Improving primary sludge dewaterability by oxidative conditioning process with ferrous ion-activated peroxymonosulfate

Xu Zhou*, Wenbiao Jin*, Lan Wang*, Wanqing Ding*, Chuan Chen**,†, Xijun Xu**,
Renjie Tu*, Song-Fang Han*, Xiaochi Feng*, and Duu-Jong Lee***,****

*Shenzhen Engineering Laboratory of Microalgal Bioenergy, Harbin Institute of Technology (Shenzhen),
518055 Shenzhen, China
**State Key Laboratory of Urban Water Resource and Environment (SKLUWRE),
Harbin Institute of Technology, 150001, Harbin, China
***Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan
****Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

Abstract—Enhancement of sludge dewaterability is key for sludge management and disposal of wastewater treatment plants (WWTP). In this study, the Fe^{2+}-peroxymonosulfate (PMS) conditioning approach was first used to oxidize the primary sludge from the primary sedimentation tank of a full scale WWTP. The combination of Fe^{2+} (0.05-0.5 g/g TSS) and PMS (0.05-0.5 g/g TSS) could significantly improve the dewaterability of primary sludge. The optimal addition amount of Fe^{2+} and PMS was 0.1 g/g TSS and 0.25 g/g TSS, respectively, under which the capillary suction time (CST) and specific resistance to filtration (SRF) of the sludge was reduced by 79% and 95%. The physicochemical properties (particle size, zeta potential, EPS composition) of the primary sludge before and after oxidative conditioning were measured. Results showed that sulfate radicals generated from Fe^{2+}-PMS system effectively reduced organic matter in different EPS fractions, further destroying sludge floc cells. Then the bound water in the sludge flocs was released, thereby improving the sludge dewaterability. The microscopic morphology also indicated that the sludge flocs have a blocky structure with tight texture before conditioning. After conditioning, the sludge flocs become smaller, and many irregular pores are formed on the surface, which facilitates the passage of internal moisture. Economic analysis showed that Fe^{2+}+PMS conditioning is more economical than the traditional Fenton method.

Keywords: Dewaterability, Oxidative Conditioning Process, Peroxymonosulfate, Primary Sludge, Ferrous

INTRODUCTION

With the acceleration of urbanization and population growth, the large amount of excess sludge generated from domestic wastewater treatment process is increasingly attracting attention. The management costs of sludge usually account for 50-60% of the total operating expense in wastewater treatment plants (WWTPs) [1,2]. A complete sludge treatment system mainly includes a series of steps in which sludge dewatering is a key step to facilitate decrease of sludge volume, thus reducing treatment and ultimate disposal costs efficiently [3]. Sludge conditioning is an effective way to improve sludge dewaterability; the sludge floc is decomposed while converting the combined water contained in the sludge into free water, which is beneficial for subsequent dewatering process [4].

At present, sludge conditioning methods mainly include physical conditioning processes (heat treatment, freeze-thaw method, ultrasonic, microwave, electricity) [5-8], acid-base process [9], flocculation process [10,11], advanced oxidation process [12-14]. Among them, the advanced oxidation process (AOP) has become a prom-

ising sludge conditioning method because of its remarkable effect on improvement of sludge dewaterability. The method generates strong oxidizing free radicals through a series of reactions, such as hydroxyl radical ·OH and sulfate radicals SO_4^-, destroying microbial cells, degrading EPS, and releasing bound water to change the structure of sludge flocs [15]. The traditional Fenton method can improve the dewaterability of sludge by the formation of ·OH by Fe^{2+} catalyzed H_2O_2 under acidic conditions [16,17]. However, H_2O_2 is chemically unstable in the Fenton reaction, so the reaction needs to be carried out at a lower pH.

Compared with ·OH (1.8-2.7 V), SO_4^- has stronger oxidation potential (2.5-3.1 V), longer life (30-40 μs), and wider application range (4<pH<9) of pH in solution [18,19]. In recent years, advanced oxidation conditioning methods based on SO_4^- have also been extensively studied. PDS and PMS, which are precursors of SO_4^-, can be activated by heat, alkali, electrolysis and transition metal ions (Fe^{2+}, Co^{2+}, Ag^+) [20,21]. PMS is more easily activated as a free radical due to its asymmetrical structure [22]. Among the activators, metal ions have the advantages of simple operation and energy saving and have become the most common method for generating SO_4^-. Fe^{2+} as the most common transition metal, requires less activation energy, is less expensive, and is more suitable as an activator [23]. Under normal conditions of temperature and pressure,

Fe^{2+} can activate PMS to produce SO_4^-, which achieves good effect of sludge dewaterability [24]. Liu et al. [25] studied the conditioning effect of Fe^{2+}-PMS system on WAS. When pH=6.8, the CST and SRF reduction rates were higher (90% and 97%) at 0.9 mmol/g VSS PMS and 0.81 mmol/g VSS Fe^{2+}. Song et al. [26] compared the conditioning effect of Fe^{2+}-persulfate and Fe^{2+}-H_2O_2 systems on ADS with 50 mg/g TS Fe^{2+} and 250 mg/g TS persulfate; the obtained reduction rate of CST can reach 90%.

Although the combined oxidative conditioning process with Fe^{2+}-PMS system has good conditioning effect, the current studies are still limited to the treatment of WAS and ADS. Meanwhile, the reaction path of the process was rarely investigated. Therefore, further studies on its effect of other sludge types as well as the reaction mechanisms are still needed. Primary sludge (PA), generated from the primary treatment process (i.e., screening, grit and grease removal, gravity-settling), is one of most typical sludge types of WWTPs [27]. Compared to WAS, PA contains both biodegradable organic and inorganic materials, and has a larger solid concentration of 2-9% [28]. Although current WWTPs mixed the two flows of primary sludge and secondary sludge in subsequent treatment and disposal processes in consideration of the actual operating overhead, an ideal WWTP was supposed to separate two sludge flows [29,30]. However, studies usually ignored the feasibility of primary sludge. Actually, many researchers have insisted primary sludge was a potential conditioner for bio-sludge in municipal and industrial sludge dewatering fields [31]. Other conditioning processes, e.g., freeze-thaw method, enzyme treatment, ultrasonication, chemical and physical conditioners, were reported about the application on primary sludge or mixed sludge [32-35]. Benitez et al. [32] employed 1.3% of a cationic copolymer coagulant (CALGON WT-2640) as chemical conditioner with 37% of bagasse as physical conditioner to enhance the dewaterability of the primary sludge from an industrial and municipal mixed wastewater treatment unit. Diak et al. [33] investigated the ability of potassium ferrate (VI) pre-treatment followed by freeze-thaw method to stabilize and dewater primary sludge simultaneously, with a gravitational reduction of sludge volume up to 79%. Xiao et al. [35] reported mixed primary and secondary sludge filterability was improved after ultrasonic pre-treatment combined with acidification (pH=2). Xiao et al. [4] further used Fe^{2+}-PMS system to oxidize five different types of sludge (containing raw mixed sludge and ultrasonic pre-treated mixed sludge) with 0.9 mmol/g VSS PMS and 0.54 mmol/g VSS Fe^{2+}. The conditioning effect of ultrasonic pre-treatment sludge was optimum (CST reduction rate was 96.19%), while thermal pre-treatment anaerobic digested sludge was the worst (CST reduction rate was 47.64%).

The advanced oxidative conditioning on primary sludge alone has rarely been reported so far. To expand the application range and technical potential of the Fe^{2+}-PMS system, this study carried out the Fe^{2+}-PMS oxidation conditioning process for the primary sludge, with CST and SRF as the main indicators of dewaterability. The effects of oxidative conditioning with different chemicals dosages and initial pH on sludge dewaterability were investigated. The properties and structures of the primary sludge (such as particle size, zeta potential, EPS composition, microscopic morphology) before and after oxidation conditioning were also studied to explore the mechanisms.

Table 1. Main characteristics of primary sludge

Parameter	Primary sludge
Moisture content (%)	94.96±0.07
Solid content (%)	4.93±0.07
TS (g/L)	51.84±1.61
TSS (g/L)	48.06±0.80
VS (g/L)	22.19±0.23
VSS (g/L)	20.77±0.10
pH	5.82±0.20
COD (mg/L)	37333±81

Table 2. Experimental design of the batch tests

Group	No.	PMS dosage (g/g TSS)	Fe^{2+} dosage (g/g TSS)
I. Effect of PMS dosage	1	0.00	0.10
	2	0.05	0.10
	3	0.10	0.10
	4	0.25	0.10
	5	0.40	0.10
	6	0.50	0.10
II. Effect of Fe^{2+} dosage	7	0.25	0.00
	8	0.25	0.05
	9	0.25	0.10
	10	0.25	0.25
	11	0.25	0.40
	12	0.25	0.50

MATERIAL AND METHODS

1. Sludge Source

The primary sludge used in the experiment was taken from the primary sedimentation tank of a full scale WWTP located in Shenzhen, China. The sludge was stored in a temperature controlled cold room at $4\,^{\circ}C$. The main characteristics of the primary sludge are shown in Table 1.

2. Batch Experiment

Two sets of batch tests were conducted to investigate the effect of PMS and Fe^{2+} dosages on primary sludge dewaterability (Table 2). Set (I) studied the effect of PMS dosage (0.05-0.50 g/g TSS, see Table 2), while the Fe^{2+} dosage was set as 0.1 g/g TSS. Set (II) aimed to study the effect of Fe^{2+} dosage (0.05-0.50 g/g TSS, see Table 2) and the PMS dosage was maintained as 0.25 g/g TSS. The selection of PMS and Fe^{2+} dosages used in this study was based on our previous studies [36].

In addition, the effect of pH on the dewaterability of the primary sludge was also studied and compared. Besides the initial pH (5.8), different pH (4.0 and 5.0) was also adjusted by adding 20% sulfuric acid.

In each batch, 100 mL of primary sludge was added to a 250 mL screw-cap bottle. Different dosages of potassium hydrogen persulfate and ferrous sulfate heptahydrate were added into the bottles at different dosages. The samples in the bottles were then mixed with

a shaker at 150 rpm or 30 min. The treated samples were then taken for CST and SRF measurements (as described in Section 2.4, 2.5).

3. Extraction and Determination of EPS from Sludge

The EPS was extracted from sludge by a modified heat extraction method [37]. Briefly, a 50 mL sludge sample was added into a centrifuge tube and centrifuged at 4,000 g for 10 min. The supernatant was collected as soluble EPS (SB-EPS). Then, the residual sludge was resuspended to 50 mL using 0.05% NaCl solution. The mixture was centrifuged at 8,000 g for 10 min and the supernatant was collected as loosely bound EPS (LB-EPS). Moreover, the residual sample was resuspended to the original volume and water-bath heated at 60 $^{\circ}$C for 30 min. After centrifugation at 12,000 g for 30 min, the supernatant was collected as tightly bound EPS (TB-EPS). Finally, three EPSs were filtered through a 0.45 μm filter and tested.

The proteins in EPS were determined by the rapid Lowry method, the polysaccharide was determined by the phenol-sulfuric acid method, the DOC was determined by the TOC analyzer, the Mv in EPS and Mv/Mn in LB-EPS were determined by high-performance size exclusion chromatography.

4. Determination of CST

CST was measured by capillary suction timer (Type 304M, Triton Electronics Ltd.) to record the time of the moisture in the sludge permeating from the inner ring probe to the outer ring probe. The needed time is the CST of the sample. Each set of experiments was repeated three times. According to the CST before and after sludge conditioning, the sludge CST reduction rate is calculated, as shown in Eq. (1):

$$R(\%) = \frac{CST_0 - CST_1}{CST_0} \times 100\% \tag{1}$$

where CST_0 represents capillary water absorption time (s) before sludge conditioning; CST_1 represents capillary water absorption time (s) after sludge conditioning.

5. Determination of SRF

SRF was measured by sludge specific resistance test device (TG-250, Shanghai Tongguang Science and Education Instrument Co., Ltd.) with a vacuum pressure of 0.03 MPa in the filter. The moisture content of the sludge before and after filtration was measured.

Each set of experiments was repeated three times.

Sludge specific resistance and reduction rate of sludge specific resistance were calculated according to Eqs. (2) and (3):

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

where SRF - sludge specific resistance (m/kg); P - experimental pressure (N/m^2); A - filtration area (m^2); b - filtration time ratio (s/m^6), the slope of the straight line obtained by V (volume of the sludge filtrate) as the abscissa, t/V is the ordinate; μ - the viscosity of the filtrate (N·s/m^2); ω - the weight of the dry sludge (kg/m^3) produced per unit volume of the filtrate.

$$R'(\%) = \frac{SRF_0 - SRF_1}{SRF_0} \times 100\% \tag{3}$$

where R′ - reduction rate of sludge specific resistance (%); SRF_0 - the specific resistance before sludge conditioning (m/kg); SRF_1 - the specific resistance after sludge conditioning (m/kg).

6. Other Analytical Methods

The sludge particle size was measured using a laser particle size analyzer (Mastersizer 2000, Malvern). The zeta potential was measured using a zeta potential analyzer (Nano ZS). Scanning electron microscopy was used to observe the microscopic morphology of the sludge. A small amount of the sample was lyophilized and pulverized. After gold spraying, it was observed by scanning electron microscopy (HITACHI SU8010).

7. Data Analysis

Graphs and statistical analyses were performed by Microsoft Excel 2016. Significant differences (P<0.05) were determined using one-way analysis of variance (ANOVA). The results were presented as mean ± the standard deviation (SD).

RESULTS AND DISCUSSION

1. Effect of Fe^{2+}-PMS Conditioning on Primary Sludge Dewaterability

As shown in Fig. 1(a), when Fe^{2+} dosage was 0.1 g/g TSS, the CST reduction rate increased first and then decreased with the increase
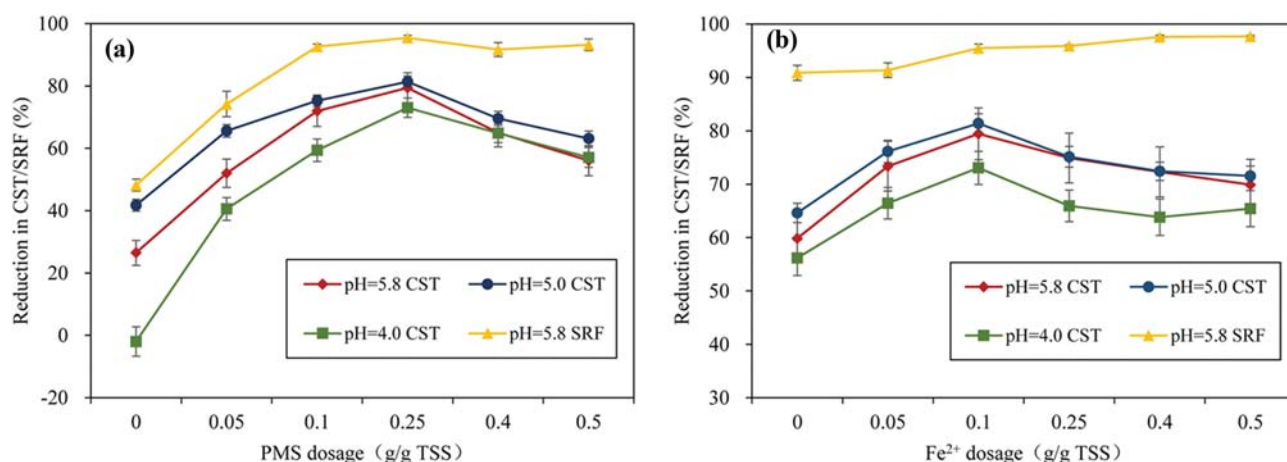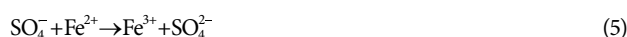

Fig. 1. Effect of different (a) PMS and (b) Fe^{2+} dosages on reduction in CST/SRF (%). In (a), the Fe^{2+} dosage was 0.1 g/g TSS. In (b), the PMS dosage was 0.25 g/g TSS. The initial CST was 253.5±9.4 s.

of PMS dosage at different pH, and the maximum CST reduction rate attained while PMS dosage was 0.25 g/g TSS. Similarly, when the PMS dosage was set as 0.25 g/g TSS, the CST reduction rate increased first and then decreased with the increase of Fe^{2+} dosage, as shown in Fig. 1(b). The highest CST reduction rate occurred when Fe^{2+} dosage was 0.1 g/g TSS.

Generally, ferrous ions activate PMS by electron transfer to produce SO_4^-, and the highly oxidizing free radicals can destroy microbial cells and effectively degrade EPS to enhance the dewaterability of sludge [38]. As shown in Eq. (4), increasing the dosage of Fe^{2+} and PMS is beneficial for producing SO_4^-. However, according to Eqs. (5) and (6), the concentration of Fe^{2+} and PMS may cause the annihilation of SO_4^-. In addition, SO_4^- itself may also be quenched (Eq. (7)) [24]. This may explain why the dewaterability of the sludge first increases and then decreases as the addition of Fe^{2+} and PMS increases.

$$Fe^{2+}+HSO_5^-\rightarrow Fe^{3+}+SO_4^-+OH^- \tag{4}$$

$$SO_4^-+Fe^{2+}\rightarrow Fe^{3+}+SO_4^{2-} \tag{5}$$

$$SO_4^-+HSO_5^-\rightarrow SO_5^-+SO_4^{2-}+H^+ \tag{6}$$

$$SO_4^-+SO_4^-\rightarrow S_2O_8^{2-} \tag{7}$$

When the pH was 5.00, the CST reduction rate was the highest under different dosage conditions, which was up to 81.40%. Meanwhile, the CST reduction rate reached 79.42% without adjustment of pH. However, there was no significant difference between the results (P>0.05). Therefore, to save operation cost, the original pH= 5.8 was selected for primary sludge conditioning. The dosing of PMS and Fe^{2+} was 0.25 g/g TSS and 0.1 g/g TSS, respectively. This is similar to the results reported by Zhen et al. [39]. When pH was between 3-8, the sludge had a higher CST reduction rate. However, when the pH was too high (>pH=10) or too low (<pH=3), the dewaterability of the sludge was deteriorated [25]. Therefore, when pH value was moderate, it could not significantly affect the effect of oxidative conditioning with Fe^{2+} and PMS.

The SRF reduction rates of the sludge with a pH of 5.80 were also measured. The SRF reduction rate reached the maximum when the PMS dosage was 0.25 g/g TSS. With the Fe^{2+} dosage increased, the SRF reduction rate was especially high when the Fe^{2+} dosage was 0.1 g/g TSS, reaching 95.46%; when the Fe^{2+} dosage was increased to 0.5 g/g TSS, the maximum reduction rate was 97.69%. However, there was no significant difference between them (P> 0.05). Therefore, the optimal dosing of PMS and Fe^{2+} was 0.25 g/g TSS and 0.1 g/g TSS, which was consistent with the results of CST studies.

2. Mechanism Analysis of Primary Sludge Dewaterability Improvement

2-1. Changes of Particle Size and Zeta Potential

According to Fig. 2, the particle size of the primary sludge decreased after conditioning at different pH values. The change of particle size was particularly significant at pH 5.80, which was 75.2± 4.2 μm before conditioning, and decreased to 42.1±2.7 μm after conditioning. It indicated that the EPS of sludge was oxidized, and the sludge floc structure was broken and became particles with smaller size. Along with the particle size reduction, the bound
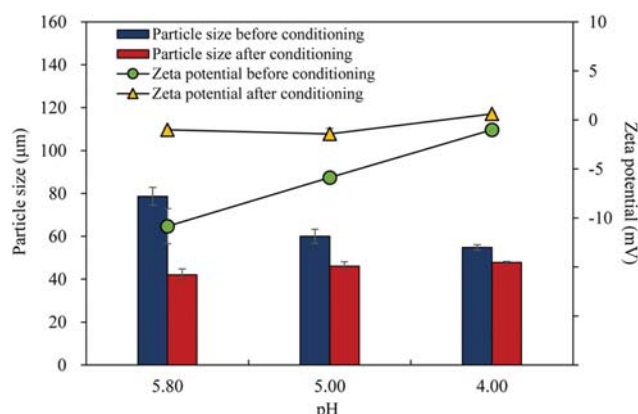

Fig. 2. Particle size and zeta potential of sludge samples before and after oxidative conditioning. Experimental conditions: Fe^{2+} dosage: 0.1 g/g TSS, and PMS dosage: 0.25 g/g TSS.

water was also released, which improved the dewaterability of the primary sludge [38].

The zeta potential of the original primary sludge before conditioning was −10.8±1.8 mV, and the surface of the sludge flocs had a large amount of negative charge. According to the DLVO theory, the increase of the negative surface charge enhanced electrostatic repulsion between the sludge particles, which was not conducive to sludge accumulation. Therefore, as the zeta potential increased, the surface charge of the sludge decreased, which led to the aggregation and precipitation of sludge and enhanced sludge dewaterability [40].

In this study, the zeta potential of the sludge changed significantly after the addition of PMS and Fe^{2+}, which became −1.01± 0.21 mV and approaching 0. This was similar to other studies using ZVI-PMS [41], the optimum treatment effect was attained when the zeta potential was −1.2±0.02 mV. Liu et al. also confirmed that when the zeta potential increased from the initial −28 mV to nearly 0 mV, the dewaterability of the bioleaching sludge was greatly improved [42]. However, because the pH value could also change the sludge zeta potential [43], it cannot be used as a single indicator for improvement of sludge dewaterability.

2-2. Changes of EPS Composition

Sludge was mainly composed of microbial cells, EPS and water. The content of protein and polysaccharide in different components of extracellular polymer has a great influence on sludge dewaterability [44]. The changes of protein, polysaccharide, DOC and molecular weight in EPS of primary sludge before and after oxidation treatment under different pH conditions are shown in Fig. 3.

The highly oxidizing SO_4^- had a significant effect on the proportion and composition of EPS in primary sludge. Before conditioning, the protein (Fig. 3(a)) was mainly concentrated in SB-EPS and TB-EPS. After the addition of Fe^{2+} and PMS, the concentration of protein was reduced in both of them. Polysaccharide (Fig. 3(b)) was mainly concentrated in TB-EPS before conditioning, and its content was up to 1.96 mg/g TSS. After conditioning, it was mainly concentrated in LB-EPS. The content of DOC (Fig. 3(c)) increased in LB-EPS after conditioning, while its content in TB-EPS decreased, indicating that oxidation process enhanced disso-
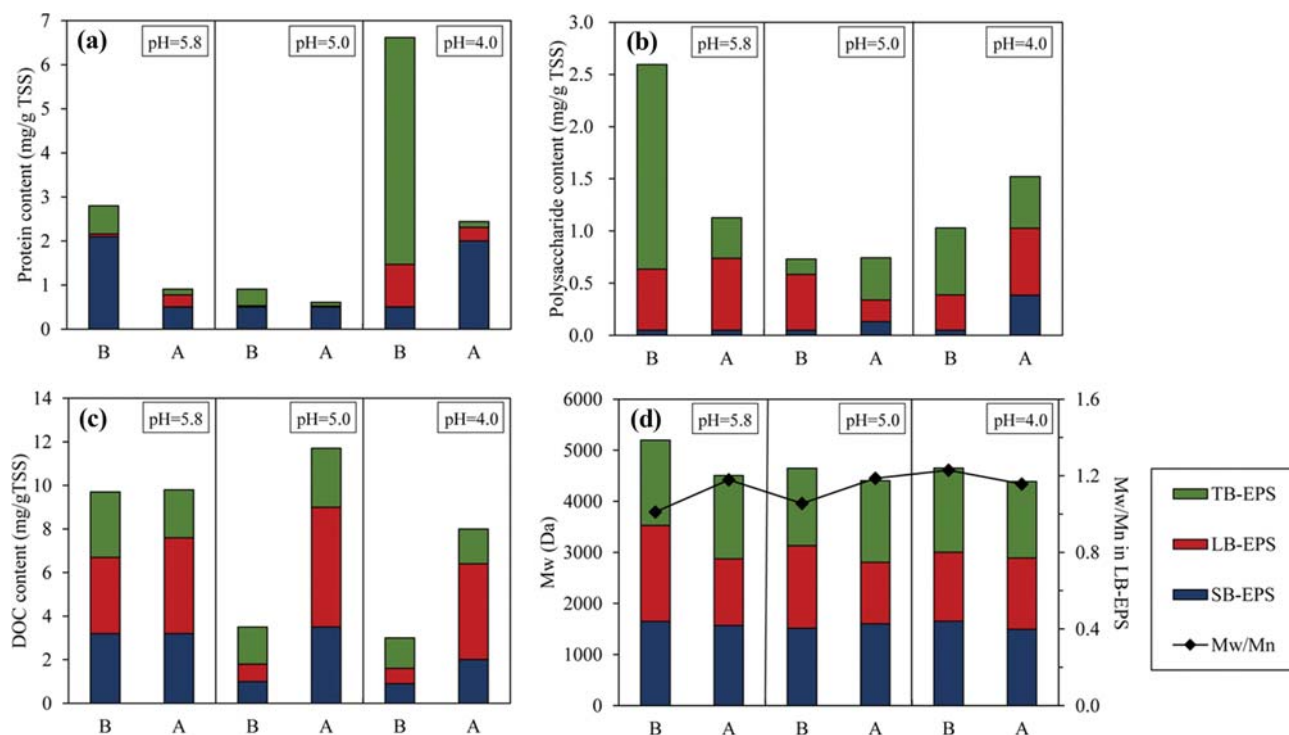
Fig. 3. Variances of (a) protein, (b) polysaccharide, (c) DOC, (d) Mw in SB-EPS, LB-EPS, and TB-EPS and (d) Mw/Mn in LB-EPS before and after oxidative conditioning. Experimental conditions: Fe^{2+} dosage: 0.1 g/g TSS, and PMS dosage: 0.25 g/g TSS. Abbreviations used: B, before Fe^{2+}-PMS oxidative conditioning; A, after Fe^{2+}-PMS oxidative conditioning.

lution of sludge components, and some organic matter was transferred from TB-EPS to LB-EPS. After oxidative conditioning, the molecular weight of EPS decreased from 5,198 Da to 4,503 Da (Fig. 3(d)), while the Mw/Mn in LB-EPS increased, indicating that some of the macromolecules had been broken down into small molecules.

After conditioning, the content of TB-EPS in the sludge decreased. This indicated that the oxidation process caused damage to the TB-EPS layer, so that the tightly bound water was released and transformed into free water that was more easily removed, thereby improving the sludge dewaterability. TB-EPS adhered to the cell surface, which acted as important protective barrier to the stability of the sludge flocs. TB-EPS contained a large amount of bound water, which impeded enhancement of sludge dewaterability [45]. The bound EPS also formed a stable gel that prevented water from leaking through the pores of sludge flocs [46]. In addition, the destruction of LB-EPS and TB-EPS also caused microbial cells to be exposed to oxidants, which were destroyed by oxidation, releasing the bound water in the sludge cells [4].

On the other hand, after oxidative conditioning, the content of protein and polysaccharide in LB-EPS and SB-EPS increased, but less than the reduction of TB-EPS, and the total amount in EPS showed a decreasing trend. This phenomenon indicated that the free radicals also have the potential to decompose loose EPS, which was beneficial to the improvement of the sludge dewaterability. The result was also consistent with previous studies on the decomposition of EPS by the Fe^{2+}-H_2O_2 system [38]. Studies also showed that the reduction of protein and polysaccharide content in EPS

increased the hydrophilicity of the sludge, which improved sludge dewaterability [47]. The reduction in protein also reduced the surface load of the sludge, making the sludge easier to aggregate [48].

Xiao et al. [35] reported that mixed primary and secondary sludge dewaterability closely correlated with the species and distribution of protein and polysaccharide in LB-EPS. In particular, compounds in the molecular weight range between 10^6-5×10^7 Da were dominant. Xiao et al. [4] also studied the physical, chemical and biological characteristics of mixed sludge after Fe^{2+}-PMS oxidative conditioning. Increases of DOC, protein, and polysaccharide concentrations in SB-EPS were observed for mixed sludge, which was similar to the present study. This likely resulted from the sludge solubilization of the constituents and oxidation elution with Fe^{2+}-PMS. Meanwhile, the content of organic matter in TB-EPS and LB-EPS as well as the bound water content decreased after Fe^{2+}-PMS treatment. A significant increase in the cell mortality rate reflected the damaging effects of strong oxidative free radicals on microbial cells. On this basis, it is proposed that the oxidative conditioning process of sludge can be divided into two stages: oxidation by SO_4^- and flocculation by Fe^{3+}. Li et al. [41] explored the oxidative conditioning process (ZVI-PMS) combined with heat treatment (ZVI-PMS-T). Both ZVI-PMS and ZVI-PMS-T conditioning could enhance sludge fluidity, and TB-EPS decomposition could lead to sludge breakage and improve sludge dewaterability. Zhen et al. [49] explored the combined effect of Fe^{2+}-PDS and microwave of gel-like flocs in WAS. The thermal effect of microwaves could promote PDS to produce more SO_4^-; the non-thermal effect of microwaves could cause cell destruction and reduce the formation of

bound water. The combined process could also cause cell disruption, thereby improving the sludge dewaterability.

In summary, this study demonstrated that the oxidative conditioning of primary sludge by SO_4^- was through three paths: (a) the degradation of organic matter in SB-EPS and LB-ESP, (b) breaking of the TB-EPS layer and releasing the combined water, and (c) destroying the cell structure to further release the bound water. These synergistic effects enhanced the sludge dewaterability.

In addition, adjustment of pH also had various effects on the EPS component. For example, when pH=4.00, the protein content in the TB-EPS increased significantly (5.15 mg/g TSS), and the increment of polysaccharide in SB-EPS was more than its reduction in TB-EPS. This might have been caused by dissolution of organic matter from the cells by excess addition of acid.

2-3. Changes of Microscopic Characteristics

To investigate the morphology and structure changes of the primary sludge, SEM was used to observe the changes of the primary sludge before and after oxidation conditioning at different pH values, as shown in Fig. 4.

The original primary sludge (Fig. 4(a)) has a blocky and plate-like structure with a tight texture and a relatively smooth surface. This morphological structure could enclose the moisture inside tightly, resulting in a low rate of sludge dewaterability. When the pH of sludge was adjusted (Fig. 4(b) and (c)), the micromorphology did not significantly change, showing a relatively flat and smooth surface. After conditioning, when pH=5.80 and 5.00 (Fig. 4(d) and (e)), the flocs became smaller after sludge conditioning, and many irregular pores were formed on the surface, which changed the structure in which the original moisture was entrapped. Meanwhile, the large sludge flocs were cracked into small particles, which was consistent with the changes of sludge particle size shown in Fig. 2. Under the condition of pH=4.00 (Fig. 4(f)), the morphology of

the sludge did not change significantly, and the sludge particles decreased, but no large number of pores was created. That might be because excessive acid addition destructed microbial cells in the sludge, dissolved intracellular material, and encapsulated sludge surface. This was also consistent with the results in Fig. 1 and Fig. 3.

Wang et al. [50] studied the effect of oxidative conditioning with EDTA chelated-Fe^{2+} activated PMS system (PMS-EDTA-Fe^{2+}) on ADS. The SEM results showed that after treatment with PMS-Fe^{2+} conditioning, the sludge cell population was destroyed by oxidation and a corroded shell-like structure was observed, but an intact cell structure still existed. Liu et al. [12] conditioned the mixed sludge using the Fenton method and used Quick lime and 42.5 ordinary Portland cement (OPC) as the skeleton construct. It could be observed from the SEM that the original sludge had a cotton wool structure and the surface was in the form of flakes, but after treatment, the sludge particles became smaller and formed columnar crystals. These irregular structures could form rigid porous structure during mechanical dewatering process with high pressure, providing channels for release of the free water.

3. Economic Analysis of Fe^{2+}-PMS Conditioning Process

The economic cost of the Fe^{2+}-PMS conditioning process compared with a classical Fenton conditioning process [51] was conducted. Fenton conditioning as a traditional AOP has been widely used in sludge dewaterability. In the economic comparison, it was assumed that two types of conditioning processes had the same efficiency for the enhancement of sludge dewaterability. Moreover, costs for sludge transportation and disposal of the two methods would be identical since the generated sludge cakes volume and mass were hypothesized to be the same. The differences between two methods were predominantly related to the types and dosages of drugs. Therefore, the economic analysis focused on the chemical consumption. On an assumption of a WWTP with a popula-
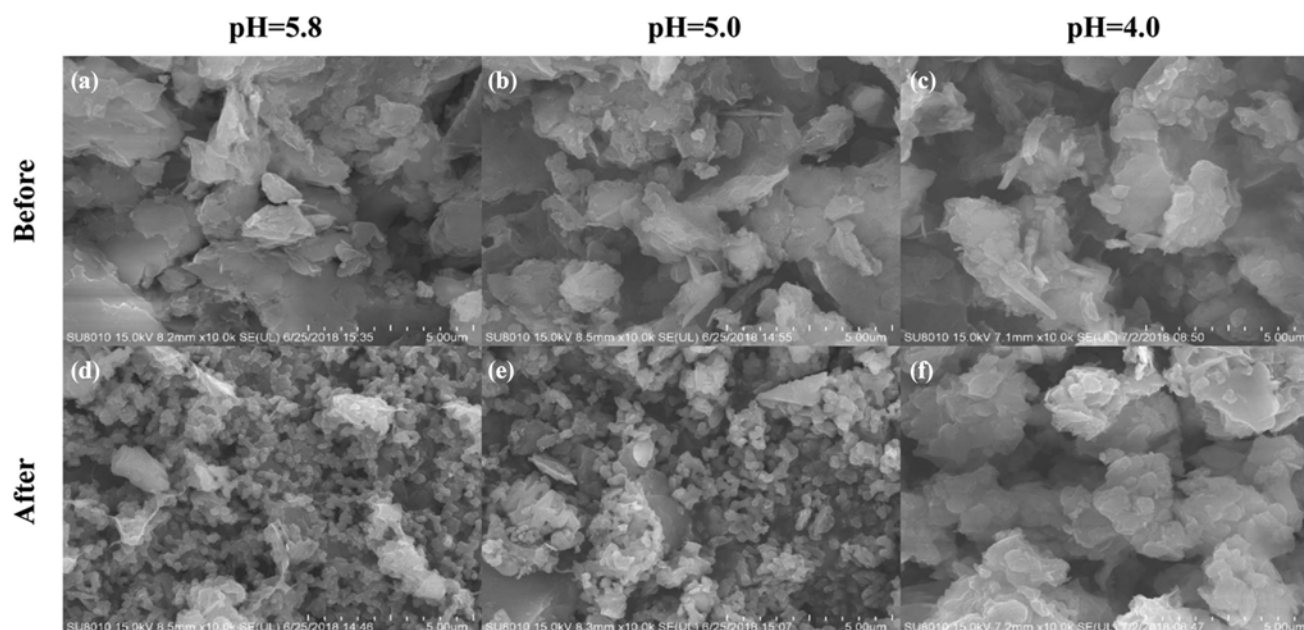

Fig. 4. SEM results of sludge samples before and after oxidative conditioning (10,000×). pH=5.8 (left), pH=5.0 (middle) and pH=4.0 (right). Experimental conditions: Fe^{2+} dosage: 0.1 g/g TSS, and PMS dosage: 0.25 g/g TSS.

Table 3. Comparison of different iron activated AOPs for sludge conditioning

AOPs	Sludge type	Solid content (g/L)	CST reduction (%)	SRF reduction (%)	Optimal dosage	pH	Reference
Fenton	Biological sludge	TSS=20.0 g/L	48.5	93.3	Fe^{2+}=5 g/L, HP=6 g/L	3	[51]
Fe^{2+}-PMS	**Primary sludge**	**TS=51.84 g/L**	**79.42**	**95.46**	**Fe^{2+}=0.1 g/g TSS, PMS=0.25 g/g TSS**	**5.8**	**This study**
Fe^{2+}-PMS	Mixed sludge	TS=16.25 g/L	89.13	nd	Fe^{2+}=0.54 mmol/g VSS, PMS=0.9 mmol/g VSS	6.04	[4]
Fe^{2+}-PMS	Ultrasonic pretreated mixed sludge	TS=14.59 g/L	96.19	nd	Fe^{2+}=0.54 mmol/g VSS, PMS=0.9 mmol/g VSS	5.97	[4]
Fe^{2+}-PDS	WAS	TSS=20.7 g/L	94.2	nd	Fe^{2+}=1.5 mmol/g VSS, PDS=1.2 mmol/g VSS	6.95	[52]
ZVI-PDS	ADS	TS=28.5 g/L	90	nd	ZVI=0.5 g/g TS, PDS=2.0 g/g TS	7.47	[53]
ZVI-HP	ADS	TS=22.3 g/L	90	nd	HP=18 mg/g TS, ZVI=2.0 g/g TS	7.72	[54]
EZP	Industrial sludge	TSS=15.9 g/L	50.1	57.6	Voltage=40 V, Na_2PDS=4.15 g/L	6.73	[55]
Fe^{2+}-Heat-PMS	WAS	TSS=13.6 g/L	92.9	nd	Fe^{2+}=0.6 mmol/g VSS, PMS=1.0 mmol/g VSS	6.7	[56]
PMS-EDTA-Fe^{2+}	ADS	TSS=51.62 g/L	60	70.6	EDTA-2Na=0.4 mmol/g VSS, Fe^{2+}=1.2 mmol/g VSS, PMS=1.0 mmol/g VSS	7.77	[50]
VTM-PMS-RH	WAS	TSS=15.4 g/L	94.8	nd	PMS=200 mg/g TSS, VTM=1 g/g TSS, RH=200 mg/g TSS	6.8	[22]

tion equivalent of 100,000, the Fe^{2+}-PMS system could save up to 100% ($462,600 per year) of the costs compared with the traditional Fenton methods. However, compared with chemical sludge conditioning methods (e.g., aluminum salt), the Fe^{2+}-PMS system needs to be further studied to continuously reduce the cost. In addition, future research should also focus on the challenges facing the application of full-scale WWTPs.

4. Comparison of Iron-activated AOPs

Table 3 compares the effects of several AOPs based on iron activation on sludge dewaterability. The effect of the oxidative conditioning process by Fe^{2+}-PMS was in the leading position among the AOPs.

Compared with the traditional Fenton method, due to the better oxidation effect of SO_4^- than ·OH, Fe^{2+}-PMS had better treatment effect and wider application range of pH between 4.0-8.0. In comparison with the ZVI activation systems, the ferrous system also had a better oxidative effect. Furthermore, although both Fe^{2+}-PMS and Fe^{2+}-PDS had similar oxidative effects, the addition amount of PMS was usually less than PDS. Table 3 also includes some combined conditioning processes based on Fe^{2+}-PMS/PDS. It can be seen that iron-activated sulfate radical processes also had the potential to combine with magnetic materials or construction of skeletal structure for the treatment of refractory sludge. Therefore, compared with other AOPs, Fe^{2+}-PMS oxidative conditioning technology had the advantages of high treatment efficiency, less chemical dosage, wide application range, and has great potential in the field of sludge treatment, which deserves further in-depth research.

CONCLUSIONS

The feasibility of improving primary sludge dewaterability based on oxidative conditioning process with combination of Fe^{2+} and PMS was investigated by a series of batch tests. The results indicated that the primary sludge dewaterability was significantly enhanced with the reduction rates of CST and SRF attained by 79% and 95% while the optimal conditioning parameters were pH=5.8, PMS was 0.25 g/g TSS and Fe^{2+} was 0.1 g/g TSS. Mechanisms for enhancement of primary sludge dewaterability were analyzed based on the changes of physicochemical properties on primary sludge. After the primary sludge was oxidized, the particle size decreased from 75.2±4.2 μm to 42.1±2.7 μm, and the zeta potential approached −1.01±0.21 mV. Sulfate radicals not only reduce the organic matter content in SB-EPS and LB-ESP, but also affect the composition of TB-EPS layer and further destroy the cell structure of sludge. After oxidative conditioning, the sludge flocs were destroyed, and loose porous structure was formed on the surface, which was easier for moisture passage, thereby improving the sludge dewaterability. Compared to the traditional Fenton method, the Fe^{2+}+PMS conditioning method could save up to 100% ($462,600 per year) of the costs based on a WWTP with a population equivalent of 100,000.

ABBREVIATIONS

ADS : anaerobic digested sludge
AOPs : advanced oxidation processes
COD : chemical oxygen demand
CST : capillary suction time
DOC : dissolved organic carbon
EPS : extracellular polymeric substances
EZP : electrolysis/electrocoagulation and zero-valent iron activated persulfate oxidation
HP : hydrogen peroxide, H_2O_2
LB-EPS : loosely bound extracellular polymeric substances
MW : microwave
Mw : weight-average molecular weight
Mn : number-average molecular weight
·OH : hydrogen radical
OPC : quick lime and 42.5 ordinary portland cement
PDS : peroxydisulfate, $S_2O_8^{2-}$
PMS : peroxymonosulfate, HSO_5^-
PMS-EDTA-Fe^{2+} : peroxymonosulfate activated by EDTA chelated-Fe^{2+} process
SB-EPS : soluble extracellular polymeric substances
SEM : scanning electron microscope
SO_4^- : sulfate radical
SRF : specific resistance to filtration
TB-EPS : tightly bound extracellular polymeric substances
TOC : total organic carbon
TS : total solids
TSS : total suspended solids
VS : volatile solids
VSS : volatile suspended solids
VTM-PMS-RH : natural vanadium-titanium magnetite-activated peroxymonosulfate oxidation coupled with rice husk as skeleton builder
WAS : waste activated sludge
ZVI : zero-valent iron

REFERENCES

1. Q. Wang, W. Wei, Y. Gong, Q. Yu, Q. Li, J. Sun and Z. Yuan, *Sci. Total Environ.*, **587-588**, 510 (2017).
2. W. Wei, X. Zhou, D. Wang, J. Sun and Q. Wang, *Water Res.*, **118**, 12 (2017).
3. X. Zhou, G. Jiang, Q. Wang and Z. Yuan, *Rsc Adv.*, **4**, 50644 (2014).
4. K. Xiao, Y. Chen, X. Jiang, Q. Yang, W. Y. Seow, W. Zhu and Y. Zhou, *Water Res.*, **109**, 13 (2017).
5. B. Cao, W. Zhang, Y. Du, R. Wang, S. P. Usher, P. J. Scales and D. Wang, *Water Res.*, **130**, 363 (2018).
6. W. Gao, *Desalination*, **268**, 170 (2011).
7. S. Guo, F. Qu, A. Ding, J. He, H. Yu, L. Bai, G. Li and H. Liang, *Rsc Adv.*, **5**, 43065 (2015).
8. L. Wang, C. Qian, J. Jiang, X. Ye and H. Yu, *Environ. Pollut.*, **231**, 1388 (2017).
9. G. Q. Su, M. X. Huo, Z. G. Yuan, S. Y. Wang and Y. Z. Peng, *Bioresour. Technol.*, **136**, 237 (2013).
10. M. B. Kurade, K. Murugesan, A. Selvam, S. Yu and J. W. C. Wong, *Bioresour. Technol.*, **217**, 179 (2016).
11. W. Zhang, P. Xiao, Y. Liu, S. Xu, F. Xiao, D. Wang and C. W. K. Chow, *Sep. Purif. Technol.*, **132**, 430 (2014).
12. H. Liu, J. Yang, N. Zhu, H. Zhang, Y. Li, S. He, C. Yang and H. Yao, *J. Hazard. Mater.*, **258**, 144 (2013).
13. X. Zhou, Q. Wang, G. Jiang, P. Liu and Z. Yuan, *Bioresour. Technol.*, **185**, 416 (2015).
14. X. Zhou, H. Chen, S. Gao, S. Han, R. Tu, W. Wei, C. Cai, P. Liu, W. Jin and Q. Wang, *Korean J. Chem. Eng.*, **34**, 2672 (2017).
15. G. Zhen, X. Lu, Y. Li, Y. Zhao, B. Wang, Y. Song, X. Chai, D. Niu and X. Cao, *Bioresour. Technol.*, **119**, 7 (2012).
16. R. Dewil, J. Baeyens and E. Neyens, *J. Hazard. Mater.*, **117**, 161 (2005).
17. E. Neyens, J. Baeyens, M. Weemaes and B. De Heyder, *J. Hazard. Mater.*, **98**, 91 (2003).
18. M. S. Kim, K. Lee, H. Kim, H. Lee, C. Lee and C. Lee, *Environ. Sci. Technol.*, **50**, 7106 (2016).
19. W. Ren, Z. Zhou, Y. Zhu, L. Jiang, H. Wei, T. Niu, P. Fu and Z. Qiu, *Int. Biodeter. Biodegr.*, **104**, 384 (2015).
20. C. Liu, B. Wu and X. Chen, *Chem. Eng. J.*, **335**, 865 (2018).
21. S. Wacławek, H. V. Lutze, K. Grübel, V. V. T. Padil, M. Černík and D. D. Dionysiou, *Chem. Eng. J.*, **330**, 44 (2017).
22. C. Liu, *Chem. Eng. J.*, **359**, 217 (2019).
23. A. Rastogi, S. R. Al-Abed and D. D. Dionysiou, *Water Res.*, **43**, 684 (2009).
24. C. Cai, H. Zhang, X. Zhong and L. Hou, *J. Hazard. Mater.*, **283**, 70 (2015).
25. J. Liu, Q. Yang, D. Wang, X. Li, Y. Zhong, X. Li, Y. Deng, L. Wang, K. Yi and G. Zeng, *Bioresour. Technol.*, **206**, 134 (2016).
26. K. Song, X. Zhou, Y. Liu, Y. Gong, B. Zhou, D. Wang and Q. Wang, *Sci. Rep-Uk.*, **6**, 24800 (2016).
27. R. Canziani and L. Spinosa *Sludge from wastewater treatment plants*, Elsevier, The Netherlands (2019).
28. V. K. Tyagi and S. Lo, *Renew. Sust. Energy Rev.*, **25**, 708 (2013).
29. H. Carrère, C. Dumas, A. Battimelli, D. J. Batstone, J. P. Delgenès, J. P. Steyer and I. Ferrer, *J. Hazard. Mater.*, **183**, 1 (2010).
30. P. Devi and A. K. Saroha, *Sci. Total Environ.*, **578**, 16 (2017).
31. T. Meyer, P. Amin, D. G. Allen and H. Tran, *J. Environ. Chem. Eng.*, **6**, 6317 (2018).
32. J. Benítez, A. Rodríguez and A. Suárez, *Water Res.*, **28**, 2067 (1994).
33. J. Diak and B. Örmeci, *J. Environ. Manage.*, **216**, 406 (2018).
34. J. Lu, S. Rao, T. Le, S. Mora and S. Banerjee, *Process Biochem.*, **46**, 353 (2011).
35. K. Xiao, Y. Chen, X. Jiang, V. K. Tyagi and Y. Zhou, *Water Res.*, **105**, 470 (2016).
36. X. Zhou, W. Jin, H. Chen, C. Chen, S. Han, R. Tu, W. Wei, S. Gao, G. Xie and Q. Wang, *Water Sci. Technol.*, **76**, 2427 (2017).
37. F. Sun, K. Xiao, W. Zhu, N. Withanage and Y. Zhou, *Water Res.*, **130**, 208 (2018).
38. X. Zhou, G. Jiang, T. Zhang, Q. Wang, G. Xie and Z. Yuan, *Bioresour. Technol.*, **192**, 817 (2015).

39. G. Zhen, X. Lu, Y. Zhao, X. Chai and D. Niu, *Bioresour. Technol.*, **116**, 259 (2012).

40. G. Zhen, X. Lu, B. Wang, Y. Zhao, X. Chai, D. Niu, A. Zhao, Y. Li, Y. Song and X. Cao, *Bioresour. Technol.*, **124**, 29 (2012).

41. Y. Li, X. Yuan, D. Wang, H. Wang, Z. Wu, L. Jiang, D. Mo, G. Yang, R. Guan and G. Zeng, *Bioresour. Technol.*, **262**, 294 (2018).

42. F. Liu, L. Zhou, J. Zhou, X. Song and D. Wang, *J. Hazard. Mater.*, **221-222**, 170 (2012).

43. K. B. Thapa, Y. Qi and A. F. A. Hoadley, *Colloids Surf. A: Physicochem. Eng. Aspects*, **334**, 66 (2009).

44. Q. Yu, H. Lei, G. Yu, X. Feng, Z. Li and Z. Wu, *Chem. Eng. J.*, **155**, 88 (2009).

45. G. Zhen, X. Lu, Y. Li and Y. Zhao, *Bioresour. Technol.*, **136**, 654 (2013).

46. G. Sheng, H. Yu and X. Li, *Biotechnol. Adv.*, **28**, 882 (2010).

47. X. Qian, Y. Wang and H. Zheng, *Water Res.*, **88**, 93 (2016).

48. B. Wilén, K. Keiding and P. H. Nielsen, *Water Res.*, **34**, 3933 (2000).

49. G. Zhen, J. Wang, X. Lu, L. Su, X. Zhu, T. Zhou and Y. Zhao, *Chemosphere*, **221**, 141 (2019).

50. J. Wang, M. Yang, R. Liu, C. Hu, H. Liu and J. Qu, *Water Res.*, **160**, 454 (2019).

51. N. Buyukkamaci, *Process Biochem.*, **39**, 1503 (2004).

52. G. Zhen, X. Lu, J. Niu, L. Su, X. Chai, Y. Zhao, Y. Li, Y. Song and D. Niu, *Chem. Eng. J.*, **233**, 274 (2013).

53. K. Song, X. Zhou, Y. Liu, G. Xie, D. Wang, T. Zhang, C. Liu, P. Liu, B. Zhou and Q. Wang, *Chem. Eng. J.*, **295**, 436 (2016).

54. Q. Wang, J. Sun, K. Song, X. Zhou, W. Wei, D. Wang, G. Xie, Y. Gong and B. Zhou, *J. Environ. Sci.-China*, **67**, 378 (2018).

55. Y. Li, X. Yuan, Z. Wu, H. Wang, Z. Xiao, Y. Wu, X. Chen and G. Zeng, *Chem. Eng. J.*, **303**, 636 (2016).

56. C. Liu, B. Wu, X. E. Chen and S. Xie, *Chem. Pap.*, **71**, 2343 (2017).