



A comprehensive insight into the combined effects of Fenton's reagent and skeleton builders on sludge deep dewatering performance



Huan Liu^{a,c}, Jiakuan Yang^{a,*}, Nairuo Zhu^a, Hao Zhang^a, Ye Li^b, Shu He^b, Changzhu Yang^a, Hong Yao^c

^a School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, PR China

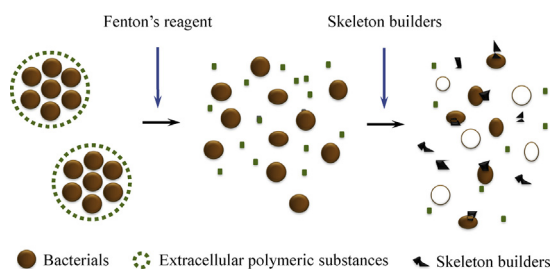
^b Universtar Science & Technology (Shenzhen) Co., Ltd., Shenzhen, Guangdong, 518057, PR China

^c State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, PR China

HIGHLIGHTS

- There is strong synergistic effect between Fenton's reagent and skeleton builders.
- Through RSM optimization, water content of sludge cake can be reduced to 49.54%.
- The composite conditioner can make sludge flocs disintegrate into small particles.
- The composite conditioner can promote senescence and death of microorganism.
- The composite conditioner can provide a rigid porous structure in sludge flocs.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 March 2013

Received in revised form 21 April 2013

Accepted 23 April 2013

Available online 30 April 2013

Keywords:

Sewage sludge
Composite conditioner
Dewaterability
Oxidation
Skeleton builders

ABSTRACT

Conditioning sewage sludge with Fenton's reagent and skeleton builders has been proved to be an effective mean to achieve deep dewatering. This work aimed to give a comprehensive insight into the mechanism involved. The results show that significant synergistic effect existed between Fenton's reagent and skeleton builders. With the optimum dosage, water content of dewatered sludge cake could be reduced to $49.5 \pm 0.5\%$. Furthermore, raw sludge existed in the form of zoogloea and its flocs surface was plate-like. After Fenton oxidation, partial of extracellular polymeric substances (EPS) was destroyed and the amounts of protein and polysaccharide dissolved in filtrate increased. Meanwhile, sludge flocs turned into smaller ones. After adding skeleton builders, constantly-changing environment promoted senescence and death of microorganism. A large area of plate-like structure disappeared, instead of which were holes. Irregular non-living things inlaid or pierced microbial cells, promoting the conversion from bound water to free water as well as further reduction of the sludge particle size. Additionally, these irregular substances could form a rigid porous structure under high pressure, which could transmit the stresses to the sludge internal parts and provide outflow channels for free water. Consequently, conditioned sludge was suitable for high pressure deep dewatering.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Sewage sludge is difficult to dewater, which is a bottleneck in sludge treatment and disposal process. Nowadays, the dewatered sludge cake which conditioned with traditional organic polymer

* Corresponding author. Tel.: +86 27 87792207; fax: +86 27 87792101.

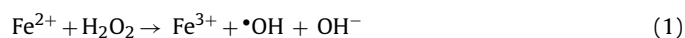
E-mail addresses: jkyang@mail.hust.edu.cn, yjiakuan@hotmail.com (J. Yang).

Table 1
Characteristics of RS.

Batch	pH	Water content (%)	COD (mg/L)	SCOD (mg/L)	TSS (g/L)	VSS/TSS (%)	Protein content (mg/L)	SRF (10 ¹³ m/kg)
1	6.0	96.6	24,900	357	31.5	0.47	4958	1.0
2	6.5	95.9	35,471	146	43.0	0.42	6097	1.5

still keeps a high water content of 75–85% (w/w) [1,2], failing to meet the increasingly stringent regulations and the requirements of subsequent disposal. Therefore, new technologies are urgently needed to enhance dewaterability so as to achieve deep dewatering of sewage sludge. According to previous researches, effective high-pressure dewatering requires making extracellular polymeric substances (EPS) dissolved, in which bound water retained [3–5], and maintaining porous structure, through which water withdraw [6,7].

Fenton peroxidation has been demonstrated to be a promising advanced sludge treatment method for degrading the EPS [8,9]. Fenton's reagent is a mixture of H₂O₂ and Fe²⁺. As presented in Eq. (1) [10], Fe²⁺ catalyzes the decomposition of H₂O₂ to form •OH, which is capable of decomposing a number of organic substances.



In recent years, there are many researches focusing on the enhancement in filtration and dewatering efficiency of sludge conditioned by Fenton's reagent [11–14]. For instance, with the extremely high addition of 5000 mg/L Fe²⁺ and 6000 mg/L H₂O₂, the specific resistance to filtration (SRF) and capillary suction time (CST) were reduced from 9.162 × 10⁹ m/kg to 6.149 × 10⁹ m/kg and from 30.5 s to 15.7 s, respectively [14]. Although Fenton peroxidation is an effective mean to destroy the structure of EPS, it cannot form porous structure in sludge cake. Thus, conditioning effects are not satisfactory. In addition, high dosage of Fenton's reagent lead to high cost, hampering its practical application at larger scales.

Meanwhile, efforts have been put into forming porous structure in highly compressible sludge cakes as well. To avoid the closure of water filtration channel under high pressure, physical conditioners (skeleton builders) are commonly used to form a permeable and rigid lattice structure in sludge cakes [7]. Hydrated lime and fly ash were the earliest skeleton builders used by Zall et al. [6]. Then a large number of studies have been conducted during the past few decades, proving the ability of coal fines, coal fly ash modified by sulfuric acid (MCFA), lignite and etc. in remaining mechanical strength and permeability of sludge cakes under relative high filter pressure [15–20]. Although using skeleton builders is an effective mean to form porous structure in sludge cake, it cannot destroy the structure of EPS. Thus, conditioning effects are also not satisfactory. In addition, large dosages of skeleton builders lead to expanding sludge volume, increasing the burden the subsequent sludge disposal.

In order to make best use of the advantages and bypass the disadvantages of Fenton's reagent and skeleton builders, our primary study [21] reported the significant enhancement in dewaterability of sludge conditioned by an inorganic composite conditioner (Fenton's reagent combined with lime and ordinary Portland cement). At optimal condition which was obtained through a series of single-factor experiments, the SRF reduction efficiency reached up to 95%. To further optimize this composite conditioning – deep

dewatering technique, a comprehensive in-depth investigation on related mechanisms are needed. Therefore, in this study, the interactions between Fenton's reagent and skeleton builders have been analyzed through response surface methodology (RSM). EPS decomposition and rigid skeleton builders' formation behavior were studied by direct observation of sludge properties.

2. Experimental

2.1. Experimental materials

Raw sludge (RS) used in this study was a mixture of sludge from the primary and secondary sedimentation tanks of a wastewater treatment plant, Wuhan, China. The main characteristics of RS, which were stored at 4 °C, are listed in Table 1. Quick lime and 42.5 ordinary Portland cement (OPC) were used as skeleton builders, which were milled and sieved to less than 0.5 mm in particle size. Their chemical compositions are summarized in Table 2.

2.2. Conditioning and dewatering process

50 L of sludge samples were carefully transferred into a conditioning tank. Although Neyens et al. [1] reported pH 3 to be more optimal, our primary study [21] has demonstrated that pH 5 was the optimal condition. In this composite conditioning process, strong acidic caused by Fenton's reagent would weaken the effectiveness of strong alkaline skeleton builders. Therefore, sludge pH was adjusted to 5 by adding H₂SO₄ (40 wt%). Afterwards, Fe²⁺ (FeSO₄) solution and H₂O₂ were added into the sludge successively. When 60 min of Fenton peroxidation was completed, the sludge mixture was further conditioned by OPC and lime. Finally, the sludge was dewatered by the filter press (shown in Fig. 1) consisting of a 40 min pressing phase with a pressure of 0.6–0.9 MPa and a 5 min filter cloth expanding phase with a pressure of 1.0–1.1 MPa.

2.3. Experimental design

A Box–Behnken experimental design [22] was chosen to evaluate the combined effects of the four independent variables at three levels (all data are based on dry sludge solids) which were determined based on preliminary tests [23], as shown in Table 3. All the experiments were conducted in triplicate and the average of the water content of the dewatered sludge cakes was taken as response (Y). When experimental data were analyzed by the RSM procedure of the statistical analysis system and fitted to an empirical quadratic model, quadratic equation for the variables was expressed as Eq. (2) [22]:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j \quad (2)$$

Table 2
Chemical compositions of the skeleton builders.

Skeleton builders	SiO ₂	CaO	Al ₂ O ₃	Cl ⁻	MgO	Na ₂ O+K ₂ O	Fe ₂ O ₃	SO ₃	LOI ^a
Lime	6.7	60.1	–	–	1.5	–	–	–	22.6
OPC	20.6	58.8	5.4	0.0	3.3	0.6	2.9	2.4	4.0

^a LOI = loss of ignition.

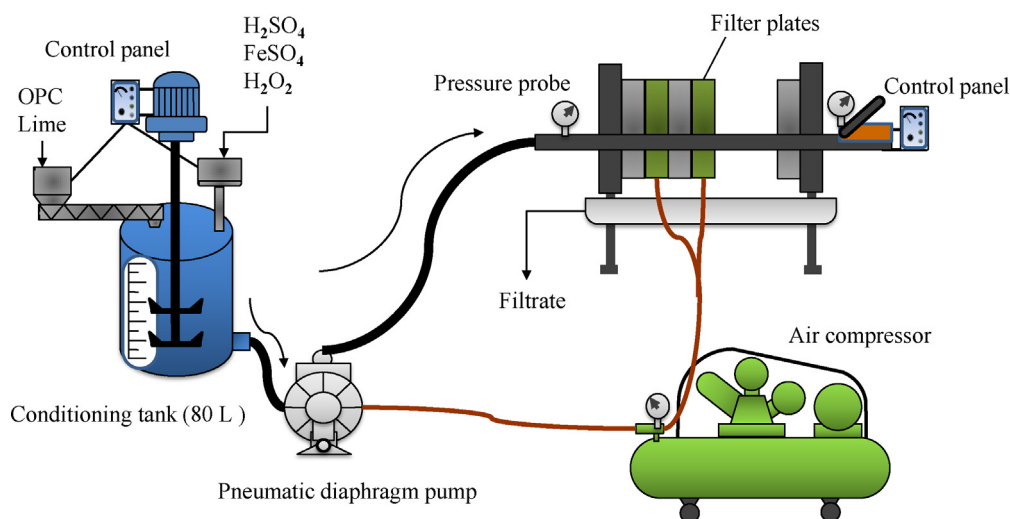


Fig. 1. Filter press dewatering system.

where Y is the predicted response, water content of sludge cakes; X_i and X_j ($i = 1, 2, 3, 4$ and $j = 1, 2, 3, 4$) are the coded value of independent variables; $\beta_0, \beta_i, \beta_{ii}$ and β_{ij} ($i = 1, 2, 3, 4$ and $j = 1, 2, 3, 4$) are the ij th model regression coefficient parameters which are estimated by multiple linear regression analysis using the software Design Expert.

2.4. Analytical methods

To clarify the conditioning mechanism of Fenton's reagents, OPC and lime, a set of experiments with different formulations (S-1: raw sludge; S-2: sludge conditioned by Fenton's reagent; S-3: sludge conditioned by OPC; S-4: sludge conditioned by lime; S-5: sludge conditioned by Fenton's reagent and OPC; S-6: sludge conditioned by Fenton's reagent and lime; S-7: sludge conditioned by OPC and lime; S-8: sludge conditioned by Fenton's reagent, OPC and lime.) were conducted. The dosages of each component are determined by the optimized results from RSM. Protein content in filtrate was determined by the modified Lowry method [24] using bovine albumin as standard, while polysaccharide content in filtrate was measured by phenol sulfuric acid method [25], using glucose as the standard. The mean particle size of the conditioned sludge flocs was determined by Mini laser particle size analyzer (Marlvern, UK), which enables the measurement in the range of 0.05–900 μm . The biosolids of conditioned sludge were detected by optical microscope (OLYMPUS BX60) directly. Simultaneously, portions of conditioned sludge were freeze-dried for scanning electron microscopy (FEI Quanta 450 FEG) observation. Ultrathin sections were prepared according to Deneux–Mustin's method [26], and then examined with a FEI Tecnai G² 20TWIN TEM at an accelerating voltage of 200 kV.

Table 3
Range and levels of natural and corresponded coded variables for RSM of the inorganic composite conditioner to condition sewage sludge.

Variable	Symbols		Range and levels		
	Natural	Coded ^a	-1	0	1
Fe ²⁺ dosage (mg/g)	ξ_3	X_1	0	40	80
H ₂ O ₂ dosage (mg/g)	ξ_4	X_2	0	32	64
OPC dosage (mg/g)	ξ_5	X_3	0	175	350
Lime dosage (mg/g)	ξ_6	X_4	0	225	450

^a $X_1 = (\xi_3 - 40)/40$; $X_2 = (\xi_4 - 32)/32$; $X_3 = (\xi_5 - 175)/175$; $X_4 = (\xi_6 - 225)/225$.

3. Results and discussion

3.1. RSM analysis

The conditioning schemes and the results of the three-level experiments based on a Box–Behnken design are presented in Table S1. The water content of sludge cakes varied from 49.9% to 77.7%.

In order to obtain the optimal conditions to achieve the lowest water content and to determine whether there were interactions between them, a multiple second-order polynomial equation was established as Eqs. (3) and (4):

$$Y_{\text{CODED}} = 57.75 - 5.11X_1 - 4.53X_2 - 4.01X_3 - 4.78X_4 + 2.09X_1X_2 + 2.38X_1X_3 + 2.54X_1X_4 - 0.30X_2X_3 + 2.42X_2X_4 + 1.11X_3X_4 + 3.61X_1^2 + 4.04X_2^2 - 0.05X_3^2 + 0.42X_4^2 \quad (3)$$

$$Y_{\text{ACTUAL}} = 94.44233 - 0.48354\xi_1 - 0.52580\xi_2 - 0.040594\xi_3 - 0.051940\xi_4 + 1.63281 \times 10^{-3}\xi_1\xi_2 + 3.40714 \times 10^{-4}\xi_1\xi_3 + 2.81667 \times 10^{-4}\xi_1\xi_4 - 5.31250 \times 10^{-5}\xi_2\xi_3 + 3.35417 \times 10^{-4} \times \xi_2\xi_4 + 2.81905 \times 10^{-5}\xi_3\xi_4 + 2.25568 \times 10^{-3} \times \xi_1^2 + 3.94808 \times 10^{-3} \times \xi_2^2 - 1.62177 \times 10^{-6}\xi_3^2 + 8.32757 \times 10^{-6}\xi_4^2 \quad (4)$$

where Y_{ACTUAL} is the response (the water content of sludge cake); X_1 is Fe²⁺ dosage; X_2 is H₂O₂ dosage; X_3 is OPC dosage; X_4 is lime dosage; $\xi_1, \xi_2, \xi_3, \xi_4$ are the coded values of the dosages of Fe²⁺, H₂O₂, OPC and lime, respectively.

Table S2 illustrates variance analysis for response surface quadratic model. The Model F -value of 20.52 implies that the model is significant. There is only a 0.01% chance that a "Model F -value" this large will occur due to noise. Values of "Prob > F " less than 0.0500 indicates that model terms are significant. The F -value of 2.72 implies that the "Lack of Fit" is not significant relative to the pure error, which is good for the model. An analysis of variance (ANOVA), conducted to check the adequacy and the significance of the response surface quadratic model, is listed in Table S3. The squared regression statistic (R^2) was 0.9535, and the "Pred R -Squared" of 0.7574 was in reasonable agreement with the "Adj R -Squared" of 0.9071, which indicated a good consistency between

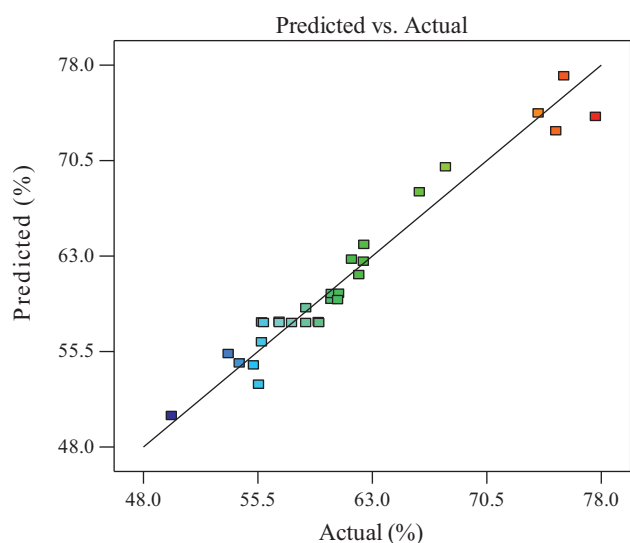


Fig. 2. Comparison of predicted and actual results.

experimental and predicted values, implying that the mathematical model was very reliable in the present study. “Adeq Precision” measures the signal to noise ratio. A ratio greater than 4 was desirable. The value of 17.475 indicated an adequate signal. In addition, the coefficient of variation was generally required to be less than 10%. The value of C.V.% (coefficient of variation), 3.48%, showed high accuracy and good reproducibility of this model. From Fig. 2, the actual and predicted experimental values were distributed along the linear function, indicating that these values were in a significant correlation. Thus, it can be concluded that the polynomial model is a reliable model to describe the composite reaction behavior in the sewage sludge conditioning.

The *F*-value denotes the significance in the model equation [27,28]. The regression and corresponding value of “Prob > *F*” less than 0.0500 indicates that model terms are significant while value greater than 0.1000 indicates the opposite. As shown in Table 4, independent factors A (Fe^{2+} dosage), B (H_2O_2 dosage), C (OPC dosage) and D (lime dosage) all have significant effects on the water content of sludge cakes. The negative coefficients demonstrates a linearly decreasing water content. The quadratic effects (A^2 , B^2) and the interactive coefficients (AC, AD and BD) also exhibit significant influences.

The three-dimensional response surfaces (Fig. 3) and their corresponding two-dimensional circular contour plots (Fig. S1) generated by Design Expert, are the visual illustration of the relations between two interacting model terms with response,

Table 4
Estimated regression coefficients.

Factor	Coefficient estimate	DF	Standard deviation	<i>F</i> -value	Prob (<i>P</i>) > <i>F</i>
Intercept	57.75	1	0.59		
A- Fe^{2+} dosage	-5.11	1	0.61	69.54	<0.0001
B- H_2O_2 dosage	-4.53	1	0.61	54.64	<0.0001
C-OPC dosage	-4.01	1	0.61	42.68	<0.0001
D-Lime dosage	-4.78	1	0.61	60.86	<0.0001
AB	2.09	1	1.06	3.78	0.0692
AC	2.38	1	1.06	5.04	0.0414
AD	2.54	1	1.06	5.70	0.0317
BC	-0.30	1	1.06	0.078	0.7835
BD	2.42	1	1.06	5.17	0.0392
CD	1.11	1	1.06	1.09	0.3137
A^2	3.61	1	0.83	18.73	0.0007
B^2	4.04	1	0.83	23.50	0.0003
C^2	-0.050	1	0.83	0.003547	0.9534
D^2	0.42	1	0.83	0.26	0.6211

while the third and fourth factors were kept constant at their respective zero levels. It can be seen from Fig. 3a that a significant reduction of water content (75.6% → 55.9%) was achieved when the Fe^{2+} and H_2O_2 concentration increased. Although the enhancement of sludge dewaterability occurred at a broad range of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ dosages, they could only significantly reduced the water content of sludge cakes when $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ dosages were more than 16/20 mg/g, respectively. The lowest water content predicted was located within high Fe^{2+} dosage of 40–80 mg/g and H_2O_2 dosage of 30–62 mg/g. At bigger dosages of H_2O_2 , the water content reduction rate was slightly affected negatively. The reason why excessive addition of H_2O_2 caused a negative impact on dewatering performance of sludge might be connected with excessive disintegration of cell membranes. In this case, macro flocs would be broke up, resulting in the production of a large amount of cell debris, which is unfavorable to sludge dewatering.

Fig. 3b reveals that Fe^{2+} dosage and OPC dosage have strong synergistic effect on the reduction of water content (75.1% → 55.9%). As shown in Fig. S1b, at Fe^{2+} dosage of 20–78 mg/g, an increase in OPC dosage has a positive effect on water content reduction. In the similar way, Figs. 3c and S1c display the significant enhancement in water content reduction when the lime dosage increases.

Figs. 3d and S1d demonstrate that an increase in H_2O_2 concentration could reduce the water content (67.8% → 55.9%) of sludge cakes on a certain range; beyond that range less reduction of water content was observed. For OPC, the larger the addition was, the lower the water content of sludge cakes was. This tendency also applied to the combination of lime and H_2O_2 , seen as Figs. 3e and S1e.

Figs. 3f and S1f present that response surface of the dosages of OPC and Lime vs. predicted water content of sludge cakes is almost flat, suggesting no significant interaction between OPC and lime. It can also be inferred that bigger dosages of OPC and lime are positively connected with lower water content.

The response surface analysis of the dosage of Fe^{2+} , H_2O_2 and the two skeleton builders provides the statistical foundation to achieve the lowest water content of sludge cakes.

Design Expert software and response surface analysis were used to determine optimum conditions of the operating variables in the composite conditioning. Since the water content of dewatered cakes and total amount of skeleton builders are the two key factors in the dewatering process, two sets of constraints were set as follows: (A) All the factors were in range while water content of dewatered cakes was minimized (at least lower than 50%). (B) The total amounts of OPC-lime addition were less than 500 mg/g while water content of dewatered sludge cakes was minimized.

Two additional experiments using each optimum operating conditions above were conducted to validate the model. The selection of the optimum dosages was both water-content-oriented and cost-oriented. The solutions of process variables and experimental results are listed in Table 5. The replicate experiments yielded dewatered cakes with water content of $49.5 \pm 0.5\%$, $51.2 \pm 1.4\%$, $53.8 \pm 0.6\%$ and $53.8 \pm 0.9\%$, respectively, which were in close agreement with the model prediction. The results clearly demonstrate the effectiveness of the model to optimize the composite conditioning effects.

3.2. Mechanism clarification

For traditional centrifugal dewatering or vacuum filtration of sludge conditioned by organic polymer, it is well known that increase in particle size and neutralization of negatively charge are in favor of improving sludge dewaterability [29,30]. But for high pressure dewatering such as filter press, different results were obtained. As shown in Fig. 4, the amount of large flocs decreased while that of small ones increased after conditioning process,

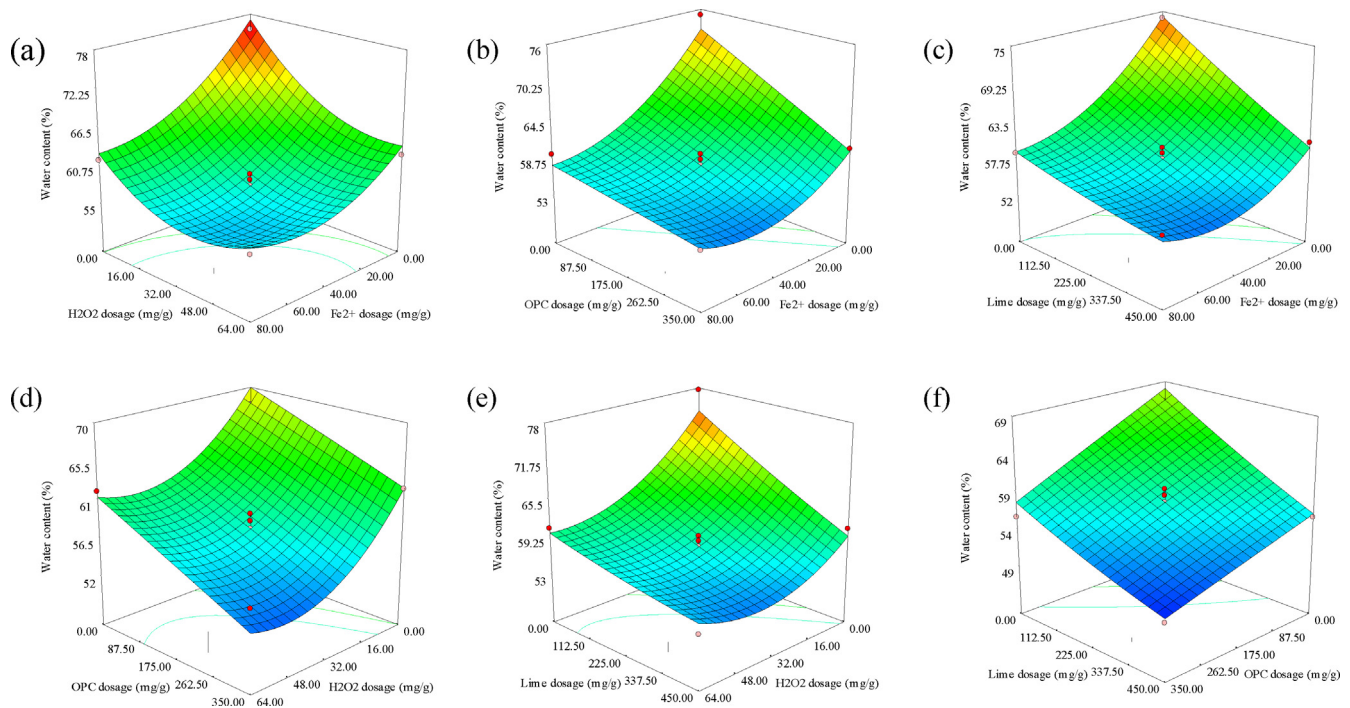


Fig. 3. Response surface plots: (a) dosages of Fe^{2+} and H_2O_2 vs. predicted water content of sludge cakes; (b) dosages of Fe^{2+} and OPC vs. predicted water content of sludge cakes; (c) dosages of Fe^{2+} and lime vs. predicted water content of sludge cakes; (d) dosages of H_2O_2 and OPC vs. predicted water content of sludge cakes; (e) dosages of H_2O_2 and lime vs. predicted water content of sludge cakes; (f) dosages of OPC and lime vs. predicted water content of sludge cakes.

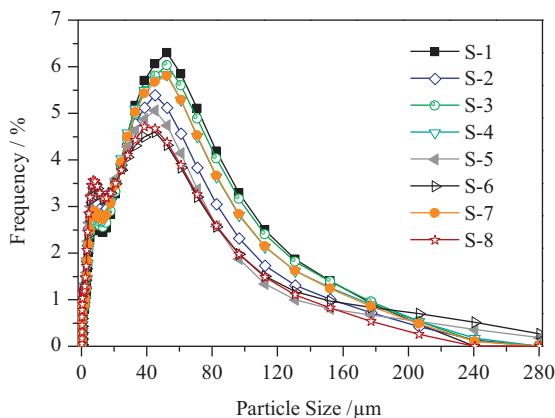


Fig. 4. Particle size distribution of sludge conditioned by different conditioners. (S-1: raw sludge; S-2: sludge conditioned by Fenton's reagent; S-3: sludge conditioned by OPC; S-4: sludge conditioned by lime; S-5: sludge conditioned by Fenton's reagent and OPC; S-6: sludge conditioned by Fenton's reagent and lime; S-7: sludge conditioned by OPC and lime; S-8: sludge conditioned by Fenton's reagent, OPC and lime).

indicating that Fenton's reagent and skeleton builders are both able to facilitate the dispersion of sludge flocs other than aggregation. This phenomenon was more obvious when combining two kinds of conditioners, which further demonstrated significant interaction between them. High active $\cdot\text{OH}$ decreased the sludge

particle size through destroying the structure of EPS, while skeleton builders functioned in sludge particle size by its alkaline. Joint usage strengthened the conditioning efficiency. In other words, dispersed small particles, compared to aggregated large flocs, are more suitable for high pressure dewatering.

EPS has been proven to be an important factor in mechanical dewatering of sewage sludge [3]. To get a clear indication on how Fenton's reagent and skeleton builders influence the EPS of sludge, the concentrations of the main components of EPS, i.e. proteins and polysaccharides, in the filtrate of untreated and treated sludge were measured. It can be seen from Fig. 5 that the changing tendencies of protein and polysaccharide concentrations were similar. The amounts of protein and polysaccharide dissolved in the filtrate of sludge conditioned by Fenton's reagent, OPC, lime, respectively, were bigger than that in RS, confirming that each of the three conditioners can destroy and dissolve EPS, thus improving sludge dewatering performance to some degree. Joint usage further increased the dissolved EPS, reconfirming the interactions between them.

Micrographs are intuitive evidence for changes in the sludge. Figs. 6a and 7a reveal that raw sludge existed in the form of zoogloea, bacteria with different shapes gathered in microcolonies, and EPS filled the voids between the microorganisms. After Fenton oxidation, the sludge particles presented as dispersion state, and floc boundaries were generally ill-defined (Figs. 6b and 7b). The presence of skeleton builders which existed as non-living things with irregular shape could also make sludge particles scatter to

Table 5
Verification experiments at optimum conditions.

Run	Fe^{2+} dosage (mg/g)	H_2O_2 dosage (mg/g)	OPC dosage (mg/g)	Lime dosage (mg/g)	Water content of sludge cakes (%)	
					Predicted	Experimental
A-5	33.8	40.3	350.0	450.0	50.1	49.5 ± 0.5
A-15	24.1	34.3	350.0	450.0	50.9	51.2 ± 1.4
B-5	53.3	44.1	218.8	281.2	54.1	53.8 ± 0.6
B-12	53.4	40.7	218.8	281.2	54.2	53.8 ± 0.9

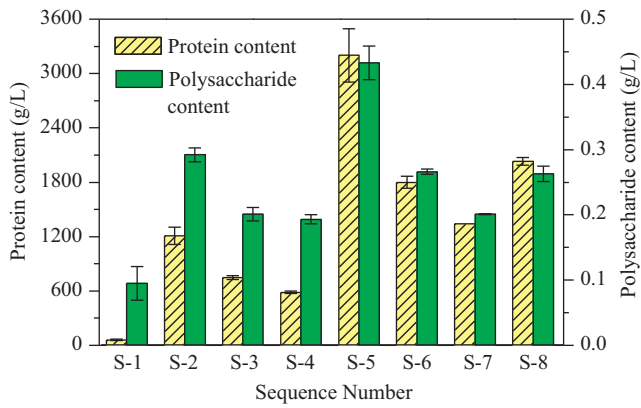


Fig. 5. Protein and polysaccharide concentration in sludge filtrate (S-1: raw sludge; S-2: sludge conditioned by Fenton's reagent; S-3: sludge conditioned by OPC; S-4: sludge conditioned by lime; S-5: sludge conditioned by Fenton's reagent and OPC; S-6: sludge conditioned with Fenton's reagent and lime; S-7: sludge conditioned by OPC and lime; S-8: sludge conditioned by Fenton's reagent, OPC and lime).

some extent due to their strong alkaline (Figs. 6c and 7c). Furthermore, the differences to RS were more obvious after sludge being conditioned by combining them. It is worth notice that joint usage can obtain several special effects: aggregates developing in the flocs (Figs. 6d and 7d), constantly-changing environment promoting senescence and death of microorganism (many empty cells, as shown in Figs. 7e). Under high pressure, the bound water in these dead cells can be easily removed. Meanwhile, non-living things with irregular shape inlaid or pierced microbial cells, promoting the conversion from bound water to free water.

TEM observations were carried out on the two-dimensional ultrathin sections. In addition, a more direct examination of flocs may be achieved using SEM on freeze-dried raw and conditioned sludge. Fig. 8a shows the morphology of raw sludge's cotton wool structure. The surface of these aggregate flocs seems to be flake like. After the composite conditioning (Fig. 8b), flake like structure disappeared, instead of which were irregular ones. Sludge particles turned smaller and column crystals emerged. These irregular substances could form a rigid permeable lattice structure under high pressure. On one hand, this hard structure can transmit the stresses to the inner parts of sludge flocs during mechanical dewatering process. On the other hand, this hard structure can provide outflow channels for free water.

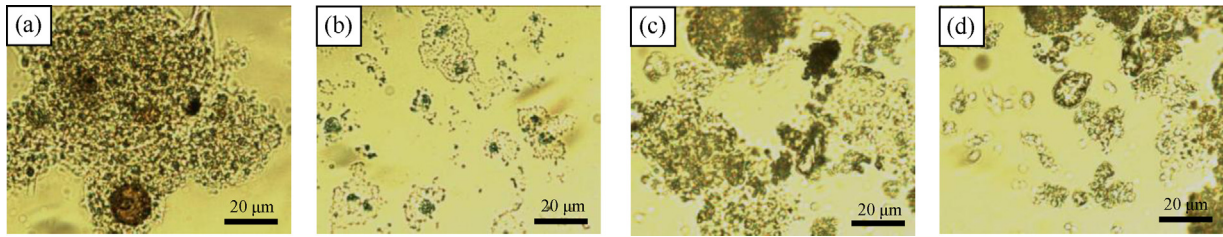


Fig. 6. Micrographs of (a) RS; (b) sludge conditioned by Fenton's reagent; (c) sludge conditioned by OPC and lime; (d) sludge conditioned by Fenton's reagent, OPC and lime.

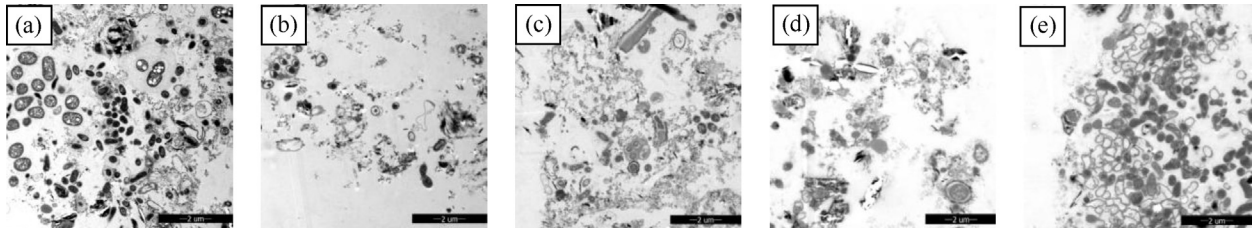


Fig. 7. TEM images of (a) RS; (b) sludge conditioned by Fenton's reagent; (c) sludge conditioned by OPC and lime; (d) and (e) sludge conditioned by Fenton's reagent, OPC and lime.

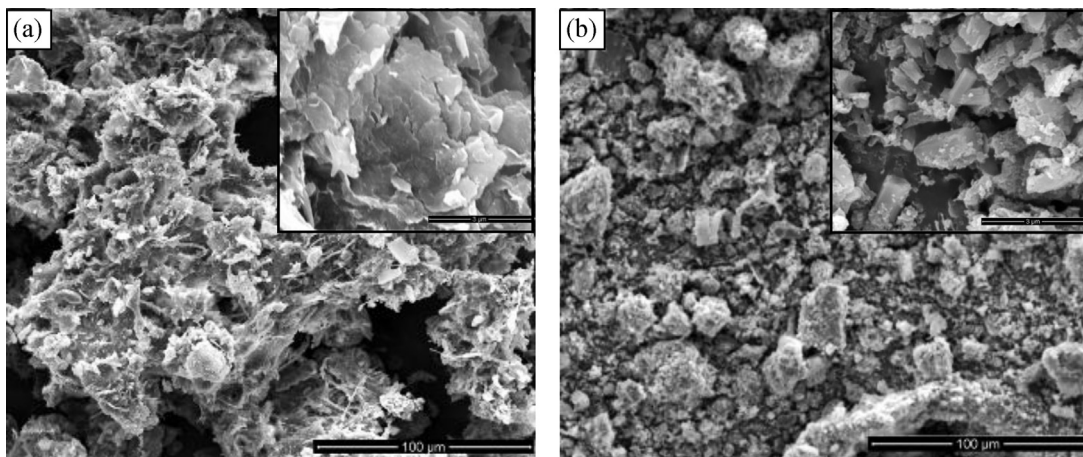


Fig. 8. SEM images of (a) RS; (b) sludge conditioned by Fenton's reagent, OPC and lime.

4. Conclusions

To further optimize the composite conditioning – deep dewatering technique, a comprehensive in-depth investigation on related mechanisms were conducted. The results indicate that each conditioner component has significant effect on sludge deep dewatering process. After RSM optimization, the water content of dewatered sludge cake could be dropped to $49.5 \pm 0.5\%$ under the conditions comprising Fe^{2+} , H_2O_2 , OPC and lime dosages of 33.8 s mg/g, 40.27 mg/g, 349.95 mg/g, 499.99 mg/g, respectively. The experimental results also demonstrated that raw sludge existed in the form of zoogloea and its flocs surface was plate-like. After Fenton oxidation, partial of extracellular polymeric substances (EPS) dissolved and sludge flocs turned into smaller ones. After skeleton builders' conditioning, constantly-changing environment promoted senescence and death of microorganism. A large area of plate-like structure disappeared, instead of which were irregular holes. Meanwhile, non-living things with irregular shape inlaid or pierced microbial cells, promoting the conversion from bound water to free water as well as further reduction of the sludge particle size. Additionally, these irregular substances could form a rigid porous structure under high pressure, which can transmit the stresses to the inner parts of sludge flocs and provide outflow channels for free water. Consequently, sludge dewatering performance was enhanced significantly.

Acknowledgments

The authors would like to appreciate the financial support from National Natural Science Foundation of China (51078162), solid waste recycling projects from New Century Excellent Talents Project of Ministry of Education (NCET-09-0392), the Fundamental Research Funds for the Central Universities (2011TS123), the Project on Technical of Research and Development of Shenzhen, China (CXY201106210008A) and the National Natural Science Foundation of China (Grant 51161140330). The authors would also like to thank the Analytical and Testing Center of Huazhong University of Science and Technology, for providing the facilities for the experimental measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2013.04.036>.

References

- [1] E. Neyens, J. Baeyens, M. Weemaes, B. De heyder, Pilot-scale peroxidation (H_2O_2) of sewage sludge, *J. Hazard. Mater.* 98B (2003) 91–106.
- [2] M. Citeau, O. Larue, E. Vorobiev, Influence of salt, pH and polyelectrolyte on the pressure electro-dewatering of sewage sludge, *Water Res.* 45 (2011) 2167–2180.
- [3] E. Neyens, J. Baeyens, R. Dewil, B. De heyder, Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering, *J. Hazard. Mater.* 106B (2004) 83–92.
- [4] X. Liu, G. Sheng, S. Yuan, J. Xu, R. Zeng, J. Wu, H. Yu, Contribution of extracellular polymeric substances (EPS) to the sludge aggregation, *Environ. Sci. Technol.* 44 (2010) 4355–4360.
- [5] G. Zhen, X. Lu, Y. Li, Y. Zhao, B. Wang, Y. Song, X. Chai, D. Niu, X. Cao, Novel insights into enhanced dewaterability of waste activated sludge by Fe(II) -activated persulfate oxidation, *Bioresour. Technol.* 119 (2012) 7–14.
- [6] J. Zall, N. Galil, M. Rehbun, Skeleton builders for conditioning oily sludge, *J. Water Pollut. Control Fed.* 59 (1987) 699–706.
- [7] Y. Qi, K.B. Thapa, A.F.A. Hoadley, Application of filtration aids for improving sludge dewatering properties – a review, *Chem. Eng. J.* 171 (2011) 373–384.
- [8] R. Dewil, J. Baeyens, E. Neyens, Fenton peroxidation improves the drying performance of waste activated sludge, *J. Hazard. Mater.* 177 (2005) 161–170.
- [9] I. Beauchesne, R.B. Cheikh, G. Mercier, J.F. Blais, T. Ouarda, Chemical treatment of sludge: In-depth study on toxic metal removal efficiency, dewatering ability and fertilizing property, *Water Res.* 41 (2007) 2028–2038.
- [10] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.
- [11] M. Lu, C. Lin, C. Liao, R. Huang, W. Ting, Dewatering of activated sludge by Fenton's reagent, *Adv. Environ. Res.* 7 (2003) 667–670.
- [12] M.A. Tony, Y.Q. Zhao, J.F. Fu, A.M. Tayeb, Conditioning of aluminium-based water treatment sludge with Fenton's reagent: effectiveness and optimizing study to improve dewaterability, *Chemosphere* 72 (2008) 673–677.
- [13] M.A. Tony, Y.Q. Zhao, A.M. Tayeb, Exploitation of Fenton and Fenton-like reagents as alternative conditioners for alum sludge conditioning, *J. Environ. Sci.* 21 (2009) 101–105.
- [14] N. Buyukkamaci, Biological sludge conditioning by Fenton's reagent, *Process Biochem.* 39 (2004) 1503–1506.
- [15] O.E. Albertson, M. Kopper, Fine-coal-aided centrifugal dewatering of waste activated sludge, *J. Water Pollut. Control Fed.* 55 (1983) 145–156.
- [16] C. Chen, P. Zhang, G. Zeng, J. Deng, Y. Zhou, H. Lu, Sewage sludge conditioning with coal fly ash modified by sulfuric acid, *Chem. Eng. J.* 158 (2010) 616–622.
- [17] K.B. Thapa, Y. Qi, S.A. Clayton, A.F.A. Hoadley, Lignite aided dewatering of digested sewage sludge, *Water Res.* 43 (2011) 623–634.
- [18] Y. Qi, K.B. Thapa, A.F.A. Hoadley, Benefit of lignite as a filter aid for dewatering of digested sewage sludge demonstrated in pilot scale trials, *Chem. Eng. J.* 166 (2011) 504–510.
- [19] J. Benitez, A. Rodriguez, A. Suarez, Optimization technique for sewage sludge conditioning with polymer and skeleton builders, *Water Res.* 28 (1994) 2067–2073.
- [20] Y. Zhao, Enhancement of alum sludge dewatering capacity by using gypsum as skeleton builder, *Colloids Surf. A* 211 (2002) 205–212.
- [21] H. Liu, J. Yang, Y. Shi, Y. Li, S. He, C. Yang, H. Yao, Conditioning of sewage sludge by Fenton's reagent combined with skeleton builders, *Chemosphere* 88 (2012) 235–239.
- [22] D.C. Montgomery, *Design and Analysis of Experiments*, 6th edition, John Wiley, New York, 2009.
- [23] H. Liu, G. Luo, H. Hu, Q. Zhang, J. Yang, H. Yao, Emission characteristics of nitrogen- and sulfur-containing odorous compounds during different sewage sludge chemical conditioning processes, *J. Hazard. Mater.* 235–236 (2012) 298–306.
- [24] O.H. Lowry, N.J. Rosebrough, A. Lewis Farr, R.J. Randall, Protein measurement with Folin phenol reagent, *J. Biol. Chem.* 193 (1951) 265–275.
- [25] M. Dubois, K.A. Gilles, J.K. Hamilton, Colorimetric method for determination of sugars and related substances, *Anal. Chem.* 28 (1956) 350–356.
- [26] S. Deneux-Mustin, B.S. Lartiges, Ferric chloride and lime conditioning of activated sludges: an electron microscopic study on resin-embedded samples, *Water Res.* 35 (2001) 3018–3024.
- [27] H. Mazaheri, K.T. Lee, S. Bhatia, A.R. Mohamed, Subcritical water liquefaction of oil palm fruit press fiber in the presence of sodium hydroxide: an optimisation study using response surface methodology, *Bioresour. Technol.* 101 (2010) 9335–9341.
- [28] S. Yang, W. Guo, X. Zhou, Z. Meng, B. Liu, N. Ren, Optimization of operating parameters for sludge process reduction under alternating aerobic/oxygen-limited conditions by response surface methodology, *Bioresour. Technol.* T102 (2011) 9843–9851.
- [29] C.H. Lee, J. Liu, Enhanced sludge dewatering by dual polyelectrolytes conditioning, *Water Res.* 34 (2000) 4430–4436.
- [30] P.R. Karr, T.M. Keinath, Influence of particle size on sludge dewaterability, *J. Water Pollut. Control Fed.* 50 (1978) 1911–1930.