various Fenton's reagent dosages (Operating parameters: pH = 6.0; reaction time = 1 min)

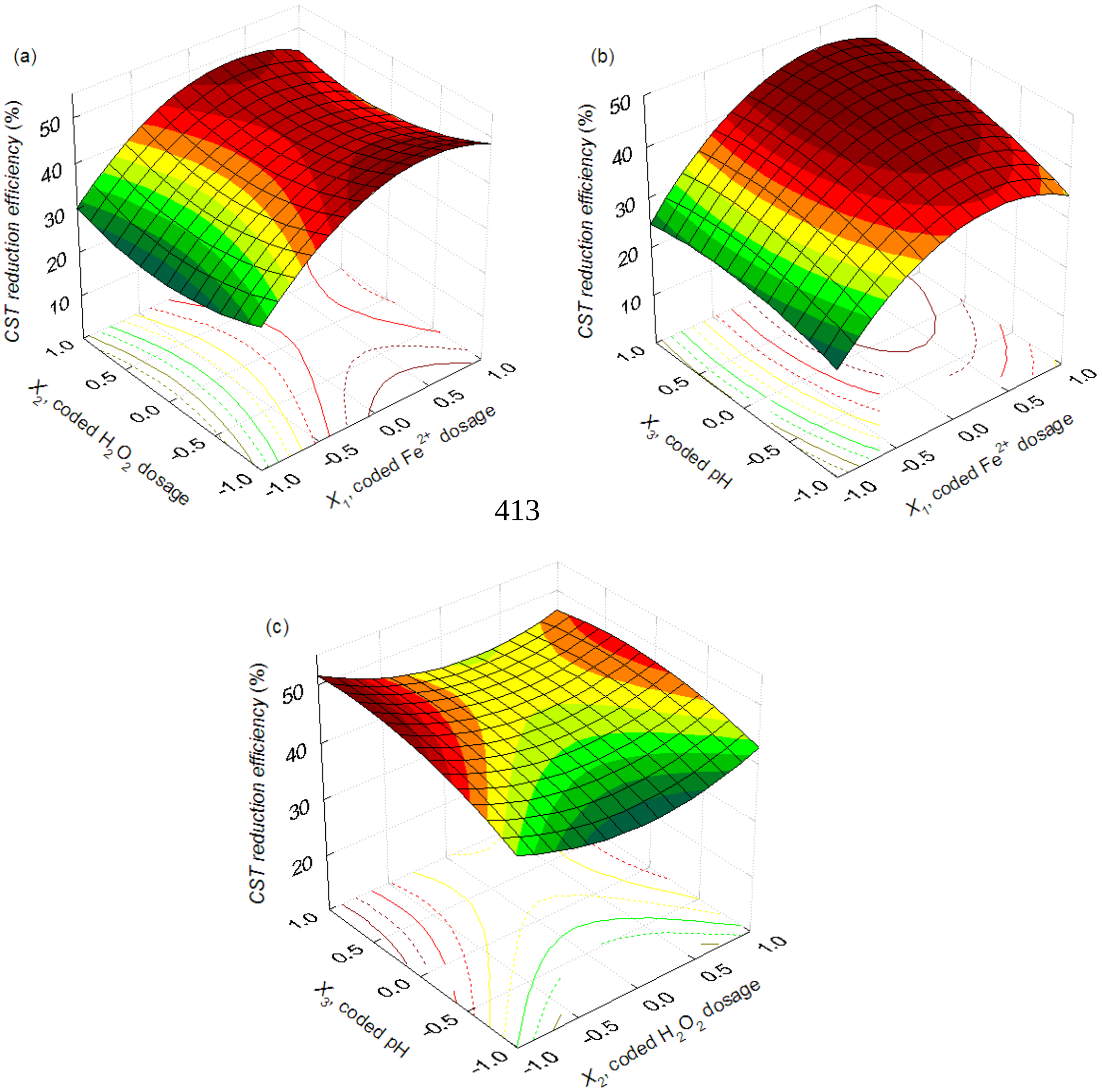

Fig. 5 Optimising Fenton reaction in alum sludge conditioning: (a) surface and contour of coded Fe^{2+} and H_2O_2 vs. predicted CST reduction efficiency; (b) surface and contour of coded $Fe^{2+}$and pH vs. predicted CST reduction efficiency; (c) surface and contour of coded H_2O_2 and pH vs. predicted CST reduction efficiency.

Table Captions

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

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

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

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

Table 5 Effects of pH (2 ~ 8) on conditioning of alum sludge with Fenton's reagent (reaction time of 1 min) at dosage of $Fe^{2+}/H_2O_2 = 14/140$ (mg g^{-1} DS^{-1})

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

Parameters	Unit	Value
Suspend solids	mg L^{-1}	2,850
pH		5.7-6.0
SRF	m kg^{-1}	6.32×10^{11}
CST	s	67.5

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^{2+} (mg g^{-1} DS^{-1})	ξ_1	X_1	3.5	14	24.5
H_2O_2 (mg g^{-1} DS^{-1})	ξ_2	X_2	105	140	175
pH	ξ_3	X_3	2.0	4.0	6.0

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

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 (E, %)	
	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

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

Reaction time (min)	After Fenton conditioning	
	Fe^{2+}/H_2O_2=3.5/17.5 (mg g^{-1} DS^{-1}), pH = 6.0	Fe^{2+}/H_2O_2=3.5/140 (mg g^{-1} DS^{-1}), pH = 6.0
1	39 ±1	30 ±2
30	40 ±1	35 ±1
90	39 ±5	40 ±2

* All sludge samples were filtered using Whatman No. 1 qualitative filter paper. Raw sludge COD = 221 ±5

Table 5 Effects of pH (2 ~ 8) on conditioning of alum sludge with Fenton’s reagent (reaction time of 1 min) at dosage of Fe^{2+}/H_2O_2 = 14/140 (mg g^{-1} DS^{-1})

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