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# Enhancement of waste activated sludge dewaterability by electro-chemical pretreatment

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ABSTRACT

The potential effects of electro-chemical conditioning on sludge dewatering treatments and its mechanism were investigated in this study. Capillary suction time (CST) and specific resistance to filtration (SRF) were used to evaluate sludge dewaterability. Extracellular polymeric substance (EPS) content and sludge disintegration degree ($DD_{SCOD}$) were also determined in an attempt to explain the observed changes in sludge dewaterability. The results indicated that application of considered low electrolysis voltages (<20 V) enhanced sludge dewaterability, while it exceeded 30 V, the dewaterability of sludge was significantly deteriorated. Also, electrolysis pretreatment slightly enhanced sludge dewaterability with short electrolysis time (<20 min), while it significantly deteriorated sludge dewaterability with long electrolysis time (>30 min). The optimal electrolysis voltage and electrolysis time to give preferable dewaterability characteristics were found to be 15–20 V, and 15–20 min, respectively, which generated sludge with optimal EPS content (15–20 mg/L) and $DD_{SCOD}$ (1.3–2.0%).



## 1. Introduction

Sludge production in the industrialized world has steadily been increasing during the last decades by the biological processes way of treating wastewater [1,2]. And sludges of biological origin such as waste activated sludge are known to exhibit very poor dewaterability. Together with more stringent disposal regulations, this has caused a demand for more efficient sludge conditioning and dewatering techniques, during which, the volume of sludge decreases, resulting in lower costs of further processing as well as transport and disposal of sludge. Thus, sludge dewatering is of paramount importance in wastewater treatment systems.

Organic polymers among many other chemicals, such as ferric salts and lime etc. are most widely employed conditioners in wastewater treatment industry. However, the use, especially the improper use, such as overdosing, of polymers may cause several problems in the supernatant water generated during sludge dewatering. As is known to all, the polymers are mainly made of acrylamide and acrylate, which can be one of the possible toxic chemicals to aquatic animals and human bodies at certain concentration even though they are sometimes biodegradable [3]. The residual polymers in dewatered sludge cakes may also pose a long-term risk to surrounding environment when the cakes are subject to landfill as the final disposal and it is usually very expensive [4]. Despite conditioning, a considerable amount of water is retained within the sludge, leading to extreme compressibility and moderate dewaterability [5]. Many new options have been investigated to enhance the sludge dewaterability, e.g. electrolysis treatment [6]. Sludge is a multiphase medium, containing water, mineral and organic substances, proteins and cells of microorganisms. The cells of microorganisms burst and the bound water could be released during the electrolysis process [7]. The disintegration of sludge flocs and disruption of microbial cell walls of sludge which lead to the lysis of large organic molecules associated with microbial cells could also be achieved by electrolysis. It was reported that the use of $Ti/RuO_2$ anode produced a series of electro-chemical steps which converted high biopolymer substances to low-molecular-weight products, and then which could be degraded easily. With that, the dewaterability of sludge could be improved. It is generally accepted that the strong water retention in sludge is related to the presence of EPSs, which form a negatively charged polymer network [8–10]. Until now, many investigations have been carried out on the role of EPS in bioflocculation, sludge settleability and dewaterability [11–17].

In this study, the effect of electrolysis conditioning on sludge dewaterability was investigated and the mechanism behind the observed changes, especially the role of EPS in sludge dewaterability was also discussed in order to accelerate understanding of electro-chemical conditioning method.

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## 2. Materials and methods

### 2.1. Test materials

Surplus sludge from secondary sediment tank was collected from Minhang wastewater treatment plant (WWTP), Shanghai, China. The plant treats 50,000 $m^3\ d^{-1}$ of wastewater with the anaerobic–anoxic–aerobic process. The sludge samples were thickened to required solid concentrations and stored at 4 °C prior to use. Maximum sludge storage period was 48 h. The water content and pH of the sludge were 98.8 ± 0.3% and 6.69 ± 0.06, respectively.

### 2.2. Experimental set-up

A series of bench-scale experiments were conducted in the electrolysis cell. The dimensions of the cell were 15 cm ($L$) × 8 cm ($W$) × 8 cm ($H$). The cell was made of glass and both the anode and the cathode were a pair of Ti/$RuO_2$ mesh. The experiment was carried out by using a highly stable power supply with the air pump of 4.5 L/h. In addition, 400 mL wastewater sludge was employed in the experiment to investigate the dewaterability of sludge.

### 2.3. Experimental procedure

Sludge samples were treated with various electrolysis voltages and electrolysis times in order to identify the optimal conditions for improving sludge dewaterability. The dewaterability of the sludge conditioned with electrolysis was assessed in terms of CST and SRF. The EPS content and sludge disintegration degree ($DD_{SCOD}$) of the sludge samples were also measured to aid our investigation into the mechanism behind the observed changes in sludge dewaterability.

Although temperature changes resulting from the heat generated during electrolysis may warrant attention during experimentation, in this work, the observed rise in sludge temperature during electrolysis was insignificant. Therefore, no effort was made to control sludge temperature. In addition, sludge pH was not regulated in order to keep the natural state.

### 2.4. Analytical methods

Sludge dewaterability was evaluated by CST, which was measured using a standard CST apparatus (model 304B, Triton, UK). The pH was measured using a digital pH-meter (pHs-3C, Leici Co., Ltd., Shanghai, China). The vacuum filtration method was also selected to measure the dewaterability of the conditioned sludge. Sludge (100 mL) was poured into a 9 cm standard Buchner funnel fitted with pre-wetted 1.2 μm glass fiber filter paper, and a constant vacuum pressure of 34.5 kPa was applied for 20 min. No additional water could be removed from the sludge then. Both the filtrate volume and the filtration time were recorded in order to assess sludge SRF. The SRF was then calculated as the slope of a linear plot of volume vs. time/volume [18]. The water content of the sludge cake trapped by the filter paper was measured in accordance with standard methods [19].

$DD_{SCOD}$ was defined by [20], comparing the electrolysis process and the maximum soluble chemical demand ($SCOD_{NaOH}$).

$$DD_{SCOD}\,(\%) = \frac{SCOD_S - SCOD_{S0}}{SCOD_{NaOH} - SCOD_{S0}} \times 100$$

$SCOD_S$ and $SCOD_{S0}$ values are for treated and untreated sludge samples, respectively. $SCOD_{NaOH}$ was obtained via an alkaline hydrolysis procedure in which the initial sludge sample was mixed with 0.5 M NaOH at room temperature for 24 h [2].

A heat extraction method [21] was modified to extract the LB-EPS (Loosely Bound EPS) and TB-EPS (Tightly Bound EPS) from the sludge. A sludge suspension was first dewatered by centrifugation in a 50 mL tube at 4000 × $g$ for 5 min. The sludge pellet in the tube was then resuspended into 25 mL of 0.9% NaCl solution. The NaCl solution for dilution was pre-heated to 70 °C to ensure that the sludge suspension reached an immediate warm temperature of 50 °C. Without any delay, the sludge suspension was then sheared by a vortex mixer (Maxi Mix II, Thermolyne) for 1 min, followed by centrifugation at 4000 × $g$ for 10 min. The organic matter in the supernatant was readily extractable EPS, and was regarded as the LB-EPS of the biomass.

For the extraction of the TB-EPS, the sludge pellet left in the centrifuge tube was resuspended in 0.9% NaCl solution to its original volume of 50 mL. The sludge suspension was heated to 80 °C in a water bath for 30 min, and the sludge mixture was then centrifuged at 4000 × $g$ for 15 min. The supernatant that was collected was regarded as the TB-EPS extraction of the sludge.

Both the LB-EPS, TB-EPS extractions and the EPS content of the sludge supernatant were analyzed for proteins and polysaccharides. They were all determined spectrophotometrically using a T6 UV/visible spectrophotometer (PGeneral, China). Proteins were determined by the Coomassie Brilliant Blue G-250 method, using casein as the standard, and its absorbance was measured at 595 nm [22]. Polysaccharides were stained with anthrone, and its absorbance was measured at 625 nm [23], using glucose as the standard. Surface structure of the sludge samples was analyzed with a scanning electron microscope (XL30, Philips, Holland).

Statistical analysis was carried out using the software SPSS version 11.0 for Windows (SPSS, Chicago, IL, USA). Each treatment was performed in triplicate and average values and standard deviations were obtained.

## 3. Results and discussion

### 3.1. Dewatering characteristics

#### 3.1.1. Sludge with electrolysis conditioning

The optimal condition as predicted by the CST and SRF tests applying electrolysis is exhibited in Fig. 1. On one hand, when the electrolysis time was set as 15 min, the CST and SRF values decreased from 60.8 s and 8.67E+11 m/kg for the unconditioned sludge to 45.5 s and 4.56E+11 m/kg for the sludge conditioned with an electrolysis voltage of 20 V. When the electrolysis voltage was increased to 50 V, both the CST and SRF values rapidly reached 79.4 s and 1.33E+12 m/kg, increases of 30.59% and 53.4%, respectively, as compared to that of the untreated sludge (Fig. 1(a)). On the other hand, when the electrolysis voltage was set as 20 V, the CST and SRF values decreased from 92.95 s and 2.06E+12 m/kg for the untreated sludge to 67.95 s and 8.56E+11 m/kg for the sludge conditioned with an electrolysis time of 15 min (Fig. 1(b)). However, along with electrolysis time extending over 20 min, both the CST and SRF values rapidly increased and even exceeded that of the unconditioned sludge. When the electrolysis time increased to 60 min, both of the CST and SRF values rapidly reached 143.8 s and 2.54E+12 m/kg, increases of 54.71% and 23.3%, respectively, as compared to that of the unconditioned sludge. Thus, a clear correlation exists between electrolysis voltage/time and CST/SRF. In conclusion, electrolysis at voltage of less than 20 V with the electrolysis time of 15 min could significantly improve sludge dewaterability, as well as the electrolysis time of less than 20 min in the use of 20 V. The phenomena were attributable to the fact that sludge flocs, which are repositories for water, are disrupted at lower electrolysis voltages and then water was released into the solution. Slight reductions in floc size and slight increases in EPS content could also explain the observed enhancement of sludge dewaterability [24,25]. While the electrolysis voltage beyond 30 V, sludge dewaterability was significantly deteriorated, and so was electrolysis

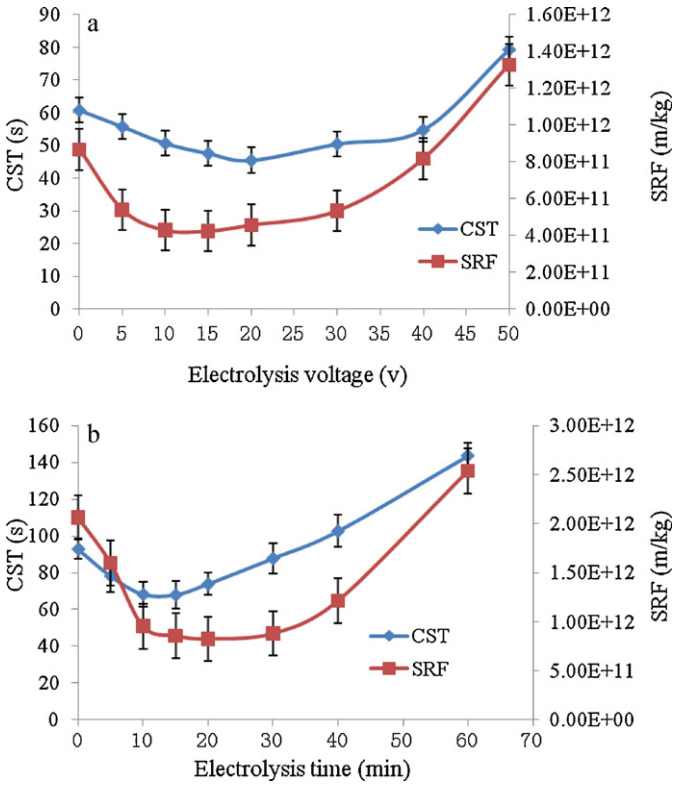


**Fig. 1.** Effect of electrolysis voltage (a) and electrolysis time (b) on dewaterability of sludge.

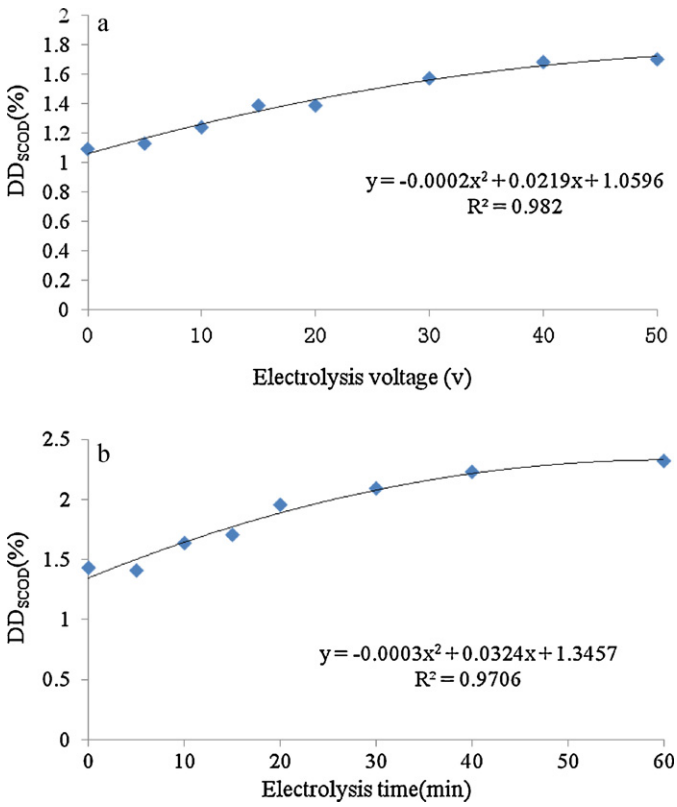


**Fig. 2.** Effect of electrolysis voltage (a) and electrolysis time (b) on sludge disintegration.

time of exceeding 30 min. The rapid decline of sludge dewaterability was attributed to the disruption of floc structure and integrity, and to the release of intracellular and extracellular materials which increase the viscosity of sludge [26,27]. The process of electrolysis also produced many fine particles, which is not beneficial for sludge dewatering. Based on the changes observed in the parameters that characterize sludge dewaterability, an optimal electrolysis voltage and time level was at 20 V with the time of 15 min observed in Fig. 1. These findings are more or less in agreement with those of Chu et al. [28], who observed that CST decreased following application of ultrasound at low power densities and for short durations, but, until now, no finding was reported in the use of electrolysis conditioning of sludge.

### 3.2. Effect of sludge disintegration on sludge dewaterability

#### 3.2.1. Changes in sludge disintegration following electrolysis conditioning

The sludge disintegration degree increased with the increasing of electrolysis voltage and time (Fig. 2). It indicated that SCOD increased gradually according to the increasing of electrolysis voltage and time. This was due to the extent of sludge floc structure disruption by electrolysis, which was also seen in the studies reported by Yu et al. [29] in the application of microwave. When the electrolysis time was short, the floc structure became relatively loose and some filamentous bacteria were exposed during this transition, but the structure change was too minimal to destroy the microorganisms. When the electrolysis time increased above a specific value, the floc structure was disrupted completely, and extracellular and intracellular biopolymers, such as proteins and polysaccharide, were released from activated sludge flocs into the soluble phase [30]. Similar effects of ultrasound treatment, microwave treatment and ozonation have also been observed [29,31,32]. Different electrolysis voltages and times generated different sludge $DD_{SCOD}$ (Fig. 2). The max value of $DD_{SCOD}$ of the sludge treated by electrolysis was between 1.7% (Fig. 2(a)) and 2.3% (Fig. 2(b)), less than that conditioned in the application of microwave reported by Yu et al. [29]. Thus, it could be concluded that temperature was a very influential parameter on sludge disintegration, because the treatment of microwave produced large heat energy. Similar conclusion was reported that temperature had a significant influence on sludge disintegration by ultrasonic sludge treatment reported by [20]. But electrolysis produced little influence in the current experimental condition for no obvious variations of temperature were observed.

#### 3.2.2. Effect of disintegration degree on CST and SRF of sludge

Slight electrolysis voltage may disrupt flocs and destroy microbial cells. Increasing electrolysis voltage and time increased both the SCOD of the supernatant and the $DD_{SCOD}$ which describes the degree of sludge disintegration. The relationship between $DD_{SCOD}$ and CST/SRF is shown in Fig. 3. The CST and SRF values decreased when $DD_{SCOD}$ increased to less than 1.3–1.8%. When $DD_{SCOD}$ increased to more than 1.8%, the CST and SRF values increased sharply. It was more or less the same as the result achieved by Yu et al. [29]. The $DD_{SCOD}$ of sludge was optimum for maximum sludge dewaterability when the CST and SRF values were at a minimum. According to the data shown in Fig. 3, the optimum value of $DD_{SCOD}$ was calculated to be approximately 1.3–1.8%. As a result, a proper $DD_{SCOD}$ was essential for the sludge dewaterability. During the electrolysis process of sludge, the sludge flocs were broken into smaller fragments, which improved the sludge dewaterability when these particles flocculated. But if electrolysis voltage and time increased to a point where the sludge $DD_{SCOD}$ was too high, and too many fine particles were produced, the sludge dewaterability gradually deteriorated. The effect of $DD_{SCOD}$ on sludge dewaterability was also reflected by the correlation between $DD_{SCOD}$ and CST/SRF under dif-

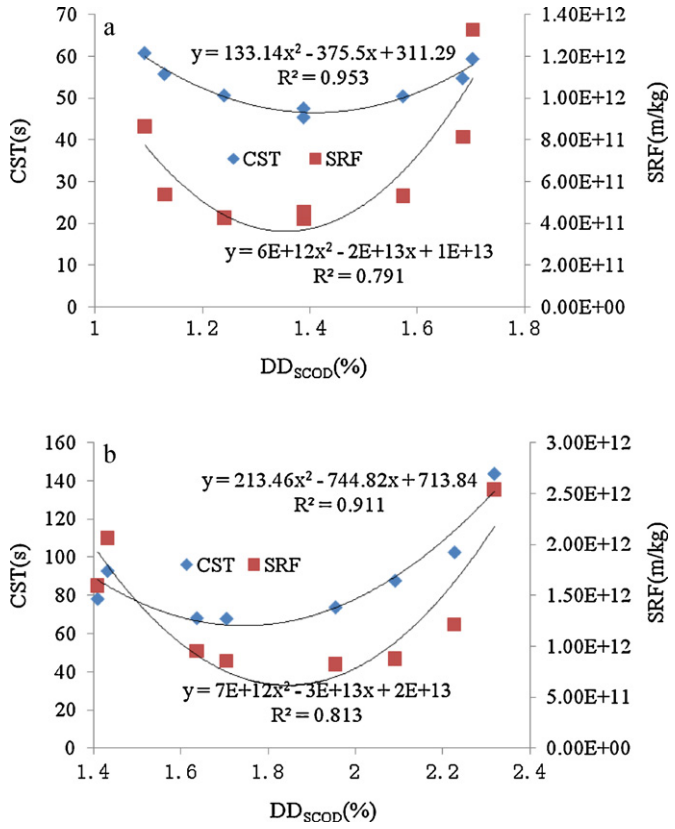


**Fig. 3.** Effect of disintegration degree on sludge dewaterability. (a) Conditioned under different electrolysis voltages and (b) conditioned under different electrolysis times.

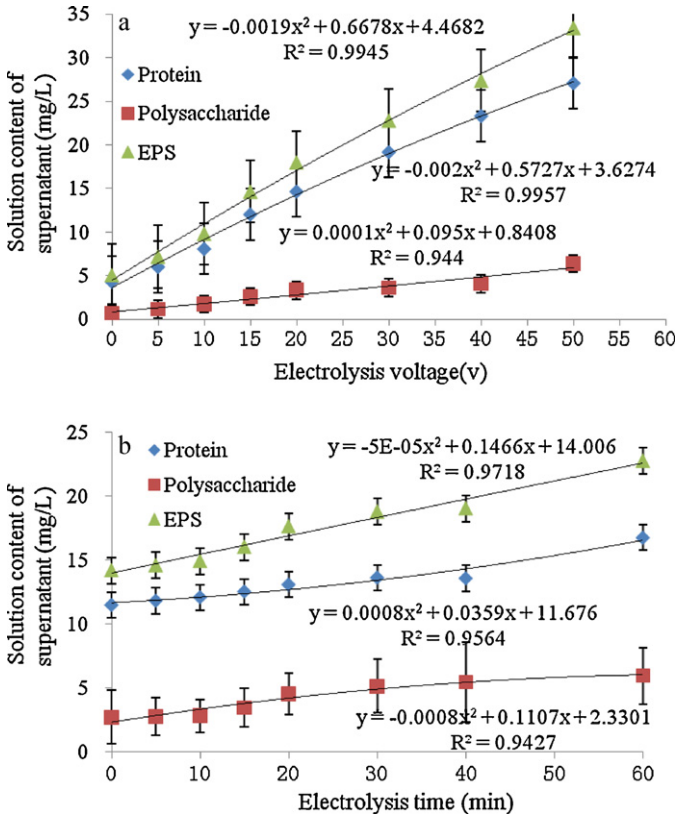


**Fig. 4.** Effect of electrolysis voltage (a) and electrolysis time (b) on EPS concentration in the sludge supernatant.

ferent electrolysis voltages ($R^2$ = 0.953 and $R^2$ = 0.791, respectively) and different electrolysis times ($R^2$ = 0.911 and $R^2$ = 0.813, respectively) as shown in Fig. 3. These results were in agreement with those reported by [20], who observed that the dewaterability was dependent on the sludge $DD_{SCOD}$ during ultrasonic treatment.

### 3.3. Effect of EPS on sludge dewaterability

#### 3.3.1. Changes in EPS concentrations of the sludge supernatant

In activated sludge, 70–80% of the extracellular organic carbon is in the form of proteins and polysaccharides [33]. These compounds aid in the retention of water and significantly contribute to the water-binding capacity of the sludge floc matrix [34]. The concentrations of proteins and polysaccharides in sludge supernatant were therefore measured in order to understand the effects of these compounds on sludge dewaterability.

The interactions of the very weak forces binding EPS components together, which are very important to the colloidal stability of flocs [35], are disrupted during electrolysis process. Proteins and polysaccharides in the sludge samples were initially estimated at concentrations of 4.33–11.5 mg/L and 0.72–2.72 mg/L, respectively. After sludge disintegration by electrolysis, the EPS and cellular substances were released into the aqueous phase, leading to an increase in protein and polysaccharide levels (Fig. 4). Otherwise, it could be seen that proteins were released to the aqueous phase more quickly than polysaccharides due to the slope of the regression line for proteins was higher than that for polysaccharides. In addition, the effect of electrolysis voltage on the releasing of EPS into the supernatant was more significant than that of electrolysis time (Fig. 4).

Furthermore, strong quadratic relationships between the EPS content and the electrolysis voltages ($R^2$ = 0.994) and electrolysis times ($R^2$ = 0.971) are observed in Fig. 4(a) and (b), respectively. Individual EPS components, such as proteins and polysaccharides, also correlated well with electrolysis voltage ($R^2$ = 0.995 and $R^2$ = 0.944) and electrolysis time ($R^2$ = 0.956 and $R^2$ = 0.942). These results were attributed to the fact that, when the wastewater sludge was disintegrated with electrolysis, cell membranes were disrupted, and the intracellular proteins and polysaccharides were released into the extracellular matrix and thereby the EPS levels increased.

#### 3.3.2. Effect of EPS on the CST and SRF of sludge

Many factors, such as EPS content, particle size distribution, specific surface area, viscosity, density, particle charge, bound water content, pH, and organic concentration, affect sludge dewatering properties [2]. EPS content is widely studied and is thought to be one of the most important factors affecting sludge dewaterability among these factors [10,36]. It has been previously mentioned that electrolysis resulted in the release of large quantities of EPS into solution (Fig. 4). EPS has a high affinity for water and thus is highly hydrated, as a result of which, the viscosity of sludge increases with the increasing of EPS concentration [37] and its dewaterability is decreased [38].

The relationship between EPS concentration and sludge dewaterability, however, is not always directly proportional. Nevertheless, these relationships are not absolute, and increasing EPS content does not always decrease sludge dewaterability. As observed in the present work, when the EPS content increased slightly at a relatively low initial value, both CST and SRF decreased (Fig. 5), similar conclusion was achieved by Sanin and Vesilind [39]. Further increases in EPS led to rapid increases in both CST and SRF values (Fig. 5). It showed that the CST and SRF values decreased with an increasing EPS concentration less than 15 mg/L in Fig. 5. When the EPS content was further increased, the CST and SRF val-

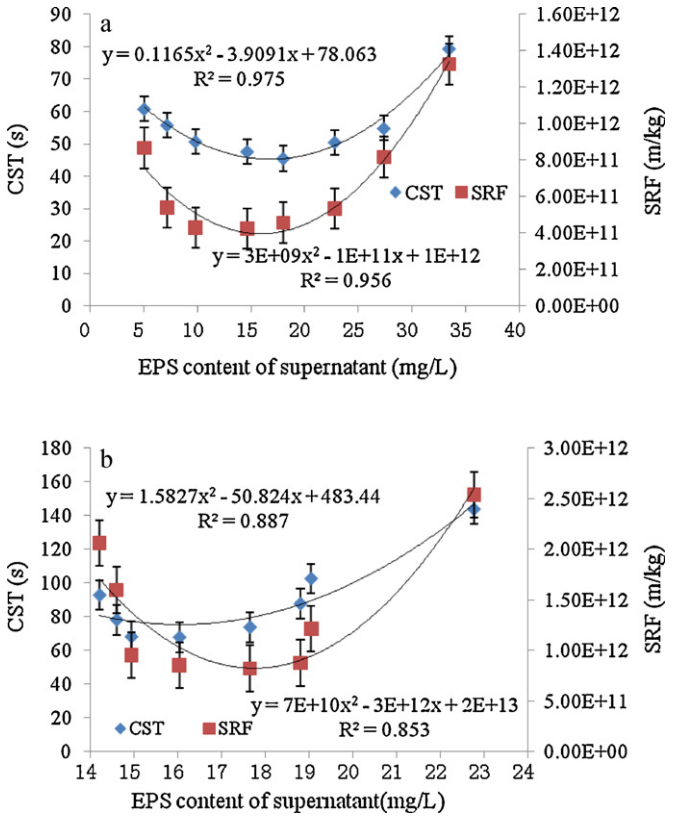


**Fig. 5.** Effect of supernatant EPS concentration on sludge dewaterability. (a) With different electrolysis voltages and (b) with different electrolysis times.

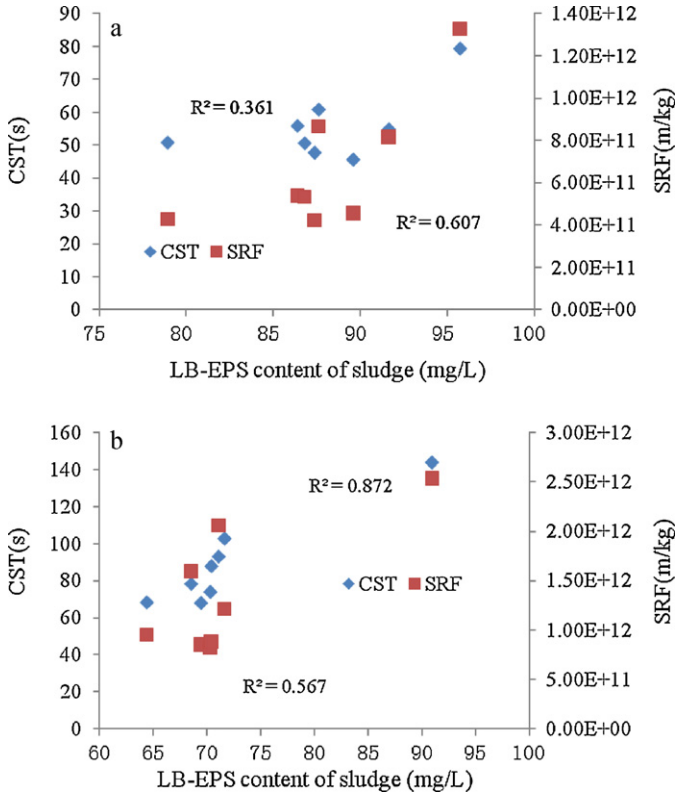


**Fig. 6.** Correlation between the EPS content of the sludge and its dewaterability as measured by SRF/CST. (a) LB-EPS content/under different electrolysis voltages; (b) LB-EPS content/under different electrolysis times; (c) TB-EPS content/under different electrolysis voltages; (d) TB-EPS content/under different electrolysis times; (e) LB + TB-EPS content/under different electrolysis voltages; and (f) LB + TB-EPS content/under different electrolysis times.

ues both increased significantly. The lowest CST and SRF values correspond to the optimum value of the EPS concentration for maximum sludge dewaterability. So, according to the regressions of the CST and SRF data (Fig. 5), the optimum value was calculated to be approximately 15–18 mg/L, which was higher than that of untreated sludge. These results also agreed with those reported by Houghton et al. [40] and Yu et al. [29], both of whom similarly observed that there existed an optimum EPS concentration at which sludge dewaterability was maximized. Flocculation reduces the number of small particles present in the sludge and thereby leads to the improvement in dewaterability characteristics [2]. When the optimal flocculation and deflocculation balance is reached, further increases in EPS content would exacerbate the sludge dewaterability. These previous observations provided a rational explanation for the observed improvement in sludge dewaterability following low voltage electrolysis.

The effect of EPS content on sludge dewaterability was also reflected by the correlation between EPS concentration and CST/SRF under different electrolysis voltages ($R^2$ = 0.975 and $R^2$ = 0.956) and electrolysis times ($R^2$ = 0.887 and $R^2$ = 0.853). These findings were in agreement with those reported by Wang et al. [37], who observed a correlation between EPS concentration and CST ($R$ = 0.9223), and with those of Houghton and Stephenson [41], who observed a strong quadratic relationship between EPS concentration and CST ($R^2$ = 0.9687), also with those of Feng et al. [2], who observed a strong quadratic relationship between EPS and CST/SRF ($R$ = 0.9576 and $R$ = 0.8314, respectively). The variations in the correlation coefficient values may be attributed to the difference of sludge types and sludge concentrations. These findings agree with those reported by Poxon and Darby [36], which showed that the relationship between EPS concentration and sludge dewaterability was dependent on digester feed composition, or that original sludge composition caused differences in this relationship.

### 3.4. Effects of LB-EPS and TB-EPS on the dewaterability of sludge

Changing the electrolysis conditions resulted in considerable variations in sludge's EPS production (Fig. 4). In general, the degree of change in LB-EPS content appeared to be more significant than that in TB-EPS. Considering that LB-EPS is located in the outer parts of cells and flocs, it is reasonable to suppose that the variety of the dewaterability of the sludge is mainly brought about by the changes of the LB-EPS content. In addition, as shown in Fig. 6(a) and (b), LB-EPS which contains abundant bound water, has been found to be positively related to the SRF/CST of sludge both applied with different electrolysis voltages ($R^2$ = 0.607 and $R^2$ = 0.361) and electrolysis times ($R^2$ = 0.567 and $R^2$ = 0.872). This finding agrees with those reported by Forster [42]. Sludge that carries a large amount of LB-EPS will therefore be more difficult to dewater if it has a higher SRF and CST values.

Otherwise, compared with the variations in LB-EPS with the changes in the electrolysis process conditions, the extent of the changes in TB-EPS was less significant (Fig. 6(c) and (d)). As is known to all, TB-EPS is located in the inner parts of cells and flocs, and it has lower level of bound water than LB-EPS. Furthermore, as shown in Fig. 6(c) and (d), TB-EPS which contains exiguous bound water, was investigated to have little relationship to the SRF/CST of sludge conditioned by electrolysis voltages ($R^2$ = 0.017 and $R^2$ = 0.110) and electrolysis times ($R^2$ = 0.000 and $R^2$ = 0.051). Fig. 6(e) and (f) shows the correlation between the LB + TB-EPS content of sludge and its dewaterability as measured by SRF/CST. Very low correlation coefficients ($R^2$ = 0.002 and $R^2$ = 0.073, conditioned with different electrolysis voltages; $R^2$ = 0.100 and $R^2$ = 0.358, conditioned with different electrolysis times) could be achieved. It

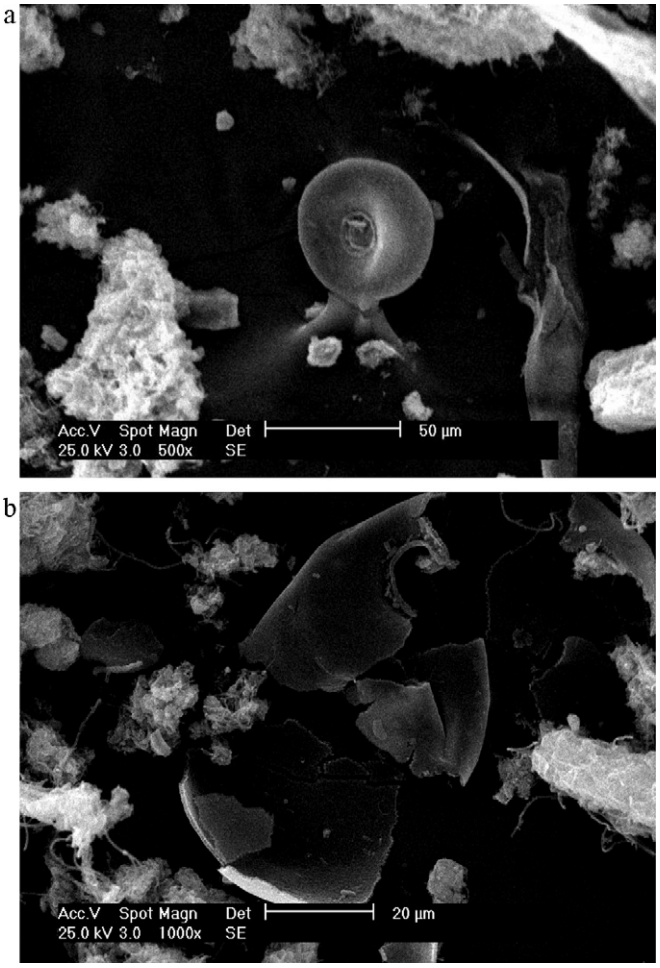


**Fig. 7.** SEM images of sludge cells: (a) unpretreated sludge and (b) electro-chemical pretreated sludge.

could be concluded that both TB-EPS and LB + TB-EPS content have less relationship than LB-EPS content with sludge dewaterability in this work, which agreed with the results of those reported by Wang et al. [43].

### *3.5. Influence of electro-chemical pretreatment on the structure of sludge*

Fig. 7 shows the scanning electron microscope (SEM) images of untreated sludge samples and electro-chemical pretreated sludge samples. The differences in sludge appearance were obvious. The surface of untreated sludge sample (Fig. 7(a)) was relatively round and smooth, while that of electro-chemical pretreated sludge sample was deformed (Fig. 7(b)). It indicated that the sludge was broken by electro-chemical treatment, and the intracellular substances would be solubilized into the solution, some of which could be degraded by electrolysis, also cell interstitial water was released into the solution, which could enhance the dewaterability of sludge.

### *3.6. Cost analysis*

Electrolysis pretreatment is feasible and can be cost effective based on this work. The total energy consumptions of electrolysis pretreatment technology would be approximately 5–10 kW h $m^{-3}$ based on this experiment result. Most importantly, electrochemical pre-treatment can significantly decrease the values both of CST and SRF. The values of CST and SRF after electrochemical pretreatment decreased from 60.8 s and 8.67E+11 m/kg to 45.5 s and 4.56E+11 m/kg as shown in this paper, respectively. The detailed cost of this technology will be evaluated in the subsequent pilot-scale experiments.

## 4. Conclusions

This research experimentally determined the influence of EPS content on the dewaterability of sludge after electro-chemical conditioning. Sludge was subjected to electrolysis at various voltage levels and times, and the effects of these parameters and EPS content on the sludge dewaterability were investigated. Treatment with 15–20 V and 15–20 min was determined to be the optimal condition based on CST and SRF results. Also, EPS content of sludge supernatant and $DD_{SCOD}$ were determined to play a vital role in the observed changes in sludge dewaterability. SEM images indicated that sludge was ruptured by electro-chemical pretreatment, and the water in the intracellular space was released into the solution which could enhance the dewaterability of sludge.

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