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Mechanism of red mud combined with Fenton's reagent in sewage sludge conditioning

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Red mud was evaluated as an alternative skeleton builder combined with Fenton's reagent in sewage sludge conditioning. The results show that red mud combined with Fenton's reagent showed good conditioning capability with the pH of the filtrate close to neutrality, indicating that red mud acted as a neutralizer as well as a skeleton builder when jointly used with Fenton's reagent. Through response surface methodology (RSM), the optimal dosages of Fe^{2+}, H_2O_2 and red mud were proposed as 31.9, 33.7 and 275.1 mg/g DS (dry solids), respectively. The mechanism of the composite conditioner could be illuminated as follows: (1) extracellular polymeric substances (EPS), including loosely bound EPS and tightly bound EPS, were degraded into dissolved organics, e.g., proteins and polysaccharides; (2) bound water was released and converted into free water due to the degradation of EPS; and (3) morphology of the conditioned sludge exhibited a porous structure in contrast with the compact structure of raw sludge, and the addition of red mud formed new mineral phases and a rigid lattice structure in sludge, allowing the outflow of free water. Thus, sludge dewatering performance was effectively improved. The economic assessment for a wastewater treatment plant of 370,000 equivalent inhabitants confirms that using red mud conditioning, combined with Fenton's reagent, leads to a saving of approximately 411,000 USD/y or 50.8 USD/t DS comparing with using lime and ordinary Portland cement combined with Fenton's reagent, and approximately 612,000 USD/y or 75.5 USD/t DS comparing with the traditional treatment.

1. Introduction

Sewage sludge, a by-product of municipal wastewater treatment, is very difficult to be dewatered, which limits its subsequent treatment and disposal. The key problems that prevent sewage sludge from dewatering are the highly hydrated nature of extracellular polymeric substances (EPS) that bind a large volume of water (i.e., bound water) within the sludge flocs and the high compressibility of sludge owing to its

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high organic content (Houghton et al., 2001; Liu et al., 2010; Sheng et al., 2010; Qi et al., 2011).

Fenton's reagent, i.e., Fe^{2+} and H_2O_2, has been widely investigated and proven to be an efficient chemical conditioner for different sludges (Lu et al., 2003; Neyens et al., 2003; Buyukkamaci, 2004; Tony et al., 2008). The effect of Fenton's reagent lies in the degradation of EPS by the hydroxyl radicals, with powerful oxidizing ability, generated through the following reaction:

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

Drawbacks associated with the use of Fenton's reagent are the safety hazards associated with using H_2O_2 and the need to firstly reduce the pH, followed by a subsequent neutralization with alkaline additives (Neyens and Baeyens, 2003). Therefore, the reduction in the dosage of Fenton's reagent can alleviate the safety hazards of using H_2O_2, and a suitable neutralizer needs to be proposed after the Fenton reaction.

Meanwhile, there are considerable researches employing physical conditioners, e.g., lime (Zall et al., 1987), gypsum (Zhao, 2002), lignite (Thapa et al., 2009) and fly ash (Chen et al., 2010), often referred to as skeleton builders for their function in building a rigid and permeable structure in sludge flocs, to decrease sludge compressibility.

Our previous studies have found that quick lime and ordinary Portland cement (OPC) as skeleton builders can significantly reduce the dosage of Fenton's reagent and enhance the dewaterability of sludge (Liu et al., 2012, 2013). However, both quick lime and OPC are non-renewable resources. The production of them consumes a massive quantity of limestone ores and emits a large amount of CO_2 in the high temperature calcination process using coal or coke as the source of energy. Moreover, the pH of the filtrate from the dewatering process of the sludge conditioned by quick lime and OPC tends to be high, usually above 12, which handicaps the subsequent recycle or disposal of the filtrate. The above-mentioned disadvantages have largely limited the application of quick lime and OPC in sludge conditioning. Thus, it is urgent to seek alternative skeleton builders capable of overcoming these weaknesses and yielding acceptable conditioning effectiveness when jointly used with Fenton's reagent.

Red mud is the solid residue from caustic soda leaching of bauxite ores to produce alumina (Yang et al., 2008). The huge global excess of red mud poses serious threats to the environment mainly due to its caustic nature (Yang and Xiao, 2008). Therefore, developing effective utilization methods for red mud is of great importance. Red mud has attracted many interests as cheap adsorbent, coagulant and catalyst in environmental protection fields (Wang et al., 2008), including wastewater treatment (Huang et al., 2008), waste gases purification (Sahu et al., 2011), soil amendment (Liu et al., 2011) and metal recovery (Wang and Liu, 2012). But the application of red mud in sludge conditioning has not been reported in literature. Red mud is superfine in particle size with a large surface area and a long-term persistence of alkalinity, which makes it a potential skeleton builder instead of lime and OPC and a potential neutralizer when jointly used with Fenton's reagent.

In this study, red mud was utilized as a novel skeleton builder in combination with Fenton's reagent to enhance sludge dewatering performance. As depicted in Fig. 1, the

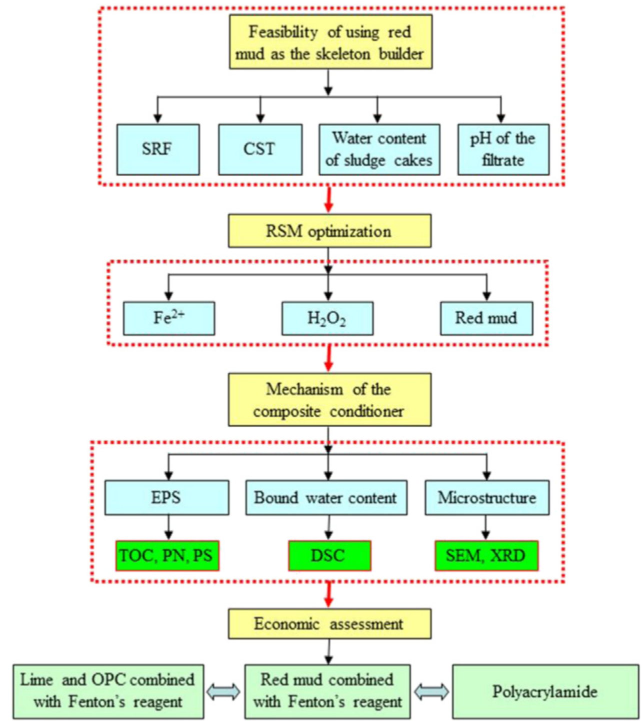

Fig. 1 – Schematic of the study.

objectives of this study were: (1) to demonstrate the feasibility of using red mud as an alternative skeleton builder by evaluating the dewaterability of the conditioned sludge and the pH of the filtrate, (2) to minimize the dosage of the composite conditioner through response surface methodology (RSM) when the water content of sludge cakes does not exceed 60%, (3) to clarify the mechanism of the composite conditioner in terms of EPS, bound water content and microstructure of sludge, and (4) to confirm the economic benefits of using red mud conditioning combined with Fenton's reagent for a wastewater treatment plant (WWTP) of 370,000 equivalent inhabitants (IE).

2. Materials and methods

2.1. *Materials*

The raw sludge (RS) used in this study was a mixture of sludge from the primary and secondary sedimentation tanks of Longwangzui municipal WWTP, Wuhan, China. Samples were transported to the laboratory in polypropylene containers and stored at 4 °C before use. The main characteristics of RS are listed in Table 1.

H_2SO_4 (analytical grade, Xinyang Chemical Company, China) was used to adjust the initial pH of sludge to 5 (Liu et al., 2012) before adding Fenton's reagent. Fe^{2+} in Fenton's reagent was prepared by making a solution of $FeSO_4$ (40 wt%). $FeSO_4 \cdot 7H_2O$ (Fe^{2+} content of 18.6 wt%) and H_2O_2 (27.5 wt%) of industrial grade were obtained from Sinopharm Chemical Reagent Company, China. Quick lime, OPC and red mud were used as skeleton builders, which were milled and sieved to

Table 1 – Characteristics of RS.

Batch	pH	Water content (%)	COD (mg/L)	TSS (g/L)	VSS/TSS (%)	SRF (10^{12} m/kg)	CST (s)
1	6.5	96.4	26,187	32.8	42	17.20	207.6
2	6.3	97.2	23,731	27.0	54	23.25	216.0

less than 1 mm particle size. The red mud was supplied by an alumina plant using the Bayer process in Zhengzhou, China. Their chemical compositions are presented in Table 2.

2.2. *Sludge conditioning and dewatering*

A sketch of the sludge conditioning and dewatering process is presented in Fig. 2. First, 20 L of raw sludge samples were transferred to a 35-L conditioning tank and then conditioned according to the following procedure: adding H_2SO_4 → 3 min of rapid mixing → adding Fe^{2+} solution → 3 min of rapid mixing → adding H_2O_2 → 30 min of slow mixing (Fenton reaction period) → adding skeleton builders → 5 min of rapid mixing. The speed of rapid mixing was set at 150 rpm while that of slow mixing was 100 rpm.

After the conditioning process, the conditioned sludge was pumped into a feed tank by the screw pump and then fed to the diaphragm filter press for the dewatering process comprising a 40-min feeding pressing phase with a pressure of 0.8 MPa and a 5-min diaphragm pressing phase with a pressure of 1.1 MPa. The pressure during the dewatering process was controlled by the air compressor.

2.3. *Sludge dewatering performance*

Sludge dewatering performance was evaluated by specific resistance to filtration (SRF), capillary suction time (CST) and water content of sludge cakes.

SRF was measured by a self-designed multi-coupled measuring device of sludge SRF (Liu et al., 2012) and calculated by

$$\mathrm{SRF} = \frac{2PA^2b}{\mu w} \tag{2}$$

where SRF is the specific resistance to filtration (m/kg), P is the filtration pressure (N/m^2), A is the filtration area (m^2), μ is the viscosity of the filtrate (N s/m^2), w is the mass of the cake solids per unit volume of filtrate (kg/m^3), and b is the slope of the filtrate discharge curve (s/m^6).

The sludge cakes were dried at 105 °C for 24 h to determine its water content. CST was measured by a CST instrument (304M, Triton). The pH of the sludge and filtrate was also measured by a digital pH-meter (PHS-3C, INESA).

2.4. *Evaluation of the feasibility of using red mud as the skeleton builder*

To determine the feasibility of using red mud as an alternative skeleton builder combined with Fenton's reagent, the conditioning effectiveness of red mud was compared with that of lime and OPC at the same dosage. Two optimized dosages in previous studies (Liu et al., 2012, 2013) were used as shown in Table 3. The first batch of raw sludge was used in this experiment.

2.5. *RSM design*

After the feasibility of using red mud as the skeleton builder was demonstrated, a Box–Behnken design (Montgomery, 2009) was chosen to optimize the dosages of the three constituents of the composite conditioner (Fe^{2+}, H_2O_2 and red mud). The range and levels of the three factors were defined based on the preliminary tests, as shown in Table 4. The water content of the dewatered sludge cakes was examined as the response. Seventeen runs were required for a complete experimental design as shown in Table A.1, and the experimental results were analyzed using the software of Design Expert 8. The criteria of the factors and response set for optimization are presented in Table 5. The optimization goal was to minimize the dosage of the composite conditioner when the water content of sludge cakes did not exceed 60%. The second batch of raw sludge was used in this optimization experiment.

2.6. *Conditioning mechanism investigation*

To elaborate the mechanism of the composite conditioner, a set of experiments with different formulations was carried out, as shown in Table 6. The dosages were determined by the RSM optimization results. The raw and conditioned sludge were analyzed for EPS, bound water content and microstructure. The second batch of raw sludge was used in this experiment.

2.6.1. *EPS extraction and analysis*

Sludge has a dynamic double-layered EPS structure of loosely bound EPS (LB-EPS) and tightly bound EPS (TB-EPS) (Poxon and Darby, 1997). A modified heat extraction method (Li and Yang,

Table 2 – Chemical compositions of the skeleton builders (wt%).

Skeleton builders	SiO_2	CaO	Al_2O_3	MgO	$Na_2O + K_2O$	Fe_2O_3	TiO_2	SO_3	Cl^-	LOI[a]
Lime	7.2	62.0	–	1.7	–	–	–	–	–	24.1
OPC	20.6	58.8	5.4	3.3	0.6	2.9	2.9	2.4	0.0	15.4
Red mud	20.4	12.9	24.5	1.0	12.3	9.5	–	0.7	0.1	4.0

[a] LOI = loss of ignition at 1200 °C.

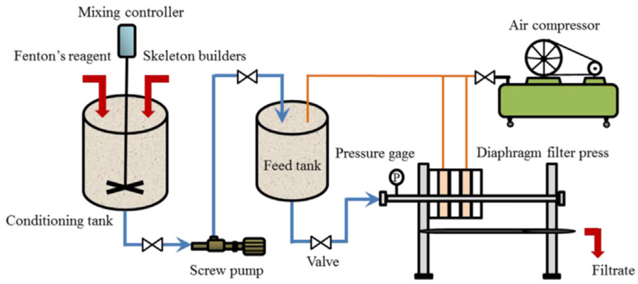

Fig. 2 – Sketch of the experimental setup for sludge conditioning and dewatering process.

2007) was applied to extract LB-EPS and TB-EPS separately from the sludge. In this method, the sludge was first centrifuged in a 50-mL tube at 4000*g* for 5 min. The centrate liquor (CL) was recovered for analysis and the sludge pellet in the tube was used for EPS extraction. All of the LB-EPS extraction, TB-EPS extraction and CL were analyzed for total organic carbon (TOC), protein (PN) and polysaccharide (PS). TOC was measured by a TOC analyzer (Multi N/C 2100, Analytik Jena). The PN content was analyzed with the modified Lowry method using bovine serum albumin as the standard, while the PS content was determined with the phenol sulphuric acid method using glucose as the standard.

2.6.2. *Bound water content measurement*

A thermal analysis method (Katsiris and Kouzeli-Katsiri, 1987) was modified to measure the bound water content. The apparatus used in this study was a differential scanning calorimetry (DSC) analyzer (Diamond, PerkinElmer) equipped with a liquid nitrogen cooling system. The sludge was first subjected to a temperature of −20 °C, assuming that all free water was frozen under this condition, and then brought back to 10 °C at a rate of 2 °C/min. The mass of the samples was in the range of 10–20 mg. The amount of free water was determined by the area of the endothermic curve below the baseline representing the amount of heat required to melt the frozen water. The amount of bound water was determined as the difference between the known total water of the sludge sample and the amount of free water. The relationship between the mass of free water and the DSC curve area can be expressed as

$$FW = K \times A \tag{3}$$

where FW is the mass of free water (mg), A is the curve area (mJ), and K is the conversion factor (mg/mJ), determined by obtaining the thermograms of pure water of known mass and measuring the curve area.

Table 4 – Range and levels of the factors in the Box–Behnken design.

Factor (mg/g DS)	Range and levels		
	−1	0	1
X_1, Fe^{2+} dosage	10	21.5	33
X_2, H_2O_2 dosage	14	30	46
X_3, red mud dosage	100	200	300

Table 5 – Criteria of the factors and response for optimization.

Variable	Goal	Lower limit	Upper limit	Importance
Fe^{2+} dosage (mg/g DS)	Minimize	0	33	3
H_2O_2 dosage (mg/g DS)	Minimize	0	46	3
Red mud dosage (mg/g DS)	Minimize	0	300	3
Water content of sludge cakes (%)	In range	0	60	3

2.6.3. *Microstructural analysis*

Microstructural characteristics of the raw and conditioned sludge samples were investigated through scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The samples were immersed in ethanol for 24 h to end the hydration reaction before analysis. Morphology study was conducted using a scanning electron microscope (Sirion 200, FEI) after the samples were freeze-dried and coated with gold. XRD analysis was conducted using an X-ray diffractometer (D8 Advance, Bruker) with Cu Kα radiation at running voltage of 40 kV and scanning rate of 0.28°/s for 2θ in the range from 5 to 75°. In addition, the particle size, specific surface area and viscosity of the raw and conditioned sludge were analyzed to supplement the SEM and XRD study. The particle size and the specific surface area were measured by a laser particle size analyzer (BT-9300ST, Bettersize), and the viscosity was measured by a rotating viscometer (NDJ-79A, Changji).

3. Results and discussion

3.1. *Feasibility of using red mud as the skeleton builder*

The results in Table 3 show clearly that the composite conditioner of Fenton's reagent and skeleton builders enhanced sludge dewaterability dramatically. Although SRF, CST and water content of sludge cakes of sludge conditioned

Table 3 – Conditioning effectiveness of the composite conditioner at two optimized dosages.

Fenton's reagent (mg/g DS)	Skeleton builders (mg/g DS)	SRF (10^{12} m/kg)	CST (s)	Water content of sludge cakes (%)	pH of filtrate
$Fe^{2+} = 40$; $H_2O_2 = 32$	Lime = 400; OPC = 300	0.98 ± 0.07	35.0 ± 1.6	49.2 ± 0.6	12.4
	Red mud = 700	1.06 ± 0.06	38.9 ± 2.7	50.3 ± 0.8	8.0
$Fe^{2+} = 33.8$; $H_2O_2 = 40.3$	Lime = 450; OPC = 350	0.72 ± 0.05	27.5 ± 2.1	46.5 ± 0.6	12.8
	Red mud = 800	0.82 ± 0.07	30.7 ± 1.4	47.3 ± 0.5	8.3

Table 6 – Different conditioning formulations for sludge.

Symbol	Sludge	Dosage (mg/g DS)		
		Fe^{2+}	H_2O_2	Red mud
RS	Raw sludge	0	0	0
F	Sludge conditioned by Fenton's reagent	31.9	33.7	0
R	Sludge conditioned by red mud	0	0	275.1
FR	Sludge conditioned by Fenton's reagent and red mud	31.9	33.7	275.1

by red mud were slightly higher than those of sludge conditioned by lime and OPC, the difference was within the standard deviation, indicating that red mud could boost sludge dewaterability similar to lime and OPC. This might be attributed to its superfine particle size and the large surface area that make red mud effective in forming rigid porous structure in sludge flocs. The pH of the filtrate collected from the dewatering process of the conditioned sludge using lime and OPC as skeleton builders was terribly high, exceeding 12 at both dosages. By contrast, the pH of the filtrate from the conditioned sludge using red mud as the skeleton builder was closer to neutrality because the alkalinity of red mud is weaker than that of lime and OPC. Therefore, it is feasible to use red mud as an alternative skeleton builder of the composite conditioner.

3.2. *RSM optimization results of the composite conditioner*

The results of the experiments based on the Box–Behnken design are presented in Table A.1. After the data fitting, a second-order polynomial equation was obtained as

$$Y = 72.61 - 6.78X_1 - 1.19X_2 - 1.73X_3 - 2.04X_1X_2 - 2.85X_1X_3 + 1.24X_2X_3 - 2.71X_1^2 + 0.57X_2^2 - 1.10X_3^2 \quad (4)$$

where Y is the predicted response (water content of sludge cakes, %), X_1–X_3 are the coded values of the dosages of Fe^{2+}, H_2O_2 and red mud, respectively.

The predicted values of the response via Eq. (4) are also shown in Table A.1. There is a good agreement between the actual and the predicted data with a regression coefficient R^2 value of 0.969. The Model F-value is 24.33, and the value of "Prob > F" is 0.0002, implying that the model is significant. Hence, it is rational to reckon that the quadratic model (Eq. (4)) is credible to represent the effects of the composite conditioner on sludge dewaterability.

The minimal coded values of the factors are as follows: $X_1 = 0.90$, $X_2 = 0.23$ and $X_3 = 0.75$. Accordingly, the dosages of Fe^{2+}, H_2O_2 and red mud are 31.9, 33.7 and 275.1 mg/g DS, at which the predicted value of the water content of sludge cakes is 60%.

To confirm the adequacy of the model, three validation experiments under the above optimal condition were carried out. The sludge cakes with the water content of 59.8 ± 0.4% were produced from the triplicate experiments. This clearly confirms the reliability of the quadratic model in optimizing the conditioning process. The pH of the filtrate was 6.8, which was lower than that in Table 3, due to the distinctly smaller dosage of red mud. The initial pH of sludge was first adjusted to 5 by H_2SO_4, and then further reduced to 3.9 after Fenton reaction. The pH reduction might result from the productions of Fe^{3+} and organic acids during the Fenton oxidation. The subsequent addition of red mud neutralized the pH of sludge to approximately 7.

3.3. *Effects of the composite conditioner on EPS*

Fig. 3a and b reveal the influence of the composite conditioner on EPS. As illustrated in Fig. 3a, the variation of TOC content in LB-EPS, TB-EPS and CL was very obvious before and after conditioning. For the raw sludge, TB-EPS had the highest TOC content, followed by CL and LB-EPS. However, TOC content in CL became the highest for the conditioned sludge. Especially for sludge conditioned by Fenton's reagent and sludge conditioned by Fenton's reagent and red mud, TOC content in CL was significantly higher than those in TB-EPS and LB-EPS. It can also be seen from Fig. 3a that TOC content in both LB-EPS and TB-EPS of the sludge conditioned by Fenton's reagent and sludge conditioned by Fenton's reagent and red mud decreased markedly in comparison with that of raw sludge, while TOC content in CL increased sharply. These results indicated that EPS were effectively degraded by Fenton oxidation. Fig. 3b shows that the variation tendencies of PN and PS, the major components of EPS (Neyens et al., 2004), were similar to that of TOC. TB-EPS had the highest PN and PS contents for the raw sludge. For sludge conditioned by Fenton's reagent and sludge conditioned by Fenton's reagent and red mud, PN and PS contents in TB-EPS and LB-EPS went down while those in CL rose sharply. This is congruous with the finding reported by Liu et al. (2012) that the amounts of PN and PS dissolved in the filtrate of the conditioned sludge were larger than those of raw sludge. It further demonstrated that EPS were degraded into dissolved organics, e.g., proteins and polysaccharides, and released into the liquid phase.

3.4. *Effects of the composite conditioner on bond water content*

Fig. 4 illustrates the DSC thermograms of pure water and sludge. *K* in Eq. (3) was calculated to be 0.0031 mg/mJ in this study from the thermograms of pure water of four different masses (Fig. 4a–d). The mass of pure water was found to be directly proportional to the curve area, with a coefficient of 1.00. The endothermic curve ranged from −5 to 10 °C, which was narrower than that reported by Katsiris and Kouzeli-Katsiri (1987), probably due to the difference of heating rates. The thermograms of the raw and conditioned sludge (Fig. 4e–h) were similar to those of pure water, despite their curves started a little earlier, which might be attributed to the change of free energy because of the presence of sludge particles as proposed by Lee and Lee (1995).

The bound water content, as depicted in Fig. 3c, decreased from 1.54 to 0.95 g/g DS after sludge was conditioned by Fenton's reagent, and further decreased to 0.90 g/g DS of sludge jointly conditioned by Fenton's reagent and red mud. It demonstrated that as EPS were degraded, approximately 42% of bound water originally retained in the EPS structure was

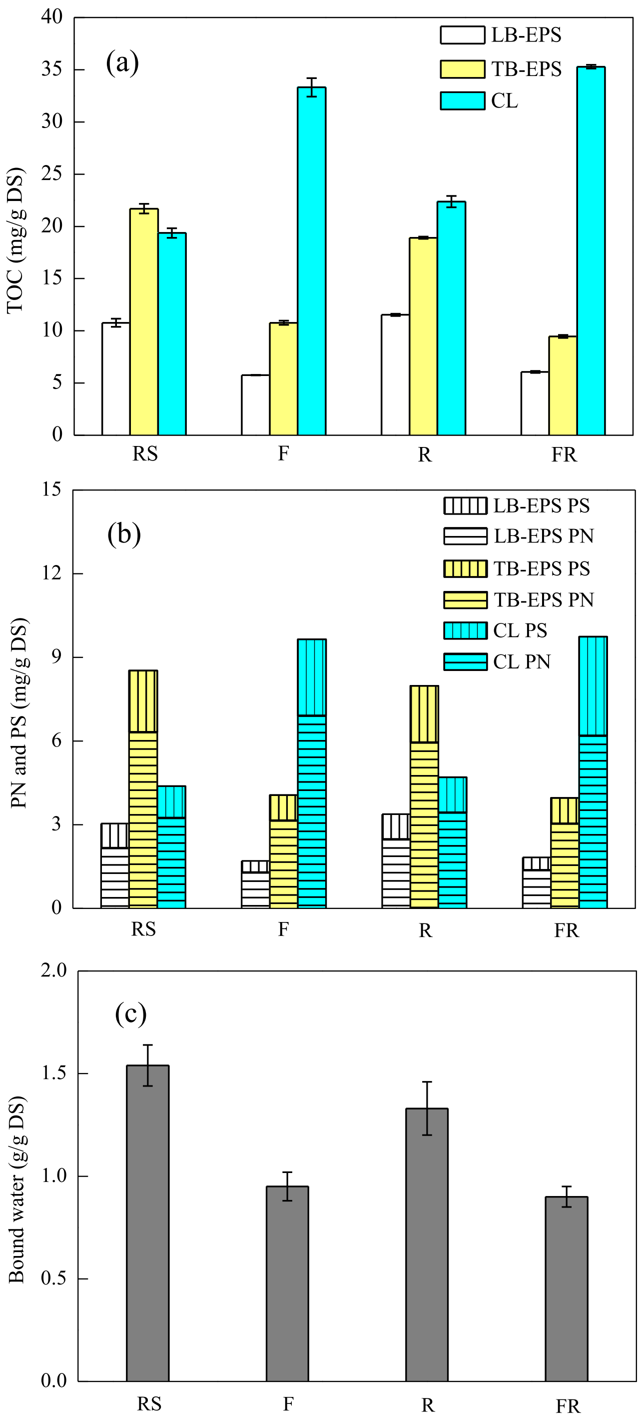

Fig. 3 – Influence of the composite conditioner on EPS and bound water: (a) TOC content of the LB-EPS, TB-EPS and CL, (b) PN and PS contents of the LB-EPS, TB-EPS and CL, (c) bound water content. RS: raw sludge, F: sludge conditioned by Fenton's reagent, R: sludge conditioned by red mud, FR: sludge conditioned by Fenton's reagent and red mud.

released and converted into free water, which is conducive to the promotion of sludge dewatering efficiency. Several references have also proposed the positive influence of releasing trapped or bound water on sludge dewatering (Foster, 1983; Kwon et al., 2004; Tony et al., 2008).

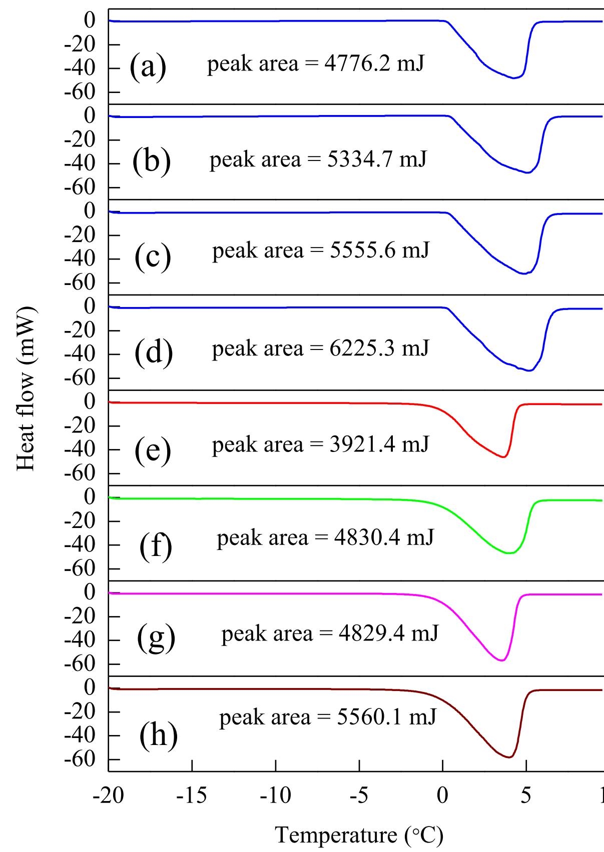

Fig. 4 – DSC thermograms of pure water and sludge: (a) pure water, 14.71 mg, (b) pure water, 16.42 mg, (c) pure water, 17.09 mg, (d) pure water, 19.16 mg, (e) raw sludge, 13.06 mg, (f) sludge conditioned by Fenton's reagent, 15.90 mg, (g) sludge conditioned by red mud, 16.30 mg, (h) sludge conditioned by Fenton's reagent and red mud, 18.58 mg.

As shown in Fig. 3, TOC, PN, PS and bound water contents in the sludge conditioned by red mud did not show significant change comparing with those in raw sludge. It can also be found that the Fenton's reagent conditioning and the composite conditioning of Fenton's reagent and red mud resulted in similar effects in TOC, PN, PS and bound water contents. It indicated that the degradation of EPS and the release of bound water were mainly attributed to the Fenton oxidation rather than the red mud. Red mud played another role as a skeleton builder to change the structure of the sludge.

3.5. *Effects of the composite conditioner on the microstructure of sludge*

Fig. 5 shows the SEM images and XRD patterns of the raw and conditioned sludge. As shown in Fig. 5a, the structure of raw sludge is compact and platy, with a continuous surface of no channels or voids. As for sludge conditioned by Fenton's reagent, it shows a discontinuous and porous structure (Fig. 5c). Furthermore, some irregularly shaped crystals embedded among sludge particles formed in the sludge conditioned by Fenton's reagent and red mud (Fig. 5e). XRD patterns indicate

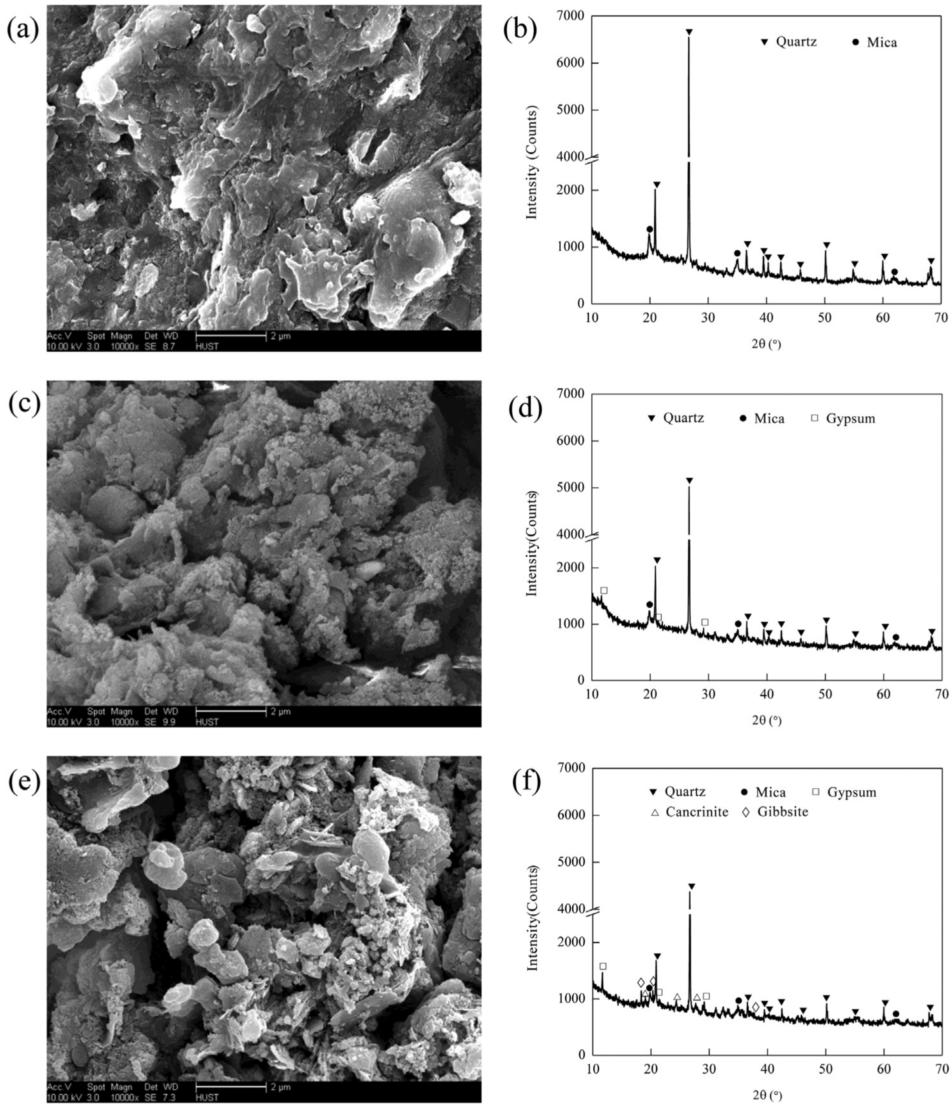

Fig. 5 – SEM images and XRD patterns of the raw and conditioned sludge: (a) SEM image of raw sludge, (b) XRD pattern of raw sludge, (c) SEM image of sludge conditioned by Fenton's reagent, (d) XRD pattern of sludge conditioned by Fenton's reagent, (e) SEM image of sludge conditioned by Fenton's reagent and red mud, (f) XRD pattern of sludge conditioned by Fenton's reagent and red mud.

that raw sludge mainly consists of quartz and mica (Fig. 5b). Gypsum was generated in the sludge conditioned by Fenton's reagent (Fig. 5d), and some new mineral phases, such as cancrinite and gibbsite, were identified after the addition of red mud (Fig. 5f). Gypsum in the sludge conditioned by Fenton's reagent was generated from the reaction of Ca^{2+} in the sludge and the SO_4^{2-} in $FeSO_4$. More gypsum was generated in the sludge conditioned by Fenton's reagent and red mud since red mud brought more Ca^{2+} that could react with the SO_4^{2-} into the system. The Al^{3+} brought by red mud accounted for the formations of cancrinite and gibbsite in the sludge conditioned by Fenton's reagent and red mud. The addition of red mud made sludge a more rigid lattice structure, capable of maintaining high porosity and permeability during high pressure filtration, thus allowing the outflow passages for free water. The microstructural results were supported by the analyses of particle size, specific surface area and viscosity. As shown in Table 7, the particle size decreased, the specific surface area increased, and the viscosity decreased after conditioning. It indicated that as the destruction of EPS bridging, dense flocs in the raw sludge were broken into smaller particles with large specific surface area, leading to a porous structure of the conditioned sludge.

3.6. *Economy of using red mud conditioning combined with Fenton's reagent*

Table 8 shows the cost estimation of the composite conditioner. The optimal dosages in Section 3.2 and that reported by Liu et al. (2013) were used for the cost estimation of the composite conditioner using red mud as the skeleton builder and that using lime and OPC as skeleton builders, respectively.

Table 7 – Effects of the composite conditioner on the particle size, specific surface area and viscosity of sludge.

Symbol	Mean particle size (μm)	Median particle size (μm)	Specific surface area (m^2/kg)	Viscosity (mPa s)
RS	60.0	46.7	203.3	4.4
F	53.4	43.1	222.2	3.5
FR	51.2	42.2	235.4	3.3

The estimated cost of the composite conditioner using red mud as the skeleton builder is only 44.0 USD/t DS, much less than that using lime and OPC as skeleton builders of 101.6 USD/t DS.

For the case of Longwangzui municipal WWTP that serves 370,000 IE with a daily sludge production of 60 g DS/IE d, the total annual sludge production is 8103 t DS/y. The annual cost of the composite conditioner using red mud as the skeleton builder and that using lime and OPC as skeleton builders are approximately 357,000 USD/y and 823,000 USD/y, respectively. The dewatered sludge from this WWTP is landfilled for disposal. The optimal water content of the dewatered sludge using red mud as the skeleton builder and that using lime and OPC as skeleton builders are 59.8 ± 0.4% and 49.5 ± 0.5%, respectively. Considering that the disposal costs of sludge with the water content of 59.8% and 49.5% are 33.6 USD/t DS and 26.8 USD/t DS, respectively, the annual disposal cost of the sludge conditioned by red mud combined with Fenton's reagent and that of the sludge conditioned by lime and OPC combined with Fenton's reagent are approximately 272,000 USD/y and 217,000 USD/y, respectively. This WWTP currently employs the traditional polyacrylamide (PAM) of 65 USD/t DS as the conditioner and produces the dewatered sludge with the water content of about 80%. The annual cost of PAM is approximately 527,000 USD/y. Considering that the disposal cost of sludge with the water content of 80% is 88.1 USD/t DS, the annual disposal cost of the sludge conditioned by PAM is approximately 714,000 USD/y. Ignoring the difference in the operation costs during the conditioning–dewatering process for these three conditioning methods, using red mud combined with Fenton's reagent as the composite conditioner leads to a saving of approximately 411,000 USD/y or 50.8 USD/t DS comparing with using lime and OPC combined with Fenton's reagent, and a saving of approximately 612,000 USD/y or 75.5 USD/t DS comparing with the traditional treatment. The filtrate of nearly neutral pH is produced from the dewatering process without the additional need to adjust the pH of the conditioned sludge. Moreover, the conditioning process occurs at ambient temperature and pressure without extra energy costs. Therefore, using red mud conditioning combined with Fenton's reagent is economical and promising for sewage sludge dewatering and disposal.

Table 8 – Cost estimation of the composite conditioner.

Constituent	Dosage (t/t DS)	Unit price (USD/t)	Cost (USD/t DS)	Total cost (USD/t DS)
H_2SO_4	0.060	100	6.0	44.0
$FeSO_4 \cdot 7H_2O$	0.171	70	12.0	
H_2O_2 (27.5 wt%)	0.123	200	24.6	
Red mud	0.275	5	1.4	
H_2SO_4	0.060	100	6.0	101.6
$FeSO_4 \cdot 7H_2O$	0.182	70	12.7	
H_2O_2 (27.5 wt%)	0.147	200	29.4	
Lime	0.450	80	36.0	
OPC	0.350	50	17.5	

4. Conclusions

Application of red mud combined with Fenton's reagent in sewage sludge conditioning has demonstrated the feasibility of using red mud as an alternative skeleton builder. Red mud conditioning combined with Fenton's reagent dramatically enhanced the dewaterability of sludge with the pH of the filtrate close to neutrality, indicating that red mud acted as a neutralizer as well as a skeleton builder. The optimal dosages of the composite conditioner were 31.9 mg/g DS of Fe^{2+}, 33.7 mg/g DS of H_2O_2 and 275.1 mg/g DS of red mud, at which the water content of sludge cakes of 59.8 ± 0.4% was achieved. The mechanism investigations illuminated that EPS were degraded into dissolved organics, e.g., polysaccharides and proteins, resulting in the conversion of bound water into free water. Besides, the conditioned sludge exhibited a discontinuous and porous structure in contrast with the compact and platy structure of raw sludge, and new mineral phases were identified in the conditioned sludge. The addition of red mud made sludge a rigid lattice structure with high permeability, allowing the outflow of free water under high pressure. The economic assessment confirms the economic benefits of using red mud conditioning combined with Fenton's reagent.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2014.04.026.

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