Water Research 95 (2016) 124–133

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Roles of iron species and pH optimization on sewage sludge conditioning with Fenton's reagent and lime

Wenbo Yu [a, 1], Jiakuan Yang [a, *], Yafei Shi [a, 1], Jian Song [a], Yao Shi [a], Jun Xiao [a], Chao Li [a], Xinyu Xu [a], Shu He [b], Sha Liang [a], Xu Wu [a], Jingping Hu [a]

[a] School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, PR China
[b] Universtar Science & Technology (Shenzhen) Co., Ltd., Shenzhen, Guangdong 518057, PR China

ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form
21 February 2016
Accepted 7 March 2016
Available online 8 March 2016

Keywords:
Sewage sludge conditioning
Fenton's reagent
pH optimization
Fe(III) coagulation
Sludge dewatering performance

ABSTRACT

Conditioning sewage sludge with Fenton's reagent could effectively improve its dewaterability. However, drawbacks of conditioning with Fenton's reagent are requirement of acidic conditions to prevent iron precipitation and subsequent neutralization with alkaline additive to obtain the pH of the filtrate close to neutrality. In this study, roles of pH were thoroughly investigated in the acidification pretreatment, Fenton reaction, and the final filtrate after conditioning. Through the response surface methodology (RSM), the optimal dosages of H_2SO_4, Fe^{2+}, H_2O_2, and lime acted as a neutralizer were found to be 0 (no acidification), 47.9, 34.3 and 43.2 mg/g DS (dry solids). With those optimal doses, water content of the dewatered sludge cakes could be reduced to 55.8 ± 0.6 wt%, and pH of the final filtrate was 6.6 ± 0.2. Fenton conditioning without initial acidification can simplify the conditioning process and reduce the usage of lime. The Fe^{3+} content in the sludge cakes showed a close correlation with the dewaterability of conditioned sludge, i.e., the water content of sludge cakes, SRF (specific resistance to filtration), CST (capillary suction time), bound water content, and specific surface area. It indicated that the coagulation by Fe^{3+} species in Fenton reaction could play an important role, compared to traditional Fenton oxidation effect on sludge conditioning. Thus, a two-step mechanism of Fenton oxidation and Fe(III) coagulation was proposed in sewage sludge conditioning. The mechanisms include the following: (1) extracellular polymeric substances (EPS) were firstly degraded into dissolved organics by Fenton oxidation; (2) bound water was converted to free water due to degradation of EPS; (3) the sludge particles were disintegrated into small ones by oxidation; (4) Fe^{3+} generated from Fenton reaction acted as a coagulant to agglomerate smaller sludge particles into larger dense particles with less bond water; (5) finally, the dewatered sludge cakes were obtained, with less small pores (1–10 nm) that contributed to water affinity, but with more large pores (>10 nm) that contributed to a permeable, rigid lattice structure. Morphology of the Fenton-conditioned sludge cake exhibited a porous structure. The estimated cost of the composite conditioner, Fenton's reagent and lime, is USD$ 43.8/t DS, which is less than that of ferric chloride and lime (USD$ 54/t DS). Furthermore, pH of the final filtrate using this composite conditioner is about 6.6. Comparatively, that using ferric chloride and lime is as high as 12.4.

1. Introduction

Sewage sludge dewatering is an effective approach for reduction of the volume and mass of sludge for subsequent treatment and disposal (Zhou et al., 2014). Water within the sludge generated in wastewater treatment plants (WWTPs) can be categorized into "free water" and "bound water" (Katsiris and Kouzeli-Katsiri, 1987). The "bound water" cannot be readily removed by mechanical means while removing "bound water" is difficult (Vesilind, 1994; Chu et al., 2005). To increase dewaterability, sludge conditioning is commonly used as a pretreatment before dewatering (Huo et al., 2014).

Many sludge conditioning methods, including physical (Show et al., 2007), chemical (Lu et al., 2003), and biological (Thomas et al., 1993) pretreatment, have been developed. Recently, considerable researches have been conducted to explore Fenton's reagent

* Corresponding author.
E-mail address: jkyang@mail.hust.edu.cn (J. Yang).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.watres.2016.03.016
0043-1354/

(Fe^{2+}/H_2O_2) as an alternative chemical conditioner for sludge conditioning (Neyens et al., 2002, 2003; Tony et al., 2009). For example, with an initial sludge pH of 3 and dosages of 1.67 mg Fe^{2+}/g DS (dry solids) and 25 mg H_2O_2/g DS, water content of the dewatered sludge cakes could be reduced to 53 wt% (Neyens et al., 2003). Hydroxyl radicals are generated through Fenton reaction (Eq. (1)), and they can degrade extracellular polymeric substances (EPS) which retain a large amount of water (Liu et al., 2010; Zhen et al., 2012).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (1)$$

Also shown in Eq. (1), Fenton reaction can generate Fe^{3+} which is an effective coagulant. Coagulation mechanisms by ferric ions include adsorption and charge neutralization, aggregation by particle transport and van der Waal's forces, and interparticle bridging (Katsiris and Kouzeli-Katsiri, 1987; Deneux-Mustin et al., 2001). Katsiris and Kouzeli-Katsiri (1987) reported that conditioning using ferric salts could significantly reduce a large amount of bound water in sludge. In traditional Fenton reaction, the molar ratios of $[Fe^{2+}]/[H_2O_2]$ is much less than 1, and Fe^{2+} mainly serve as a catalyst. As the molar ratio of $[Fe^{2+}]/[H_2O_2]$ is close to 1, a large amount of Fe^{2+} ions are converted to Fe^{3+}. Fe^{3+} species could act as a coagulant that could enhance sludge dewaterability (Katsiris and Kouzeli-Katsiri, 1987). Oxidation effect in Fenton conditioning has widely been noted and studied. However, few studies on the role of Fe^{3+} species in conditioning by using Fenton's reagent could be found in literature.

The main drawbacks associated with using of Fenton conditioning are the necessity of the initial acidification to prevent iron precipitation, followed by subsequent neutralization using alkaline additive to neutralize the filtrate (Neyens and Baeyens, 2003). Acidic pH of around 3 is often considered as an optimal condition for Fenton oxidation (Arnold et al., 1995). Liu et al. (2012) claimed that the specific resistance to filtration (SRF) reduction efficiency of the conditioned sludge reached a maximum peak at an initial pH of 5, when Fenton's reagent and skeleton builders were combinedly used. Lu et al. (2001) reported that initial pH in a wide range of 2–7 had insignificant effects on filtration efficiency and had a minor effect on sludge cake moisture, when the sludge was conditioned by Fenton's reagent. Tony et al. (2008) reported that pH of 6 was optimal to achieve the highest reduction efficiency of capillary suction time (CST). However, optimal initial pH for Fenton reaction in sludge conditioning has not been fully defined in previous literature. With regard to neutralization after sludge conditioning by Fenton's reagent, Neyens et al. (2003) suggested addition of 55.6 g $Ca(OH)_2$/kg DS after Fenton reaction. Zhang et al. (2014) suggested a dosage of 275.1 mg red mud/g DS as both a neutralizer and a skeleton builder. However, addition of a neutralizing reagent would increase the cost. So, the dosage of the neutralizer should be minimized. Lime is commonly used as a neutralizer to adjust the pH of sludge conditioned by Fenton's reagent.

Although both initial pH and final filtrate pH should be important parameters, previous studies did not make a consistent conclusion on the optimal initial pH. Furthermore, the initial pH, Fenton's reagent conditioning performance and the dosage of the neutralizer were seldom considered combinedly. The schematic of this study is shown in Fig. 1. The objectives of this study were to: (1) optimize the dosages of H_2SO_4 used in the acidification pretreatment, Fe^{2+}, H_2O_2, and lime used as neutralizer, in order to achieve water content of <55 wt% in the dewatered sludge cakes and filtrate pH between 6.5 and 7; (2) explore the mechanisms of both Fenton oxidation and coagulation by Fe(III) generated in Fenton reaction; and (3) preliminarily evaluate the cost of using optimal dosage of Fenton's reagent and lime for sewage sludge dewatering.

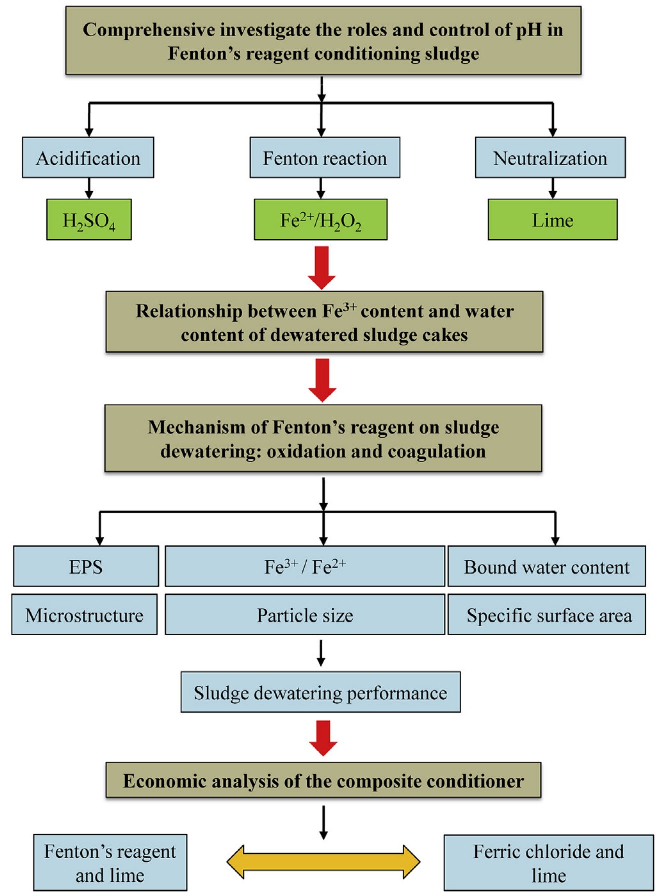

Fig. 1. Schematic of the study.

2. Methods

2.1. Materials

Raw sludge (RS) used in this study was the secondary sludge after sludge thickening from Tangxun Lake Municipal WWTP, Wuhan, China. Samples were transported to the laboratory in polypropylene containers and stored at 4 °C before used. All the tests were completed within one week. The main characteristics of RS are tabulated in Table 1.

Analytical grade H_2SO_4 (40 wt%, Xinyang Chemical Company, China) was used for initial pH adjustment before Fenton's reagent. Fe^{2+} in the Fenton's reagent was prepared from $FeSO_4 \cdot 7H_2O$ (analytical grade, Sinopharm Chemical Reagent, China) and H_2O_2 (30 wt%, Sinopharm Chemical Reagent, China) was of analytical grade. Lime (Xinyang Chemical Company, China) used in this study was industrial grade with free-CaO content of 81.7 wt%. Fe^{3+} was prepared from $FeCl_3 \cdot 6H_2O$ (analytical grade, Sinopharm Chemical Reagent, China).

2.2. Sludge conditioning and dewatering

The sludge conditioning and dewatering process is presented in Fig. S1. 25 kg RS was transferred to a conditioning tank and then conditioned using the following procedure: H_2SO_4 addition → 150 rpm stirring for 3 min → addition of Fe^{2+} → 150 rpm stirring for 5 min → H_2O_2 addition → 100 rpm stirring for 30 min → addition of lime → 150 rpm stirring for 5 min.

Table 1
Characteristics of RS.

Batch	pH	Water content (%)	SCOD[a] (mg/L)	TSS (g/L)	VSS/TSS[b] (%)	SRF ($\times 10^{13}$ m/kg)	CST (s)
1	6.76	96.8	833	30	47.8	2.2	157.7
2	6.75	96.8	975	31	58.9	2.5	332.9

[a] SCOD: Soluble chemical oxygen demand.
[b] VSS/TSS: the ratio of volatile suspended solids to total suspended solids.

After conditioning, the conditioned sludge was pumped into a feeding tank, in which the internal pressure was controlled by air to feed the sludge to a laboratory–scale diaphragm filter press with three diaphragm plates (250 mm $\times$ 250 mm, 10 mm depression) and got six sludge cakes at each test. The dewatering procedure comprised of a feeding pressing phase (0.8 MPa for 30 min) and a diaphragm pressing phase (1.2 MPa for 10 min). This deep dewatering process of diaphragm filter press was commonly used (Neyens and Baeyens, 2003; Zhai et al., 2012). In this deep dewatering process, the water content of the dewatered cakes were about 60 wt%, compared with traditional centrifuge and belt press with the water content of the dewatered cakes of about 80 wt%. A quarter of each sludge cake was sampled for measuring water content in order to obtain a representative of the dryness of the cake. Water content of the dewatered cake was determined after being dried at 105 °C for 24 h and used to determine the performance of dewatering. The pH was determined by using a PHS-3C pH-meter (Leici, China). pH, TN (Total nitrogen), TP (Total phosphorus), and SS (Suspended solids), were carried out according to the standard methods (APHA, 1998).

2.3. SRF and CST

SRF and CST were also used to evaluate sludge dewatering performance (Skinner et al., 2015). SRF was measured by a multi-coupled measuring device, as described in Liu et al. (2012). The CST was measured by a 304 M CST instrument (Triton, UK).

2.4. RSM design

A Central Composite Design (Montgomery, 2009) was used to optimize dosages of H_2SO_4 used in acidification pretreatment, Fe^{2+}, H_2O_2 and lime. Ranges and levels of these four constituents were defined based on the preliminary tests, as shown in Table 2. The water content (Y_1) of the dewatered sludge cakes and the pH of the filtrate (Y_2) were considered as the responses. Thirty runs were required for a complete set of the experimental design as shown in Table S1, and the experimental results were analyzed by the Design Expert 8 software. The criteria and response sets for optimization are presented in Table 3. The goal of optimization was to minimize the dosage of the four constituents to achieve the water content of <55 wt% for the dewatered cake and the filtrate pH close to neutrality between 6.5 and 7. The water content of <55 wt% is below to the limit in Chinese Standard for quality of sludge for co-landfilling (GB/T 23485-2009) (GAQSIQ, 2009). The first batch of RS was used in this optimization experiment.

Table 2
Ranges and levels of the factors in the optimization experiments by Central Composite Design.

Factors	Ranges and levels				
	−2	−1	0	1	2
X1, H_2SO_4 dosage[a] (mL/kg RS)	0	0.92	1.84	2.76	3.69
X2, Fe^{2+} dosage (mg/g DS)	16	32	48	64	80
X3, H_2O_2 dosage (mg/g DS)	12	24	36	48	60
X4, Lime dosage (mg/g DS)	30	40	50	60	70

[a] As H_2SO_4 dosage was 0, 0.92, 1.84, 2.76, 3.69 mL/kg RS, the initial pH of the acidified sludge was 6.76, 6.17, 5.53, 4.71 and 4.26, respectively.

2.5. Fe^{3+}/Fe^{2+} extraction and analysis

Fe^{3+} and Fe^{2+} in the dewatered sludge cakes (~5 g) were extracted by 200 mL of 0.5 M HCl under room temperatures for 24 h (Schnell et al., 1998). After the extraction, both Fe^{3+} and Fe^{2+} in the sludge cakes were dissolved into a liquid phase. The concentration of Fe^{2+} and $Fe(total)_{HCl}$ in the extraction solution and the filtrate were analyzed by 1,10-phenanthroline at a wavelength of 510 nm using a DR/2000 spectrophotometer (Hach, USA). Fe^{3+} content was calculated as the difference between Fe^{2+} and $Fe(total)_{HCl}$. Before being analyzed, the extraction solution and the filtrate were passed through 0.45 μm membrane.

2.6. Statistical analysis

The fitting data obtained from thirty runs of RSM optimization experiments included Fe^{3+} content and water content of the sludge cakes. Data were fitted and analyzed by the SPSS statistical software (SPSS version 19.0, SPSS Inc).

2.7. Investigations of the conditioning mechanism

To elucidate mechanisms and roles of each constituent in the Fenton conditioning, a set of experiments with different formulations were conducted (Table 4). The dosages of the constituents were from the RSM optimization study. RS was used as the control. As shown in Table 4, sludge conditioned by Fenton's reagent and lime, sludge conditioned by Fenton's reagent, sludge conditioned by $FeSO_4$, sludge conditioned by $FeCl_3$, sludge conditioned by H_2O_2 at pH of 3 were noted as Fenton-L, Fenton, Fe(II), Fe(III), and H_2O_2, respectively. The RS and the various conditioned sludges were analyzed for water content, SRF, CST, Fe^{3+}/Fe^{2+} content, EPS content, bound water content, particle size of sludge, specific surface area of sludge, and microstructure. The contents of Fe^{3+} and Fe^{2+} in the filtrates of the raw and the conditioned sludges were also analyzed. The second batch of RS was used in these experiments.

2.7.1. EPS extraction and analysis

Microbial EPS of sludge, including loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS), have significant effects on biomass flocculation, sludge settlement and dewaterability (Li and Yang, 2007). A modified heat extraction method (Li and Yang, 2007) was used to extract the LB-EPS and TB-EPS in this study. In this method, the sludge was first centrifuged in a 50-mL tube at 4000g for 5 min. The centrifugal liquor (CL) was analyzed and the sludge pellet in the tube was used for EPS extraction (Zhang et al., 2014). Test samples were passed through a 0.45 μm membrane before being analyzed. All the LB-EPS extraction, TB-EPS extraction, and the CL were analyzed for total organic carbon (TOC), protein (PN) and polysaccharide (PS). TOC was measured by a Multi N/C 2100

Table 3
Criteria of the factors and response for optimization.

Variable	Goal	Lower limit	Upper limit	Importance
X1, H_2SO_4 dosage (mL/kg RS)	Minimize	0	2.76	3
X2, Fe^{2+} dosage (mg/g DS)	Minimize	0	64	3
X3, H_2O_2 dosage (mg/g DS)	Minimize	0	48	3
X4, Lime dosage (mg/g DS)	Minimize	0	60	3
Water content of the dewatered sludge cakes (wt%)	In range	0	55	3
pH of the filtrate	In range	6.5	7	3

Table 4
Different conditioning procedures for sludge.

Symbol	Conditioners	Initial pH of the sludge	Dosage (mg/g DS)				Conditioning procedures
			Fe^{2+}	H_2O_2	Fe^{3+}	Lime	
RS	None	6.75	0	0	0	0	150 rpm/5 min → 100 rpm/30 min → 150 rpm/5 min
Fenton-L	Fe^{2+}/H_2O_2 and lime	6.75	47.9	34.3	0	43.2	Fe^{2+} solutions → 150 rpm/5 min → H_2O_2 → 100 rpm/30 min → lime → 150 rpm/5 min
Fenton	Fe^{2+}/H_2O_2	6.75	47.9	34.3	0	0	Fe^{2+} solutions → 150 rpm/5 min → H_2O_2 → 100 rpm/30 min → 150 rpm/5 min
Fe(II)	$FeSO_4$	6.75	47.9	0	0	0	Fe^{2+} solutions → 150 rpm/5 min → 100 rpm/30 min → 150 rpm/5 min
Fe(III)	$FeCl_3$	6.75	0	0	47.9	0	Fe^{3+} solutions → 150 rpm/5 min → 100 rpm/30 min → 150 rpm/5 min
H_2O_2	H_2O_2	3	0	34.3	0	0	H_2SO_4 → 150 rpm/5 min → H_2O_2 → 100 rpm/30 min → 150 rpm/5 min

TOC analyzer (Analytik Jena, GER). The PN content was analyzed by the modified Lowry method using bovine serum albumin (Frølund et al., 1996). The PS content was analyzed by the anthrone method using glucose as the standard (DuBois et al., 1956).

2.7.2. Particle size and specific surface area

The particle sizes of the RS and the conditioned sludges were measured by a BT-9300ST laser particle size analyzer (Bettersize, China).

The sludge cakes of the RS and the conditioned sludges were first frozen at −40 °C for 24 h. Then, samples were transferred to a FD-1-50 freeze dryer (Biocool, China) at −60 °C and freeze-dried at a pressure lower than 10 Pa for 48 h. The surface area and the pore structure of the freeze-dried samples were determined by a JW-BK122W surface area and pore size analyzer (JWGB, China) on nitrogen adsorption principle (at 77 K). The specific surface area was calculated by the Brunauer-Emmet-Teller (BET) equation (Brunauer et al., 1938). The pore size distributions were estimated using the Barrett-Joyner-Halenda (BJH) approach (Barrett et al., 1951).

2.7.3. Bound water content measurement

The bound water content was determined using a Q2000 differential scanning calorimetry (DSC) analyzer (TA, USA). The methods reported in literature were based on an assumption that bound water does not freeze at temperatures below the freezing point of free water (Katsiris and Kouzeli-Katsiri, 1987; Vaxelaire and Cézac, 2004). In this study, the amount of water that did not freeze at −20 °C was determined as bound water. The sludge was first freezed to a temperature of −20 °C, assuming that all free water was frozen under this condition, and then brought back to 20 °C at a rate of 2 °C/min. The mass of the samples was in the range of 15–30 mg. Details for the DSC analytical procedure can be found in Katsiris and Kouzeli-Katsiri (1987) and Zhang et al. (2014).

2.7.4. Microstructural analysis

Scanning electron microscopy (SEM) technique was utilized to investigate the microstructural characteristics of the RS and the conditioned sludge cakes after freeze-drying (the detail of freeze-drying was presented in Section 2.7.2). Morphology study was conducted using a Sirion 200 scanning electron microscope (FEI, NL) at 10 kV after the samples coated with gold.

3. Results and discussion

3.1. RSM optimization results

Experimental results were evaluated using the Central Composite Design to yield approximative functions for dependent variables: water content of the sludge cakes (Y_1), and pH of the filtrate (Y_2). The following fitting polynomial Eqs. (2) and (3) were obtained from data fitting.

$$\begin{aligned} Y_1 = {} & 55.33 - 0.53\,X_1 - 1.51\,X_2 - 1.04\,X_3 - 0.096\,X_4 \\ & + 0.67\,X_1\,X_2 + 0.14\,X_1\,X_3 + 0.15\,X_1\,X_4 + 0.051\,X_2\,X_3 \\ & - 0.44\,X_2\,X_4 + 0.2\,X_3\,X_4 - 0.44\,X_1^2 + 1.02\,X_2^2 + 0.42\,X_3^2 \\ & - 0.26\,X_4^2 \end{aligned} \quad (2)$$

$$Y_2 = 6.13 - 0.32\,X_1 - 0.82\,X_2 - 0.12\,X_3 + 0.43\,X_4 \quad (3)$$

where X_1, X_2, X_3 and X_4 are the coded values of the dosages of H_2SO_4, Fe^{2+}, H_2O_2 and lime, respectively.

The predicted water content of the sludge cakes (%) via Eq. (2) is shown in Table S1. A good agreement between the experimental and the predicted data was obtained with a regression coefficient (R^2) of 0.834. The model f-value is 5.39, and the value of "Prob > F" is 0.0012, which is less than 0.05, implying that the model is significant. The predicted pH value of the filtrate via Eq. (3) is also shown in Table S1. The R^2 value between the experimental and the predicted values is 0.888. The model f-value was 49.32, and the value of "Prob > F" is less than 0.0001, implying that the model is significant. Thus, it can be concluded that the above two models (Eqs. (2) and (3)) are reliable to describe the behavior of the composite conditioner on sludge dewaterability and pH of the filtrate.

The goal of optimization was to minimize the dosage of the composite conditioner to achieve the water content of <55 wt% for the dewatered cakes and the filtrate pH between 6.5 and 7. To achieve this goal, the optimal coded values of the factors are $X_1 = -2.000$, $X_2 = -0.004$, $X_3 = -0.142$, $X_4 = -0.679$. Accordingly, the dosages of H_2SO_4, Fe^{2+}, H_2O_2, and lime are 0, 47.9, 34.3, and 43.2 mg/g DS, respectively.

Three validation experiments under the above-mentioned optimal conditions were carried out to validate the accuracy of the model. The results of the triplicate experiments showed that the water content of the dewatered sludge cakes were 55.8 ± 0.6 wt% and the pH of the final filtrate was 6.6 ± 0.2. The experimental results validated the reliability of the model. The TN, TP, and SS in filtrate were 75.6 ± 8.5, 1.1 ± 0.1, and 107.3 ± 15.6 mg/L, respectively (Table S2). The SS in the filtrate is acceptable (Long et al., 2014).

Using the optimal condition, there is no need to adjust the initial pH of RS. After addition of $FeSO_4$, the pH of the sludge dropped from 6.76 to 5.96. The molar ratio of $[Fe^{2+}]/[H_2O_2]$ was 0.85, which was close to 1. H_2O_2 rapidly oxidized most of Fe^{2+} to Fe^{3+} via Eq. (1). When Fe^{2+} was converted into Fe^{3+} after the addition of H_2O_2, the pH of the sludge further dropped to 3.94. The subsequent addition of lime neutralized the pH of the sludge to 6.66. It is a common belief that oxidation of Fenton's reagent is most effective at pH = 3, to prevent iron precipitation (Bokare and Choi, 2014). In this study, sludge without initial acidification pretreatment could obtain optimal dewaterability, which implies that oxidation effect is not the only role of Fenton conditioning. Furthermore, the conditioning process without acid addition can be simplified and requires a smaller amount of lime.

3.2. Relationship between Fe^{3+} content and water content of the sludge cakes

Values of water content of the sludge cakes from the RSM optimized experiments were used to correlate with their Fe^{3+} contents. As shown in Fig. 2, the experimental data indicated a good correlation between Fe^{3+} content and the water content of the dewatered sludge cakes. The regression equation was shown in Eq. (4) below.

$$y = 0.0069x^2 - 0.7429x + 74.3622 \ (R^2 = 0.66) \qquad (4)$$

where y is the water content (wt%), and x is the Fe^{3+} content (mg/g DS) of the dewatered sludge cakes. The value of "Prob > F" is 1.4×10^{-13}, which is less than 0.01. Thus it indicates that model terms are significant. When the Fe^{3+} content was lower than 53.8 mg/g DS, a greater Fe^{3+} content in the sludge cakes resulted in a reduction in water content. The lowest water content of the sludge cake was 54.4 wt% when the Fe^{3+} content was 53.8 mg/g DS. A further increasing in the Fe^{3+} content of the sludge cake did not lead to additional reduction in water content. This result implies that the coagulation effect of Fe^{3+}, produced from the Fenton's reagent, has a notable positive correlation with sludge dewatering performance. It should be noted that this limit data of 53.8 mg Fe^{3+}/g DS could be only deduced in the used H_2O_2 dosage range in RSM experiments. The limit data of Fe^{3+} content in sludge cakes could be varied at the different molar ratio of $[Fe^{2+}]/[H_2O_2]$ and different H_2O_2 dosage.

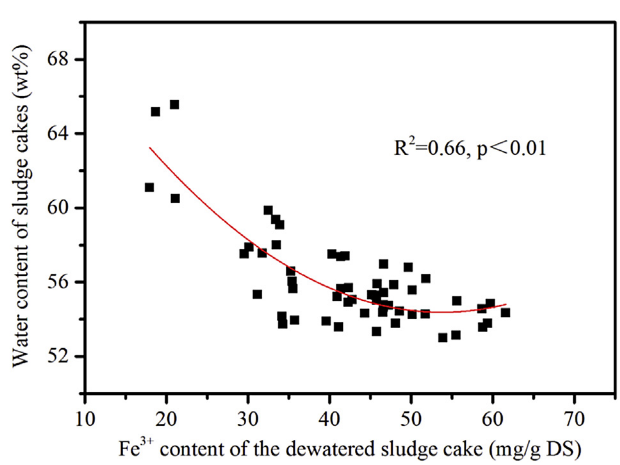

Fig. 2. Correlation between water content and Fe^{3+} content of dewatered sludge cakes.

3.3. Results of mechanism investigation

3.3.1. Sludge dewatering performance

The organic content of the second batch of RS was larger than that of the first batch, which resulted in a poorer dewatering performance. The water content of the sludge cake, as shown in Fig. 3a, decreased from 86.9 to 63.7 wt% after sludge was conditioned by Fenton's reagent, and further decreased to 62.9 wt% after sludge was jointly conditioned by Fenton's reagent and lime (Fenton-L). Because of the small dosage of lime (43.2 mg lime/g DS), the addition of lime only attributes to neutralize the pH of sludge. The water content of the sludge cake conditioned by Fe(III) alone was 69.7 wt%. The water content of the sludge cakes conditioned by Fe(II) and by H_2O_2 individually were as high as 83.3 wt% and 78.2 wt%, respectively. It indicated that individual usage of Fe(II) or H_2O_2 could obtain a much poorer dewatering efficiency, when compared with Fenton's reagent with synthetic effect of Fe^{2+}/H_2O_2.

As shown in Fig. 3b, SRF and CST of RS were 2.53×10^{13} m/kg and 332.9 s, respectively. Sludge conditioned by Fenton's reagent and lime (Fenton-L), Fenton's reagent, and Fe(III) reduced SRF and CST dramatically to 2.83×10^{12} m/kg and 35.5 s, 1.87×10^{12} m/kg and 34.5 s, and 2.7×10^{12} m/kg and 42.5 s, respectively. On the other hand, individual usage of Fe(II) or H_2O_2 slightly reduced SRF and CST to 2.05×10^{13} m/kg and 239.2 s, and 1.48×10^{13} m/kg and 129.2 s, respectively. It is consistent with the result of the water content of dewatered sludge cakes, as shown in Fig. 3a.

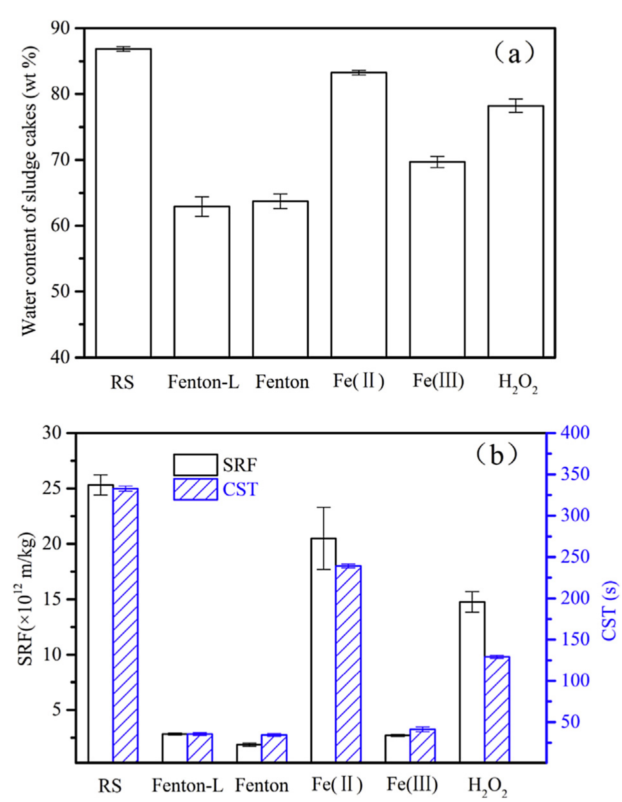

Fig. 3. Sludge dewatering performance: (a) water content of dewatered sludge cakes, (b) SRF and CST.

3.3.2. Fe^{3+}/Fe^{2+} content of the sludge cakes and filtrate

Compared to Fe^{2+}, Fe^{3+} is a very good coagulant which could significantly reduce a large amount of bound water in sludge (Katsiris and Kouzeli-Katsiri, 1987). So the concentration of Fe^{3+} content of the sludge cakes could be used as an indicator of the coagulation effect of the sludge.

As shown in Table 5, sludge conditioned by Fenton's reagent and lime (Fenton-L) and sludge conditioned by Fenton's reagent (Fenton) contained a large amount of Fe^{3+}, which were 31.9 and 33.3 mg/g DS, respectively. 28.16 mg Fe^{3+}/g DS was in the sludge cake of the sludge conditioned by Fe(III) alone. However, the sludge cakes of RS, sludge conditioned by Fe(II) alone and sludge conditioned by H_2O_2 alone contained less Fe^{3+}, which were only 0.24, 1.96, and 3.83 mg/g DS, respectively. Due to the anaerobic settlement and storage, the dominant iron species in the RS was 10.5 mg Fe^{2+}/g DS by microbial activities, compared to 0.24 mg Fe^{3+}/g DS (Rasmussen and Nielsen, 1996).

3.3.3. EPS

As illustrated in Fig. 4a, the TOC contents in the TB-EPS of the RS and the conditioned sludges are larger than those of the LB-EPS, which is consistent with the finding of Li and Yang (2007). The TOC contents in CL are in the following order: H_2O_2 > Fenton-L > Fenton > RS ≈ Fe(II) > Fe(III). TOC content of CL in sludge conditioned by oxidizing reagents, i.e., H_2O_2, Fenton-L, and Fenton, was apparently larger than that in RS, which implied that part of EPS was degraded and dissolved into liquid, and degradation of EPS was mainly attributed to oxidation effects. However, the content of TOC in CL of sludge conditioned by Fe(II) or Fe(III) alone was nearly similar to that of RS. It implies that individual addition of Fe(II) or Fe(III) alone did not change EPS significantly, and neither Fe(II) nor Fe(III) could contribute to EPS degradation in a significant manner.

As shown in Fig. 4b, the distributions of PN and PS in TB-EPS and LB-EPS of the RS and the conditioned sludges are similar to those of TOC (i.e., PN content in TB-EPS > PN content in LB-EPS, PS content in TB-EPS > PS content in LB-EPS, and TOC content in TB-EPS > TOC content in LB-EPS). In contrast to RS, the contents of PN and PS in CL of the sludge conditioned by H_2O_2, Fenton-L, and Fenton dramatically increased. The result implies that parts of EPS in the sludge were degraded into dissolved proteins and polysaccharides due to oxidation. However, The contents of PN and PS in CL of sludge conditioned by Fe(II) or Fe(III) alone were less than those in CL of the sludge conditioned by H_2O_2, Fenton-L, and Fenton. It is consistent with the results of TOC in CL, as shown in Fig. 4a.

3.3.4. Bound water content

Free water content of sludge is the amount of "freezable" water which can be calculated from the DSC endothermic curve area (Katsiris and Kouzeli-Katsiri, 1987; Zhang et al., 2014), as shown in Fig. S2, and Eq. (5). Fig. S3 illustrates the relationship between mass

Table 5
Fe^{3+}/Fe^{2+} content in the dewatered sludge cakes and filtrate.

Symbol	Iron species in dewatered sludge cakes (mg/g DS)		Iron species in filtrate (mg/L)	
	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}
RS	0.24	10.5	1.81	2.26
Fenton-L	31.9	12.27	1.89	14.57
Fenton	33.3	12.56	2.84	128.08
Fe(II)	1.96	35.16	0	624.68
Fe(III)	28.16	6.14	9.46	555.77
H_2O_2	3.83	6	2.11	2.08

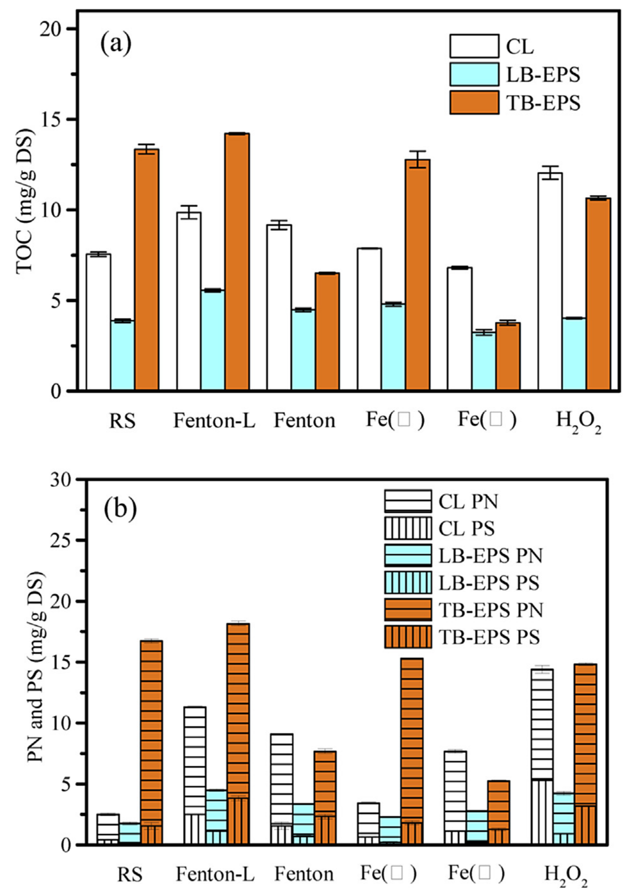

Fig. 4. (a) TOC content of CL, LB-EPS, and TB-EPS and (b) PN and PS content of CL, LB-EPS, and TB-EPS of the RS and the conditioned sludges.

of free water and the DSC endothermic curve area, as shown in Eq. (5) below:

$$FW = 0.00289 \times A + 0.09377 \quad (5)$$

where FW is the mass of free water (mg), and A is the endothermic curve area (mJ). Bound water of sludge is the amount of "unfreezable" water which is calculated as the difference between total and free water.

As shown in Fig. 5, the conditioned sludge of Fenton-L can reduce bound water of RS from 2.9 to 1.47 g/g DS. Bound water contents of the conditioned sludge of Fenton's reagent, Fe(III), H_2O_2, and Fe(II) are 1.58, 1.83, 2.36, and 2.66 g/g DS, respectively. The results agree well with the sludge dewatering performance, as shown in Fig. 3, which indicates that the more bound water in sludge, the poorer the sludge dewatering performance.

3.3.5. Particle size

As shown in Fig. 6, particle sizes of different sludges are in the following order: Fe(III) > Fe(II) > RS > Fenton ≈ Fenton-L > H_2O_2. Coagulants of Fe(III) and Fe(II) salts could neutralize the surface charge of the particles and the sludge particles would be destabilized. Sludge particles rapidly aggregated into large flocs. Then, sludge flocs densification was caused by double electric layer compression (Niu et al., 2013). The coagulation capability of Fe(III) is much better than that of Fe(II). Thus, the particle size of the sludge conditioned by Fe(III) was larger than that of sludge conditioned by Fe(II). The result is similar to Oikonomidis et al. (2010) who reported that flocs of activated sludge dosed with Fe(II) were

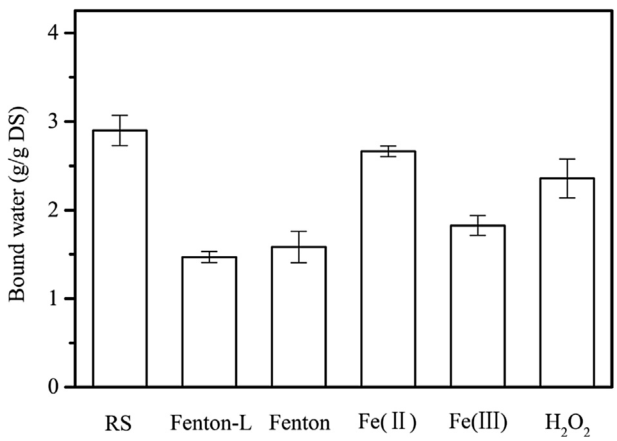

Fig. 5. Bound water content of the RS and the conditioned sludges.

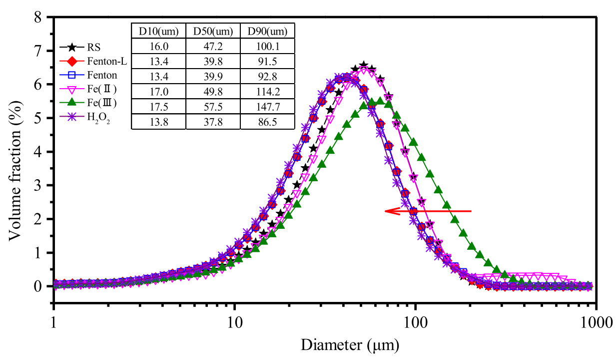

Fig. 6. Particle size distributions of the RS and the conditioned sludges.

more compact and smaller in size than those with Fe(III). So, the particle size of sludge conditioned by Fe(III) was apparently larger than sludge conditioned by Fe(II) or RS.

Sludge conditioned by H_2O_2 alone could effectively decrease the sludge particle size due to destruction of the EPS structure and breakage of dense sludge flocs into smaller particles by oxidation. Consequently, the particle size of the sludge conditioned by H_2O_2 alone is the smallest among all the specimens, as shown in Fig. 6. Fenton reaction degraded the organics from large molecular sizes into small ones via highly reactive hydroxyl radicals (Neyens et al., 2004; Tony et al., 2008). Therefore, the particle size of the sludge conditioned by Fenton's reagent was smaller than that of RS. Since the size of flocs with Fenton and Fenton-L are smaller than RS, Fenton and Fenton-L might be not suitable for use with belt filter press or centrifuge. However, Fenton and Fenton-L are proved to be effective for the deep dewatering for use with a diaphragm filter press in many studies (Neyens et al., 2004; Liu et al., 2013).

It is notable that the particle sizes of the conditioned sludge of Fenton or Fenton-L are apparently larger than those of the sludge conditioned by H_2O_2 alone. Fenton oxidation effect in sludge conditioning could degrade large sludge flocs into small ones. At the same time, Fe(III) generated in Fenton reaction can act as a coagulant. Thus the particles sizes of Fenton or Fenton-L are larger than those of the sludge conditioned by H_2O_2 alone.

On the basis of above-mentioned results and analysis, a two-step mechanism (Fenton oxidation and Fe(III) coagulation) was proposed, as shown in Fig. 7. In the first step, oxidation attributes to reactive hydroxyl radicals from Fenton reaction, and leads to EPS degradation and release of bound water, as shown in Figs. 4 and 5. Large particles of the sludge flocs were degraded and destructed into smaller particles, as shown in Fig. 6. In the second step, Fe^{3+} generated in Eq. (1) plays the role of coagulant, which agglomerates the smaller sludge particles with less bound water into larger dense particles. This Fenton oxidation and Fe(III) coagulation mechanism model could be further proven by the results of specific surface area and microstructural characterization.

3.3.6. *Specific surface area*

The prime sludge characteristics affecting dewatering performance appear to be the vast surface area of the finely divided particles (Karr and Keinath, 1978). Sludge particle surface is relatively large and highly active, which is typically associated with a large amount of water, which is hard to be dewatered (Katsiris and Kouzeli-Katsiri, 1987).

As shown in Table 6, the specific surface areas of the RS, the conditioned sludge of H_2O_2, and Fe(II) were comparatively large, at 153.2, 147.2, and 131.2 m^2/g, respectively. The specific surface areas of the conditioned sludge of Fenton-L, Fenton, and Fe(III) are comparatively smaller, at 49.0, 51.9, 56.9 m^2/g, respectively. The significant differences of specific surface area among those sludges are related to different Fe^{3+} contents of the sludge cakes (Table 5). The high Fe^{3+} content in the sludge results in a small specific surface area of the conditioned sludge. The less specific surface area of the sludge flocs contributes to less associated water, and it can improve sludge dewatering. Combinedly considering the results in Table 6 and Fig. 3, sludge with a smaller specific surface area shows lower SRF and CST and lower water content of sludge cakes, thus exhibiting better sludge dewatering performance.

In addition, as shown in Fig. 8, sludge with a higher Fe^{3+} content has less pore volume of small pores (1–10 nm) and more pore volume of large pores (>10 nm) than those of sludges with less Fe^{3+} content. This phenomenon can be attributed to the ability of charge neutralization and double electric layer compression of Fe^{3+} coagulation which changes the sludge surface morphology. Porosity is normally classified as macro pores (>50 nm), meso pores (2–50 nm), and micro pores (<2 nm) (Shi, 1996). The small pores (1–10 nm) consist of micro and small parts of meso pores. The decrease in small pores can reduce water affinity of sludge flocs. The large pores (>10 nm) mainly consist of meso and macro pores. These large pores in sewage sludge can act as channels of water flow in a permeable and porous structure, and then it can improve permeability of sludge under mechanically dewatering.

In summary, as shown in Fig. 8, the dewatered sludge cakes conditioned by Fenton-L, Fenton, and Fe(III) have less small pores (1–10 nm) contributing to the affinity of water in sludge, but more large pores (>10 nm) contributing to a permeable, rigid lattice structure in sludge cake. These characteristics of pores distributions of sludge cakes are consistent with the sludge dewaterability.

3.3.7. *Microstructure*

As shown in Fig. 9, the microstructures of the RS appeared continuously dense, which revealed poor water permeability and poor dewaterabilty (Fig. 9a). On the other hand, porous structures were generated from sludge conditioned by Fenton-L and Fenton's reagent, which revealed good water permeability and an excellent dewaterabilty (Fig. 9b and c). The microstructure of the sludge conditioned by Fe(II) was similar to that of RS, which had dense morphology and was less porous (Fig. 9d). Agglomerated sludge particles and porous structure appeared in the sludge conditioned by Fe(III) (Fig. 9e), possessed a good water permeability and dewaterabilty. Few pores appeared on the surface of the sludge conditioned by H_2O_2, and no flocs agglomeration was observed (Fig. 9f), which revealed a poor water permeability and poor dewaterabilty. Generally, morphologies of RS and various conditioned sludges further illustrated the results of conditioning and

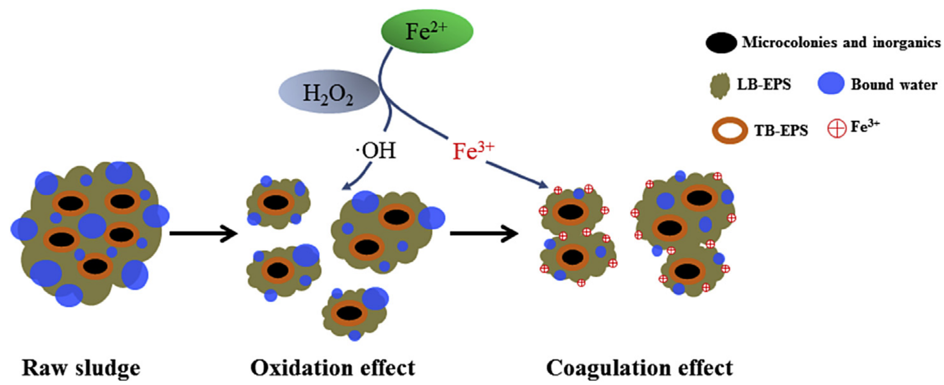

Fig. 7. Fenton oxidation and Fe(III) coagulation two-step mechanism of Fenton conditioning of sewage sludge.

Table 6
BET surface area of the dewatered sludge cakes.

Symbol	BET surface area (m^2/g)
RS	153.2
Fenton-L	49.0
Fenton	51.9
Fe(II)	131.2
Fe(III)	56.9
H_2O_2	147.2

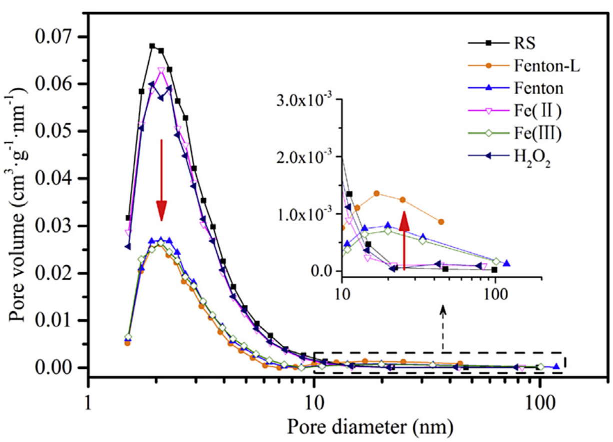

Fig. 8. BJH mesopore size distributions of the RS and the conditioned sludges.

dewatering experiments, and also provided the support of microstructure characteristics for our proposed two-step mechanism.

3.4. Economic analysis

Table 7 shows a preliminary cost estimate on sludge conditioning with optimal Fenton-L. The optimal dosages in Section 3.1 were used for this economic analysis on the composite conditioner of Fenton's reagent and lime (Fenton-L). On the other hand, ferric chloride and lime, which was commonly used in sludge deep-dewatering (Deneux-Mustin et al., 2001). The organic matter of Fenton-L conditioned sludge cake was 54.7 wt%. Compared with 58.9 wt% organic matter of raw sludge, the addition of Fe^{2+} and lime in Fenton-L increased a little inorganic matter in the final dryness of the sludge cake. Fenton-L has oxidation effect and better coagulation effect (31.9 mg Fe^{3+}/g DS, as shown in Table 5) compared with sludge conditioned by ferric chloride and lime (10.37 mg Fe^{3+}/g DS). Therefore, the dose of Fenton-L was smaller than $FeCl_3$ and lime (0.28 g/g DS (ignore H_2O_2) vs 0.55 g/g DS), the dewatering performance was almost the same (water content of sludge cakes was 62.4 wt% vs 61.8 wt%). The calculated cost of the composite conditioner using Fenton's reagent and lime is USD$ 43.8/t DS, which is much less than that of commonly used ferric chloride and lime (USD$ 54/t DS). Due to a much large dosage of lime, the filtrate pH of the sludge conditioned by ferric chloride and lime is 12.4, compared to pH of 6.6, close to neutrality, by using the optimal composite Fenton-L conditioner in this study.

For the case of 100,000 m^3/d Tangxun Lake Municipal WWTP with a daily dry sludge production of 16 t/d, the total generation of dry sludge is 5840 t DS/y. The annual costs of the composite conditioners using Fenton's reagent and lime, and using ferric chloride and lime are USD$ 255,792/y, and USD$ 315,360/y, respectively. The dewatered sludge cakes are transported to a landfill for final disposal at a cost of USD$ 8/t of sludge cake. Considering that ferric iron and overdosed lime are still remained in the sludge cakes, the annual production of the sludge cakes that are conditioned by Fenton's reagent and lime and by ferric chloride and lime are 16,296 t and 22,914 t, respectively. Therefore, the landfilling cost of the conditioned sludge cakes are USD$ 130,268/y and USD$ 183,312/y, respectively. Additional USD$ 8/t DS or USD$ 46,720/y is needed for filtrate neutralization of sludge conditioned by ferric chloride and lime. Hence, the final disposal costs of sludge cakes conditioned by Fenton's reagent and lime and conditioned by ferric chloride and lime are USD$ 22.3/t DS and USD$ 39.4/t DS, respectively.

The total operational cost of Fenton's reagent and lime is USD$ 66.1/t DS or USD$ 385,864/y, which leads to a saving of USD$ 27.3/t DS or USD$ 159,527/y, compared to using ferric chloride and lime.

4. Conclusions

After the RSM optimization, the water content of the sludge cakes could be reduced to 55.8 ± 0.6 wt%, and the pH of the filtrate was 6.6 ± 0.2 when dosages of H_2SO_4, Fe^{2+}, H_2O_2, and lime were 0, 47.9, 34.3 and 43.2 mg/g DS, respectively. Fenton conditioning of sludge without acidification pretreatment could also obtain a good dewatering efficiency, which implies that Fenton oxidation is not the only role in sludge conditioning. The Fe^{3+} ions from the Fenton reaction worked as coagulants. Furthermore, without addition of acid in pretreatment can simplify the conditioning process and reduce the dosage of the subsequent neutralizer.

Based on the experimental results, a two-step mechanism of Fenton oxidation and Fe(III) coagulation was proposed to explain the conditioning effect of Fenton reaction. Oxidation first degraded

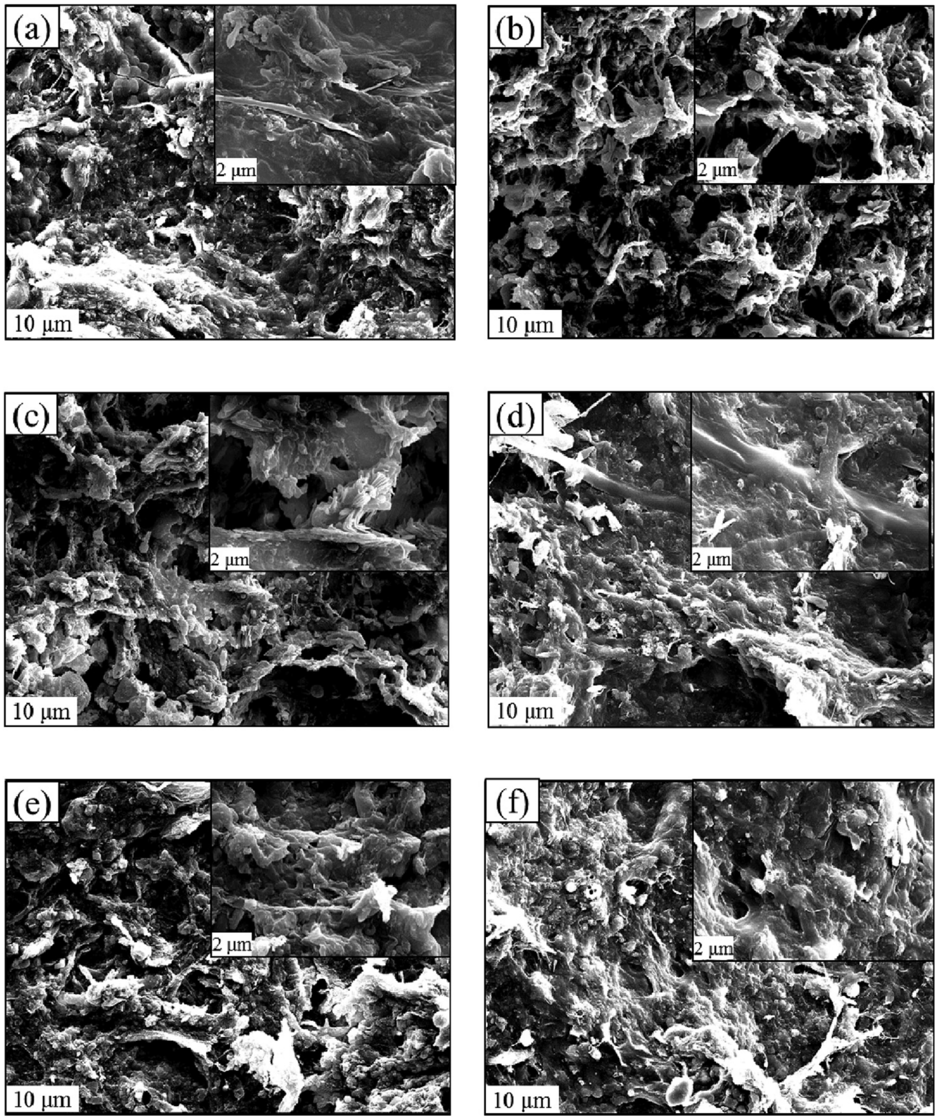

Fig. 9. SEM images of dewatered sludge cakes: (a) the RS, (b) the sludge conditioned by Fenton's reagent and lime, (c) the sludge conditioned by Fenton's reagent, (d) the sludge conditioned by ferrous sulfate, (e) the sludge conditioned by ferric chloride, and (f) the sludge conditioned by hydrogen peroxide.

Table 7
Run cost analysis of sludge conditioning with optimal Fenton-L in this study compared with traditional conditioners of $FeCl_3$ and lime.

Conditioners	Dosage (t/t DS)	Unit price (USD$/t)	Cost (USD$/t DS)	Total cost	Water content of dewatered sludge cake (wt%)	VSS/TSS (%)	pH of filtrate
$FeSO_4 \cdot 7H_2O$	0.240	70.0	16.8	43.8	62.4	54.7	6.6
H_2O_2	0.124	200.0	24.8				
Lime	0.043	50.0	2.2				
$FeCl_3 \cdot 6H_2O$	0.050	580.0	29.0	54.0	61.8	35.8	12.4
Lime	0.500	50.0	25.0				

EPS and reduced the sludge particle size. Fe(III) coagulation then agglomerated the small particles into large and compact particles. The high Fe^{3+} content in sludge sharply reduced the specific surface area of sludge particles. Sludge conditioned by Fenton's reagent could convert a large amount of bound water to free water. Porous structure and coagulation phenomenon appeared in the sludge conditioned by Fenton's reagent or Fe(III). Using a composite conditioner of optimal Fenton-Lime presents advantages in sludge dewatering and subsequent disposal.

Acknowledgments

The research is supported by the National Natural Science Foundation of China (51508214), the Project of Innovative and Interdisciplinary Team of HUST (2015ZDTD027), and the Research Project of Chinese Ministry of Education (113046A). Additionally, we thank Dr Huijie Hou (an associate Professor in HUST) for paper revision. We would also like to thank the Analytical and Testing Center of Huazhong University of Science and Technology for

providing experimental measurements.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.03.016.

References

APHA, 1998. Standard Methods for the Examination of Water and Wastewater, nineteenth ed. American Public Health Association, Washington, D.C.

Arnold, S.M., Hickey, W.J., Harris, R.F., 1995. Degradation of atrazine by fenton's reagent: condition optimization and product quantification. Environ. Sci. Technol. 29 (8), 2083–2089.

Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J. Am. Chem. Soc. 73 (1), 373–380.

Bokare, A.D., Choi, W., 2014. Review of iron-free fenton-like systems for activating H_2O_2 in advanced oxidation processes. J. Hazard. Mater. 275, 121–135.

Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60 (2), 309–319.

Chu, C.P., Lee, D.J., Chang, C.Y., 2005. Energy demand in sludge dewatering. Water Res. 39 (9), 1858–1868.

Deneux-Mustin, S., Lartiges, B.S., Villemin, G., Thomas, F., Yvon, J., Bersillon, J.L., Snidaro, D., 2001. Ferric chloride and lime conditioning of activated sludges: an electron microscopic study on resin-embedded samples. Water Res. 35 (12), 3018–3024.

DuBois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric method for determination of sugars and related substances. Anal. Chem. 28 (3), 350–356.

Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. Water Res. 30 (8), 1749–1758.

General Administration of Quality Supervision, 2009. Inspection and quarantine of the People's Republic of China (GAQSIQ). In: Disposal of Sludge from Municipal Wastewater Treatment Plant- Quality of Sludge for Co-landfilling (GB/T 23485-2009), pp. 2.

Huo, M., Zheng, G., Zhou, L., 2014. Enhancement of the dewaterability of sludge during bioleaching mainly controlled by microbial quantity change and the decrease of slime extracellular polymeric substances content. Bioresour. Technol. 168, 190–197.

Karr, P.R., Keinath, T.M., 1978. Influence of particle size on sludge dewaterability. J. Water Pollut. Control Fed. 50, 1911–1930.

Katsiris, N., Kouzeli-Katsiri, A., 1987. Bound water content of biological sludges in relation to filtration and dewatering. Water Res. 21 (11), 1319–1327.

Li, X.Y., Yang, S.F., 2007. Influence of loosely bound extracellular polymeric substances (EPS) on the flocsculation, sedimentation and dewaterability of activated sludge. Water Res. 41 (5), 1022–1030.

Liu, X.-M., Sheng, G.-P., Luo, H.-W., Zhang, F., Yuan, S.-J., Xu, J., Zeng, R.J., Wu, J.-G., Yu, H.-Q., 2010. Contribution of extracellular polymeric substances (EPS) to the sludge aggregation. Environ. Sci. Technol. 44 (11), 4355–4360.

Liu, H., Yang, J., Shi, Y., Li, Y., He, S., Yang, C., Yao, H., 2012. Conditioning of sewage sludge by fenton's reagent combined with skeleton builders. Chemosphere 88 (2), 235–239.

Liu, H., Yang, J., Zhu, N., Zhang, H., Li, Y., He, S., Yang, C., Yao, H., 2013. A comprehensive insight into the combined effects of Fenton's reagent and skeleton builders on sludge deep dewatering performance. J. Hazard. Mater. 258, 144–150.

Long, B., Yang, C.Z., Pu, W.H., Yang, J.K., Shi, Y.F., Wang, J., Bai, J., Zhou, X.Y., Jiang, G.S., Li, C.Y., 2014. The stability of aerobic granular sludge treating municipal sludge deep dewatering filtrate in a bench scale sequencing batch reactor. Bioresour. Technol. 169, 244–250.

Lu, M., Lin, C., Liao, C., Ting, W., Huang, R., 2001. Influence of pH on the dewatering of activated sludge by fenton's reagent. Water Sci. Technol. 44 (10), 327–332.

Lu, M.C., Lin, C.J., Liao, C.H., Huang, R.Y., Ting, W.P., 2003. Dewatering of activated sludge by Fenton's reagent. Adv. Environ. Res. 7 (3), 667–670.

Montgomery, D.C., 2009. Design and Analysis of Experiments, sixth ed. John Wiley, New York.

Neyens, E., Baeyens, J., 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. J. Hazard. Mater. 98 (1–3), 33–50.

Neyens, E., Baeyens, J., Weemaes, M., De Heyder, B., 2002. Advanced biosolids treatment using H_2O_2-oxidation. Environ. Eng. Sci. 19 (1), 27–35.

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

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

Niu, M., Zhang, W., Wang, D., Chen, Y., Chen, R., 2013. Correlation of physicochemical properties and sludge dewaterability under chemical conditioning using inorganic coagulants. Bioresour. Technol. 144, 337–343.

Oikonomidis, I., Burrows, L.J., Carliell-Marquet, C.M., 2010. Mode of action of ferric and ferrous iron salts in activated sludge. J. Chem. Technol. Biotechnol. 85 (8), 1067–1076.

Rasmussen, H., Nielsen, P.H., 1996. Iron reduction in activated sludge measured with different extraction techniques. Water Res. 30 (3), 551–558.

Schnell, S., Ratering, S., Jansen, K.-H., 1998. Simultaneous determination of iron (III), iron (II), and manganese (II) in environmental samples by ion chromatography. Environ. Sci. Technol. 32 (10), 1530–1537.

Shi, H., 1996. Activated carbons and double layer capacitance. Electrochimica Acta 41 (10), 1633–1639.

Show, K.-Y., Mao, T., Lee, D.-J., 2007. Optimisation of sludge disruption by sonication. Water Res. 41 (20), 4741–4747.

Skinner, S.J., Studer, L.J., Dixon, D.R., Hillis, P., Rees, C.A., Wall, R.C., Cavalida, R.G., Usher, S.P., Stickland, A.D., Scales, P.J., 2015. Quantification of wastewater sludge dewatering. Water Res. 82, 2–13.

Thomas, L., Jungschaffer, G., Sprössler, B., 1993. Improved sludge dewatering by enzymatic treatment. Water Sci. Technol. 28 (1), 189–192.

Tony, M.A., Zhao, Y.Q., Fu, J.F., Tayeb, A.M., 2008. Conditioning of aluminium-based water treatment sludge with Fenton's reagent: effectiveness and optimising study to improve dewaterability. Chemosphere 72 (4), 673–677.

Tony, M.A., Zhao, Y.Q., Tayeb, A.M., 2009. Exploitation of Fenton and Fenton-like reagents as alternative conditioners for alum sludge conditioning. J. Environ. Sciences China 21 (1), 101–105.

Vaxelaire, J., Cézac, P., 2004. Moisture distribution in activated sludges: a review. Water Res. 38 (9), 2215–2230.

Vesilind, P.A., 1994. The role of water in sludge dewatering. Water Environ. Res. 66 (1), 4–11.

Zhai, L.-F., Sun, M., Song, W., Wang, G., 2012. An integrated approach to optimize the conditioning chemicals for enhanced sludge conditioning in a pilot-scale sludge dewatering process. Bioresour. Technol. 121, 161–168.

Zhang, H., Yang, J., Yu, W., Luo, S., Peng, L., Shen, X., Shi, Y., Zhang, S., Song, J., Ye, N., 2014. Mechanism of red mud combined with Fenton's reagent in sewage sludge conditioning. Water Res. 59, 239–247.

Zhen, G., Lu, X., Li, Y., Zhao, Y., Wang, B., Song, Y., Chai, X., Niu, D., Cao, X., 2012. Novel insights into enhanced dewaterability of waste activated sludge by Fe (II)-activated persulfate oxidation. Bioresour. Technol. 119, 7–14.

Zhou, X., Wang, Q., Jiang, G., Zhang, X., Yuan, Z., 2014. Improving dewaterability of waste activated sludge by combined conditioning with zero-valent iron and hydrogen peroxide. Bioresour. Technol. 174, 103–107.