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Influence of pretreating activated sludge with acid and surfactant prior to conventional conditioning on filtration dewatering

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Abstract

Chemical conditioners have been employed widely to improve sludge mechanical dewaterability, but there is still a large quantity of water in the flocculating constituent of activated sludge, which leads to the difficulty in further reducing the water content of dewatered sludge. The presence of extracellular polymers (ECP) is believed to be one of the unfavorable elements in activated sludge dewatering. This paper investigated the effect of removal of ECP from the solid surface by the use of surfactant and acid before commonly used conditioners utilized on activated sludge filtration dewatering. The moisture content of dewatered sludge dropped by 3–5% if activated sludge was pretreated with acid or surfactant ahead of the conventional conditioners used, which decreased by 7–11% in the case of combining the utilization of acid and surfactant. It was found that the use of acid and surfactant pretreatments before conditioning with polyacrylamide or calcium oxide and ferric chloride reduced the sludge water content from around 82 and 80% to about 75 and 69% when sludge MLSS was 12.5 and 9.9 g/l, respectively, which resulted in an almost 28 and 35% reduction in dewatered sludge volume compared to that without surfactant and acid pretreatments.

Keywords: Activated sludge; Filtration dewatering; Pretreatment; Acid; Surfactant

1. Introduction

Activated sludge has been widely applied to treat wastewater, especially municipal wastewater. It has been found that there are many organic polymers in activated sludge. Most of these polymers are the metabolic products of bacteria. These extracellular polymers (ECP) include polysaccharide, protein and DNA [1]. Li and Ganczarczyk [2] found that ECP are the third main component in an activated sludge floc after the water and cells.

In the course of using activated sludge to treat wastewater, a large amount of excess sludge is produced, which will cause environmental pollution if it is not disposed. Thus, the wastewater treatment plant should not only purify wastewater, but also treat surplus sludge. As the activated sludge contains more than 99% water, and handling and disposal of excess sludge incur a rather large expenditure in wastewater treatment [3], reducing sludge volume by dewatering is economically valuable.

Chemical conditioning is widely used to improve the dewatering. The sludge water content can be reduced to almost 80% when it is treated with commonly used conditioners such as calcium oxide, ferric chloride and polyacrylamide, and then dewatered with a mechanical device. However, the presence of ECP makes it difficult to pack sludge aggregates as ECP are highly viscous, highly hydrated and are able to bind a large volume of water in activated sludge [4,5]. Kang et al. [6] found that addition of ECP to different sludges increased specific filtration resistance. The studies of Liao et al. [1] indicate that the presence of high concentration of ECP had a negative effect on sludge compressibility in the course of dewatering. All these might be an explanation for the difficulty in further reducing its water content to below 80% when activated sludge is conditioned with the commonly used conditioners then the mechanically dewatered. Since the sludge volume can be decreased by 20% as its water content is reduced from 80 to 75%, there may be significant benefits in improving sludge dewatering by removing ECP.

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Nelson et al. [7] and Thomas et al. [8] used enzymes to digest ECP to improve activated sludge dewatering. However, the fact that enzymes are expensive, and the complexity of ECP requires the use of multiform enzymes has limited the application of this method. It has been found that some chemical elements such as pH value and surfactant can cause cell materials (CM) to leave the solid surface [9,10]. Since the ECP of activated sludge are also composed of CM-like materials adhering to the sludge surface, in the previous papers a different strategy for reducing activated sludge ECP was reported, and the water content of activated sludge was observed to be significantly decreased when sludge was treated with surfactant or acid followed by mechanical dewatering [11,12]. In this paper, the effects of pretreating activated sludge with surfactant and acid prior to conditioning it with conventional conditioners on sludge filtration dewatering were investigated, and the reasons for dewaterability improvement were also discussed.

2. Materials and methods

2.1. Activated sludge

Waste activated sludge was taken from Shanghai Quyang sewage treatment plant, China, a full-scale plant. This plant is designed for treating domestic wastewater by the traditional activated sludge process. Sludge water content, pH value and mixed liquor suspended solids (MLSS) were 99.5%, 6.8 and 6.1 g/l, respectively. Thickened sludges with MLSS of 9.9 and 12.5 g/l were obtained by settling activated sludge at 4 °C for 10 and 24 h, respectively. Sludges were stored at 4 °C prior to use.

2.2. Chemicals

Chemicals used were analytical grade except for the bovine serum albumin (BSA) and deoxyribonucleic acid(calf thymus) were biochemical. All chemicals were purchased form Shanghai reagent company (China). The molecular weight of cationic polyacrylamide was $(4–5) \times 10^6$. The water used for analysis was deionized water.

2.3. Filtration dewatering of activated sludge

Filtration dewatering was done in a Buchner funnel with a 0.45 μm membrane filter under 0.05 MPa vacuum.

Duplicate concentrated activated sludge of 100 ml was put into a beaker of 250 ml, and the chemicals were then added according to the following sequence: 16 mol/l sulfuric acid to adjust the pH value, surfactant (dodecyl betaine), polyacrylamide (0.05% solution in water), or ferric chloride (20% solution in water) and calcium oxide (10% solution in water). The resulting mixture was stirred rapidly with a magnetic stirrer for 1 min at a speed of 220 rpm, and followed by a slow agitation of 170 rpm for 5 min. The treated activated sludge was poured into a Buchner funnel to filter for 30 min. In the control test, the chemicals were not used.

The water content (WC) of dewatered activated sludge was determined according to the following equation:

$$\mathrm{WC} = \frac{W_1 - W_2}{W_1} \times 100\%$$

where W_1 is the weight of wet filter cake and W_2 is the weight of filter cake after drying at 105 °C for 2.5 h.

2.4. Settling test of activated sludge

Duplicate surplus activated sludges of 100 ml with a MLSS of 6.1 g/l were used to study its settleability. The procedures for treating and stirring the activated sludge were the same as described above for dewatering test. The resulting mixture was poured into a cylinder of 100 ml, and the settled sludge volume was measured at intervals over a 60 min period. In the blank test, no chemicals were utilized.

2.5. Analysis

Protein was determined according to the method of Lowry et al. [13] with BSA as standard. Polysaccharide was assayed by the phenol–sulfuric method of Dubois et al. [14] with glucose as standard. DNA was measured by the diphenylamine assay of Burton [15] with calf thymus DNA as standard. All assays were conducted in duplicate. If the protein, polysaccharide and DNA appeared in the filtrate after surfactant/acid treatment, it was believed that these ECP were from activated sludge.

The viscosity (η_s) of the sludge was measured using a viscosity analyzer (model HAAKE VT501) at 30 °C. MLSS was measured as 105 °C dry sludge weight per volume, which was collected on a 0.45 μm membrane filter.

3. Results and discussion

CST (capillary suction time) and SRF (specific resistance to filtration) have been widely used as means of gauging sludge dewatering. However, they measure only the filterability and this need not correspond with the water content in the dewatered sludge. Some water in the sludge flocs is bound, and difficult to dewater mechanically. It is possible therefore that the sludge is easily filterable, but there is a high amount of residual water in the dewatered sludge. As a result, the water content of dewatered sludge was applied in this paper to measure the dewaterability.

3.1. Effect of acidic pH pretreatment before ferric chloride and calcium oxide conditioning

As cheap conditioners, ferric chloride and calcium oxide were applied to condition activated sludge in this study.

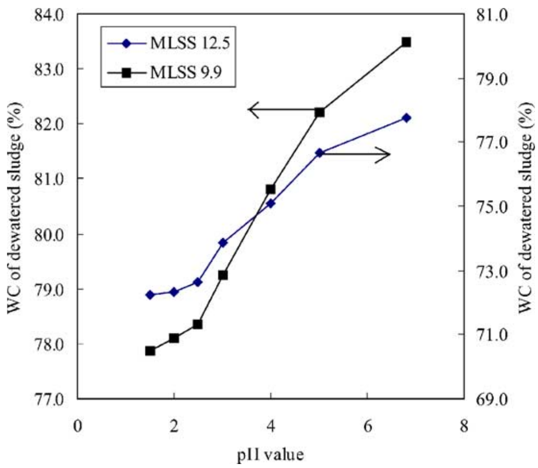

Fig. 1. Effects of acid pretreatment prior to ferric chloride and calcium oxide conditioning on filtration dewatering.

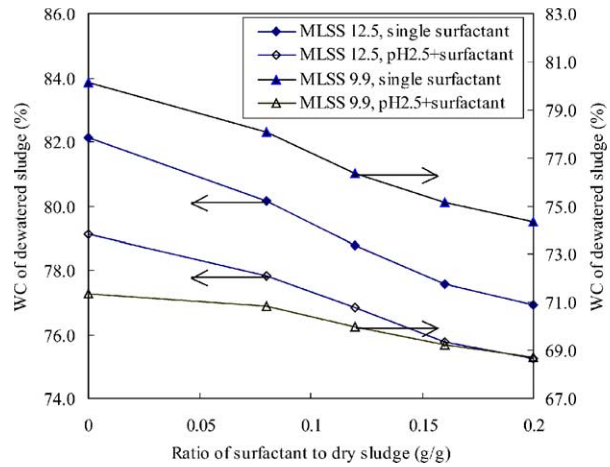

Fig. 2. Effects of surfactant or surfactant together with pH 2.5 pretreatment before ferric chloride and calcium oxide conditioning on filtration dewatering.

However, it was observed that if the activated sludge was pretreated with acid before ferric chloride and calcium oxide were employed, the filtration dewaterability could be improved (Fig. 1). Fig. 1 was obtained under conditions of a 0.167 and 0.2 g/g ratio of ferric chloride and calcium oxide to dry sludge, respectively. As shown in Fig. 1, the water content of dewatered sludge in the case of sludge MLSS 12.5 g/l was around 82% when the pH was not adjusted (i.e. pH = 6.8). However, the water content was reduced to 80.56% when pH was lowered to 4, which was further declined to 79.12% if pH was reduced to 2.5. It is clear that the water content of dewatered sludge decreased with pH. However, when the pH was less than 2.5, the water content was not significantly reduced with lowering pH value. Same results were found even when the amounts of ferric chloride and calcium oxide changed.

The fact that decreasing pH led to the reduction of water content of dewatered sludge was observed to be independent of sludge concentration (MLSS). When MLSS was 9.9 g/l, it can be seen from Fig. 1 that the water content of dewatered sludge was 80.13% at pH 6.8, which was reduced to 78.86% at pH 5. Further reduction of water content could be achieved by further decreasing pH value. At pH 2.5, the water content became 74.33%. Nevertheless, the trend of water content reduction with decreasing pH was not obvious if pH was below 2.5. The water content was decreased from 74.33 to 73.50% when pH value varied in the range of 2.5–1.5. It seems that the suitable pH should be controlled to 2.5 when sulfuric acid is applied to pretreat activated sludge.

3.2. *Effect of surfactant employed ahead of ferric chloride and calcium oxide conditioning*

The use of surfactant or its combination with pH 2.5 ahead of ferric chloride and calcium oxide conditioning was also found to improve sludge dewaterability. Fig. 2 shows its addition influencing filtration dewatering under the same ferric chloride and calcium oxide additions as in Fig. 1. For sludge with MLSS 12.5 g/l, the water content of dewatered sludge was declined from 82.11 to 76.93% as surfactant to dry sludge ratio was increased to 0.2 g/g. If surfactant was used together with pH 2.5, the sludge water content was decreased from 79.12 to 75.24% as surfactant to dry sludge ratio was increased from 0 to 0.2 g/g. But the results in Fig. 2 also indicate that the reduction of water content was slowed down as surfactant to dry sludge ratio exceeded 0.15 g/g whether pH 2.5 was used or not.

The results with sludge MLSS 9.9 g/l in Fig. 2 show that the use of surfactant pretreatment also benefited filtration dewatering. When only surfactant was employed, the water content was dropped from 80.13 to 74.34% with increasing surfactant to dry sludge ratio to 0.2 g/g. Even surfactant was utilized with pH 2.5, the sludge filtration dewatering was still improved. The water content declined from 74.33 to 68.71% under conditions of pH 2.5 and surfactant to dry sludge ratio changing from 0 to 0.2 g/g. Also it can be seen from Fig. 2 that the reduction of water content was not notable while surfactant to dry sludge ratio was more than 0.15 g/g for either single surfactant or pH 2.5 plus surfactant pretreatment.

3.3. *Effect of acid pretreatment prior to polyacrylamide conditioning*

Polyacrylamide (PAM) is another frequently used conditioner. It has been observed in our studies that before PAM is applied to condition activated sludge, the employment of surfactant/acid can also improve sludge mechanical dewaterability. Fig. 3 illustrates the influence of pH on filtration dewatering under conditions of 0.24% PAM dosage (based on dry sludge weight). The water content with sludge MLSS 12.5 g/l was decreased obviously with the increase of acidity, i.e. from 81.62 to 78.65% in the range of pH 6.8–2.5.

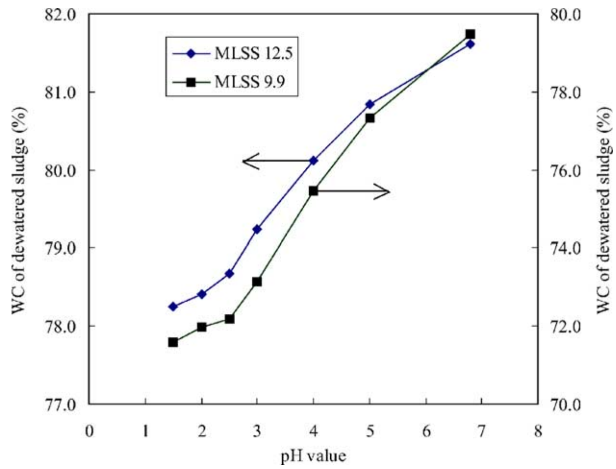

Fig. 3. Effects of acid pretreatment prior to PAM conditioning on filtration dewatering.

However, the water content was not significantly reduced in the case of pH below 2.5 suggesting that the suitable pH for pretreating activated sludge with acid before PAM conditioning should be controlled at 2.5.

The same observations were made when sludge MLSS was 9.9 g/l. The water content declined from 79.46 to 74.2% within pH 6.8–2.5, but it decreased very little (from 74.2 to 73.6%) when pH changed from 2.5 to 1.5. As a consequence, pH 2.5 was chosen as the suitable pH value for acid pretreating activated sludge with MLSS varying between 9.9 and 12.5 g/l.

3.4. Effect of surfactant used before PAM conditioning

The addition of surfactant to the activated sludge ahead of PAM conditioning provides another way to increase the dewatering performance. Fig. 4 describes the influence of surfactant used individually or together with pH 2.5 on filtration dewatering under the same PAM dosage as that in

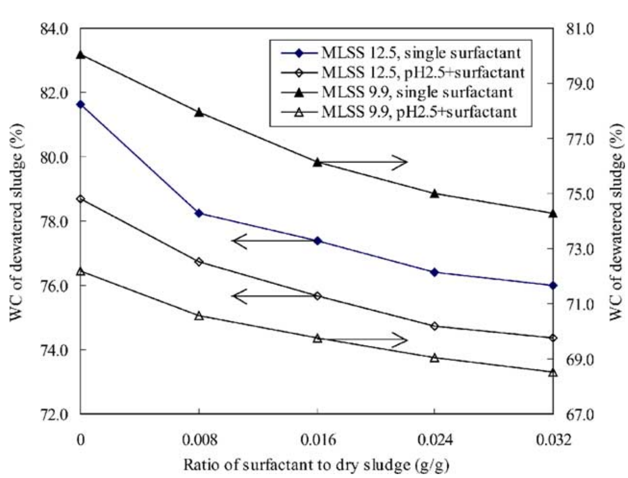

Fig. 4. Effects of surfactant used with or without pH 2.5 ahead of PAM conditioning on filtration dewatering.

Fig. 3. As shown in Fig. 4, the water content, with sludge MLSS 12.5 g/l and only surfactant pretreatment, dropped from 81.62 to 76.41% as surfactant to dry sludge ratio increased to 0.024 g/g, but there was only a 0.4% decline in water content (from 76.41 to 76.01%) as surfactant to dry sludge ratio was raised from 0.024 to 0.032 g/g. Similar results were observed if surfactant was employed together with pH 2.5, i.e. the water content decreased from 78.65 to 74.72% with increasing surfactant to dry sludge ratio from 0 to 0.024 g/g. Although the water content could be further reduced to 74.38% by raising surfactant to dry sludge ratio to 0.032 g/g, the reduction was not significant.

For sludge with 9.9 g/l of MLSS, it was also found that the influences of surfactant on water content reduction were obvious at surfactant to dry sludge ratios below 0.024 g/g. The water content decreased by almost 5% for both single surfactant and surfactant plus pH 2.5 pretreatments, i.e. from 80.04 to 74.98% with only surfactant application, and from 74.2 to 69.05% with the combined pretreatment of pH 2.5 and surfactant. Further increasing surfactant to dry sludge ratio to 0.032 g/g resulted in only a 0.74% (from 74.98 to 74.24%) and 0.53% (from 69.05 to 68.52%) water content decline for only surfactant and surfactant plus pH 2.5 pretreatment, respectively.

It should be noted that although only one dosage of ferric chloride, calcium oxide and PAM was reported in this paper, it was observed that surfactant and sulfuric acid pretreatments reducing the water content of dewatered sludge occurred independently of the dosages of these conditioners (data not shown). The ratio of ferric chloride, calcium oxide and PAM to dry sludge investigated was in the range of 0.1–0.33, 0.15–0.3, and 0.0012–0.003 g/g, respectively.

Form the above experimental results it is very interesting to note that the surfactant to dry sludge ratios used with ferric chloride and calcium oxide were different from those used with PAM, but the reason is unclear. One explanation might be that calcium hydroxide reacted with surfactant, and more surfactant was therefore required.

3.5. Possible reasons for acid and surfactant pretreatment improving sludge dewatering

One of the possible explanations for acid/surfactant pretreatments improving activated sludge filtration dewaterability can be arrived from the perspective of ECP. It was observed that ECP left the activated sludge surface in the case of acidic conditions or surfactant. Fig. 5 shows the effect of pH on the ECP concentration in the filtrate when activated sludge with MLSS 12.5 g/l was treated with only sulfuric acid and then filtered. Results in Fig. 5 reveal that polysaccharide, protein and DNA were released from the activated sludge under acidic conditions, and their amounts were increased with the acidity. However, the release of ECP increased slowly when pH was below 2.5.

Fig. 6 is the release of ECP after activated sludge (sludge MLSS = 12.5 g/l) was treated only with surfactant or sur-

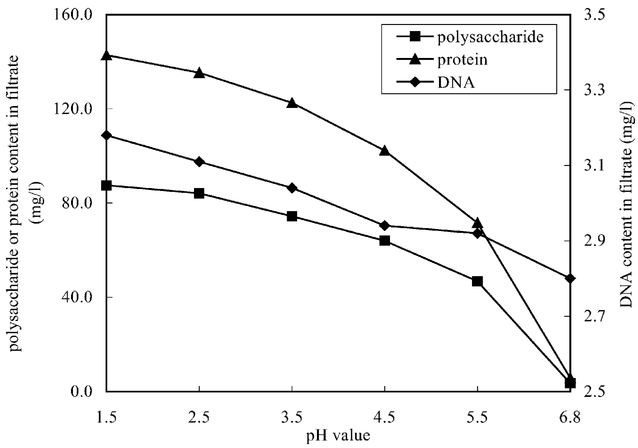

Fig. 5. Effects of pH value on ECP in filtrate.

factant plus pH 2.5 (without employing ferric chloride and calcium oxide or PAM). The results with single surfactant treatment indicate that the amount of ECP in the filtrate increased with the surfactant dosage. Also, it can be seen from Fig. 6 that there was more ECP released when surfactant and pH 2.5 were utilized together than when only surfactant was used, and the ECP were also increased with surfactant under pH 2.5 condition. It can be concluded therefore that the application of surfactant resulted in the reduction of sludge ECP.

In this study, the comparison between the use of two conditioners, ferric chloride and calcium oxide, and PAM alone (without using sulfuric acid) affecting the release of ECP and the water content of dewatered sludge was also made, and the results are shown in Fig. 7 (sludge MLSS = 12.5 g/l). As seen form Fig. 7, there were some differences in the ECP contents in the filtrate between two conditioners. All of the polysaccharide, protein and DNA were higher with ferric chloride and calcium oxide than with PAM. However, there was no significant difference in the water content of dewatered sludge. The water content was 82% with ferric chloride and calcium oxide, and 81.62% with PAM.

The study of Forster [4] shows that modifying the ECP will also modify the viscosity of the sludge. It was observed in this investigation that the sludge viscosity changed when sludge was treated with sulfuric acid and surfactant, and some results are shown in Fig. 8. The sludge MLSS in Fig. 8 was 12.5 g/l, and the ratio of surfactant to dry sludge was 0.08 g/g. Clearly, the sludge viscosity was reduced significantly after pH 2.5 treatment, and dropped further when surfactant was employed. Sanin and Vesilind [16] also observed that ECP removal reduced sludge viscosity. Thus, the sludge appeared more compact, which caused the improvement of mechanical dewaterability.

Also, in our study the sludge settleability was observed to be increased when surfactant or acid was applied (Fig. 9). The surfactant addition in Fig. 9 was 0.04 g/g, and sludge MLSS was 6.1 g/l. Since the sludge ECP and viscosity were reduced, the sedimentation velocity of activated sludge was enhanced in the case of surfactant or pH 2.5, and was increased further by their combined use. It seems that a good settleability of activated sludge always corresponded to a good dewaterability [7].

The isoelectric point of activated sludge would be usually between pH 1 and 3 [17]. In this study the water content of dewatered sludge was not further decreased with pH in the case of pH less than 2.5. Thus, it is likely that the isoelectric point of activated sludge used in this study was around pH 2.5. Apparently, the sludge exhibited the greatest dewaterability at the isoelectric point.

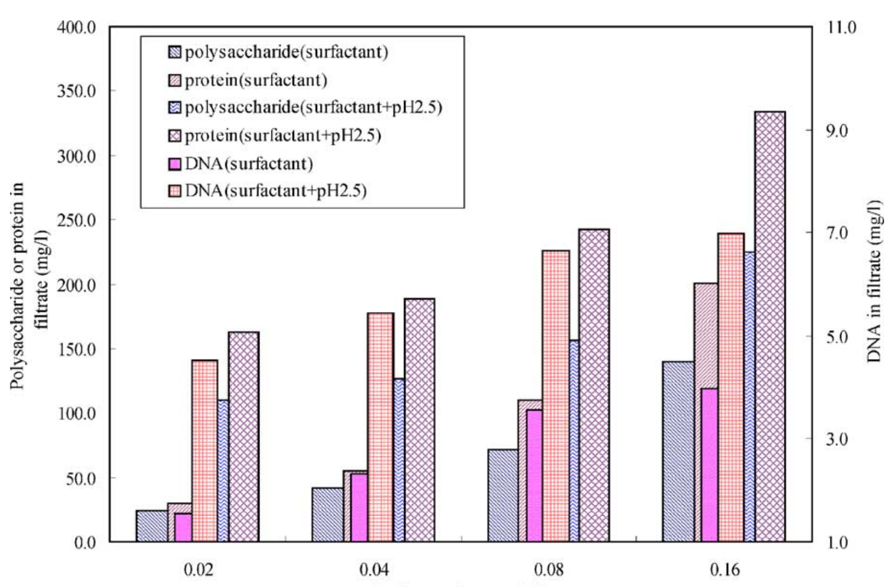

Fig. 6. ECP concentrations in filtrate after sludge pretreated with surfactant/acid.

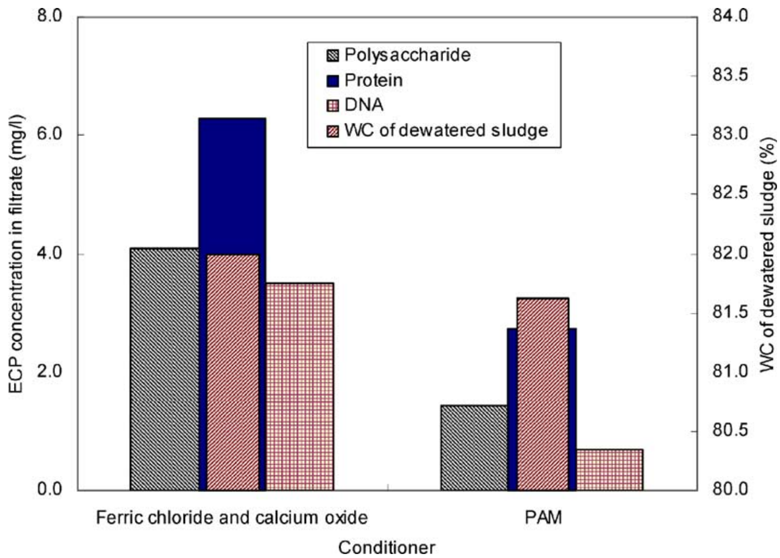

Fig. 7. Comparison between two conditioners used alone affecting ECP in filtrate and water content of dewatered sludge.

In addition, it is well known that surfactant can lower the water–solid interfacial tension, which might also be one reason for surfactant improving activated sludge dewatering. Due to this function, surfactants have been used as “dewatering aids” in increasing vacuum filtration dewatering efficiency of iron ore sludge [18]. If the filter cake of activated sludge is considered as solids with a series of capillaries between the particles, then according to the Laplace–Young relationship

$$P = \frac{2r_{\mathrm{GL}}\cos\theta_{\mathrm{SL}}}{r_{\mathrm{C}}}$$

Where P is the pressure, r_{GL} the surface tension, θ_{SL} the solid–liquid contact angle, and r_{C} is the capillary radius. When r_{GL} is reduced, the force retaining water in the filter cake can be reduced, and much moisture can be removed.

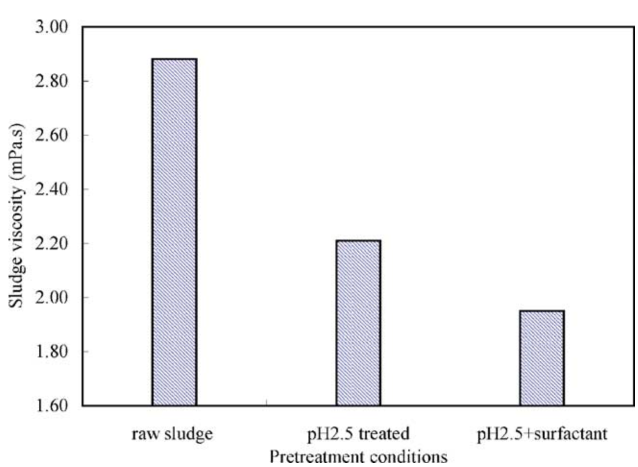

Fig. 8. Effects of pH 2.5 and surfactant pretreatment on sludge viscosity.

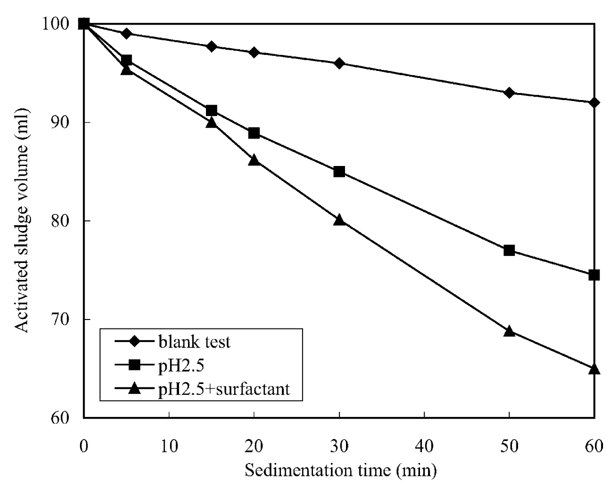

Fig. 9. Settlement curve of activated sludge under different conditions.

4. Conclusions

The effects of acid and surfactant pretreating activated sludge before the application of conventional conditioners (ferric chloride and calcium oxide, and PAM) on sludge filtration dewatering were investigated. The main conclusions from this study were as follows:

(1) The water content of dewatered sludge produced by conventional conditioning and filtration dewatering was 80–82%, but it could be reduced to 74–78% by acid or surfactant pretreatment alone.
(2) Acid plus surfactant pretreatments further reduced the water content to around 69% (sludge MLSS = 9.9 g/l) and 75% (sludge MLSS = 12.5 g/l).
(3) The acid and surfactant pretreatment caused the release of sludge ECP, reduced sludge viscosity and increased

sludge settleability. As a consequence, the sludge appeared more compact, and much more water could be removed during filtration dewatering.

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