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Fenton's Oxidation to Improve the Filterability and Dewaterability of Excess Activated Sludge by Affecting Extracellular Polymeric Substances

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This paper investigated the effect of Fenton's reagent pretreatment on the filterability and dewaterability of the excess activated sludge. Fenton's reagent pretreatment greatly improved the filterability and dewaterability of the sludge measured by the capillary suction time (CST) and moisture of sludge cake, respectively. The suitable conditions of Fenton pretreatment on the sludge filterability were as following: pH 2.5-3.0; 60-70 °C; treatment time of 2-3 h. The filterability and dewaterability of the sludge increased by 81 and 12 %, respectively, at pH 2.5 under 68 °C for 2.5 h reaction time when the sludge was treated by Fenton reagent with H_2O_2/Fe^{2+} ratio of 8. There was no significant difference in the filterability and dewaterability at various ratios of H_2O_2/Fe^{2+}. The contents of loosely bound extracellular polymeric substances (EPS) (LB-EPS), tightly bound EPS (TB-EPS), polysaccharides (PS) in LB-EPS, PS in TB-EPS and proteins (PN) in TB-EPS all reduced, but protein content in LB-EPS increased after Fenton's pretreatment. Protein in TB-EPS was strongly correlated with capillary suction time and moisture of sludge cake. A significant reduction of extracellular polymeric substances concentration was the major reason for the observed changes in the sludge filterability and dewaterability.

Keywords: Excess activated sludge, Fenton's reagent, Dewaterability, Extracellular polymeric substances, Capillary suction time.

INTRODUCTION

The activated sludge process produces large quantities of excess activated sludge (WAS), which generally contains the water content of over 95 %. It is necessary to dewater the sludge to allow a reduction in volume, facilitation of transportation, decreasing of energy used in case of drying or incineration. Unfortunately, it is well known that the sludge is hard to be dewatered due to its biological gel structure property and only about 20-25 % dry solids (DS) can be obtained[1]. Obtaining higher dry solids can be done with pretreatment processes to destroy the floc structure and to release the bound water in the sludge.

One of the main reasons for difficulty in sludge dewatering is due to the presence of extracellular polymeric substances (EPS). By binding cells and particle together, EPS also change the particle size distribution of the sludge, which again affects the dewatering characteristics. The floc matrix is likely to have a dynamic double-layered EPS structure of loosely bound EPS (LB-EPS) diffused from the tightly bound EPS (TB-EPS) that surrounds the cells[2]. Considering the high water binding property of EPS and high content of EPS in the activated sludge, it is envisaged that degrading the EPS can enhance the dewatering efficiency of the activated sludge. From previous reports, advanced oxidation methods improved the sludge dewaterability by affecting the EPS in two ways: (1) they have the potential to degrade EPS and; (2) they affect the multi-functional groups of the EPS and promote their participation in several interactions[3,4].

Several researchers have reported that Fenton's reagent can be used to improve the dewatering of the sludge efficiently[5-7]. However, as far as is known, little information is available about the EPS changes of the excess activated sludge after being pretreated by Fenton's reagent and mechanism of improving the dewaterability. Neyens and Baeyens[3] indicated that the peroxidation of the sludge enhanced the dewaterability. The responsible mechanism was not fully understood, but the oxidative pretreatment might be based on particle oxidation and rearrangement of the surface components of the sludge flocs.

To understand the action of the Fenton's oxidation technology in the sludge dewaterability, the essential role played by the EPS must be assessed and understood. Additionally, it is necessary to establish optimal conditions for a volume and mass reduction of the sludge. The aim of this study is thus to examine EPS content and chemical constituents and to analyze how the sludge dewaterability is influenced by Fenton's reagent. This work may provide some insights into the changes of the filterability and dewaterability of the sludge. It will be important to elucidate the role that EPS have in the dewatering phenomena in the sludge to address sludge-liquid separation problems.

EXPERIMENTAL

The sludge samples were taken from the settling tank of a municipal wastewater treatment plant in Ningbo, China. Table-1 shows the characteristics of the sludge samples. The sludge was stored in filled plastic containers placed in an ice cooler during the transportation from the plant site to the laboratory. The excess activated sludge was not conditioned with any conditioner. Sample tests started immediately and were completed within 20 h, while being kept refrigerated at 4 °C.

Sludge pretreatment with Fenton's reagent: The preliminary conditions test was carried out in several 250 mL beakers. The sludge samples (100 mL) were adjusted to the desired pH value using H_2SO_4, then rapidly mixed with different dosage of ferrous sulfate and H_2O_2 (30 %) at a speed of 200 rpm for 3 min to start the pretreatment processes and then slowly stirred to allow to react for desired time at desired temperatures. For the experiments of optimal temperature, the sludge with Fenton reagent was set up to 12 °C, 45 °C, 68 °C, 100 °C and 120°C, respectively. For the experiments of optimal reaction time, the sludge was reacted with Fenton reagent for immediately (0 h), 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, 3.5 h, 4.0 h, 4.5 h and 5.0 h at 60 °C, respectively.

The H_2O_2/Fe ratio test was carried out in a 500 mL beaker. The sludge samples (350 mL) in a 500 mL beaker were adjusted to pH 2.5 using H_2SO_4, then rapidly mixed with a certain dosage of ferrous sulfate and different amounts of H_2O_2 at a speed of 200 rpm for 3 min to start the pretreatment processes and then slowly stirred to allow to react for 2.5 h at 68 ± 2 °C. Additionally, in order to assess the thermal effect during Fenton reaction, the filterability and dewaterability of the sludge being conventionally heated at 68 °C for 2.5 h without Fenton's reagent were also investigated.

Sludge filterability and dewaterability tests: The capillary suction time was measured by a capillary suction time instrument (Triton, Model 304 M, Essex, UK) as detailed in APHA[8] with a capillary suction time paper purchased from Triton Ltd. The test was made in triplicate with a relative standard deviation of 5 %. 50 mL sludge samples were centrifuged at 2215 × g for 10 min and then the sludge cake after centrifuged were dried by an oven at 105 °C to evaluate the moisture of the sludge cake. The solids content was analyzed following the standard methods[8].

Extraction of EPS and determination of EPS components: The sludge sample was fully mixed prior to commencing the extraction procedure. Extracellular polymeric substances extraction was carried out using a sonication/thermal extraction process according to Li and Yang[2]. The activated sludge was harvested by centrifugation (6000 × g, 10 min) and washed with distilled water prior to extraction to remove the loose slime polymers found in the sludge. The dewatered sludge pellet was resuspended in a 0.05 % w/w NaCl solution with several glass beads, sonicated at 20 kHz for 2 min, shaken horizontally at 150 rpm for 10 min, sonicated again for an additional 2 min. The liquor was centrifuged at 8000 × g for 10 min to separate solids and supernatant. The collected supernatant was regarded as the LB-EPS of the sludge sample (LB-EPS). The residual sludge pellet left in the centrifuge tube was resuspended in a 0.05 % w/w NaCl solution, sonicated for 2 min, then heated at 60 °C for 0.5 h, finally centrifuged at 11000 × g for 0.5 h to collect supernatant. The collected supernatant was regarded as the TB-EPS in the sludge sample (TB-EPS).

Analytical methods: The suspended solid (SS) was determined according to APHA[8]. The LB-EPS and TB-EPS extractions were analyzed for total organic carbon (TOC), protein and polysaccharide. Total organic carbon was measured by a TOC analyzer (Elementar, Liqui TOC/TNb, Germany) and expressed as mg TOC/g suspended solid. Proteins were determined by an adaptation of the Lowry method using casein (Shanghai Sangon Biotechnology, China) as the standard. Polysaccharides were determined using the anthrone method with a glucose standard. All samples were made in triplicate.

Statistical analysis: Statistical analysis was carried out with SPSS software version 11.0 for Windows (SPSS, Chicago, IL, USA). Correlations were considered statistically significant at a confidence interval ($p < 0.05$).

RESULTS AND DISCUSSION

Fig. 1 shows that capillary suction time decreased with the increase of the temperature at first, then increased. The temperature higher than 100 °C did not improve and even decreased the filterability, which implied that moderate temperature (< 100 °C) could help Fenton reaction. The adverse impact of thermal effect due to high temperature (> 100 °C) might counteract the effect of Fenton oxidation. Neyens *et al.*[9] also found that Fenton operation at higher temperature improved the peroxidation results. Fig. 2 showed that the proper pH was 2.5-3.0, which was in accord with the characteristics of Fenton reagent. In Fig. 3, capillary suction time reduced by 75 and 77 % at 2 h and 3 h of reaction time, respectively. However, capillary suction time did not decrease after 3 h, even increased slightly. The result was not consistent with the result by Lu *et al.*[6] who found that no significant effect occurred at different times. The difference might be due to the fact that the Fenton solution was added into the sludge after it is prepared, so the Fenton reaction was started for a period of time before it reacted with the sludge in the experiment by Lu *et al.*[6]. In the present study, the Fenton reaction was started in the sludge. Based on the results above, it could be concluded

TABLE-1
CHARACTERISTICS OF THE EXCESS ACTIVATED SLUDGE SAMPLES

	TSS (g/L)	VSS (g/L)	pH	Conductivity (mS/cm)	COD (mg/L)	SCOD (mg/L)
Sludge sample	13.65 ± 1.22	8.77 ± 0.89	6.92	7.44	18,096 ± 612	225 ± 14

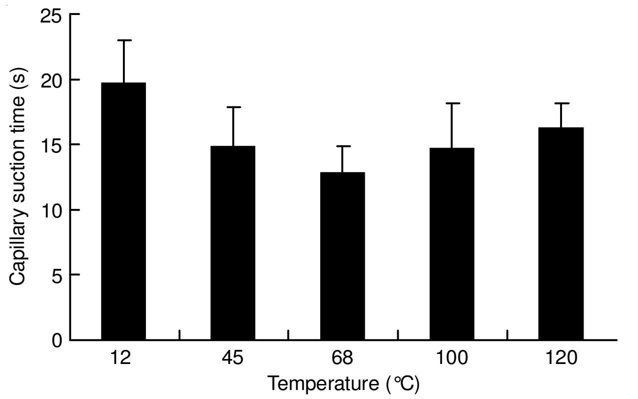

Fig. 1. Comparison of different temperatures on the capillary suction time. (Experimental conditions: Fe^{2+} = 1.0 g/L; H_2O_2 = 3.0 g/L; reaction time of 1 h; pH = 3.0)

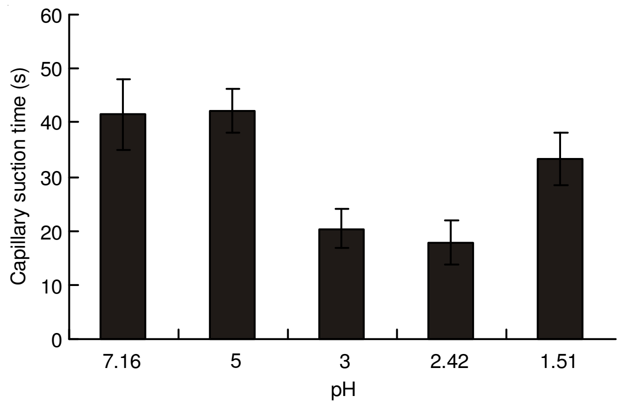

Fig. 2. Comparison of different pH on the capillary suction time. (Experimental conditions: Fe^{2+} = 1.0 g/L; H_2O_2 = 3.0 g/L; reaction time of 1 h; 68 °C)

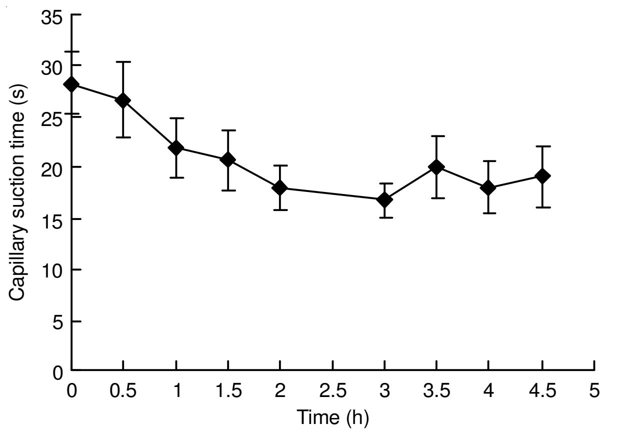

Fig. 3. Comparison of different reaction times on the capillary suction time. (Experimental conditions: Fe^{2+} = 1.0 g/L; H_2O_2 = 3.0 g/L; pH = 3.0; 68 °C)

that the suitable conditions of Fenton oxidation to improve the filterability of the sludge were as following: pH 2.5-3.0; 60-70 °C; treatment time of 2-3 h.

Effects of H_2O_2/Fe^{2+} ratio on the filterability and dewaterability of the sludge: It is possible that the sludge is easily filterable, but there is a high amount of residual water in the dewatered sludge[10]. Therefore, capillary suction time and moisture of sludge cake were applied together in this study to measure the filterability and dewaterabilty, respectively. Because the amount of ferrous ions and H_2O_2 directly affects the production of hydroxyl radicals, it was expected that H_2O_2/Fe^{2+} ratio had great influence on the filterability and dewaterability of the sludge. However, the researchers were not unanimous in the optimum H_2O_2/Fe^{2+} ratio. Neyens *et al.*[9] found mechanical dewatering is significantly improved after hydrogen peroxide treatment and the optimum H_2O_2 dosage and Fe^{2+} concentration were 0.037 g/100 mL sludge and 1 mg/100 mL, respectively. This implied that the optimum H_2O_2/Fe^{2+} ratio was 37. Mustranta and Viikari[11] found that the optimum H_2O_2 concentration was 15 mM/L at 0.02 mM $FeSO_4·7H_2O$, *i.e.* 455 of H_2O_2/Fe^{2+} ratio. Therefore, the effects of H_2O_2/Fe^{2+} ratio on the filterability and dewaterability of the sludge was investigated at pH 2.5 under 68 ± 2 °C for 2.5 h reaction time. In this experiment, 3 g/L Fe^{2+} concentration and different amounts of H_2O_2 were added to observe the changes of capillary suction time and moisture of sludge cake. Results in Fig. 4a indicated that heat treatment alone at 68°C without Fenton's reagent, did not enhance the filterability, even was detrimental to the filterability of the sludge, *i.e.* capillary suction time value increased by 31 % compared with untreated sludge. But, Neyens *et al.*[4] demonstrated that capillary suction time decreased when sludge was treated at 120 °C for 1 h reaction time. It can be seen that capillary suction time declined by 81 % when the H_2O_2/Fe^{2+} ratio was 8. The optimal H_2O_2/Fe^{2+} ratio was 7-12, but there was no great difference in capillary suction time values among different H_2O_2/Fe^{2+} ratios. The results were comparable with the findings by Buyukkamaci[12]. They found that capillary suction time decreased after Fenton's reagent conditioning, capillary suction time decreased with H_2O_2 (Fe^{2+}) dosage and there was no significant different among different H_2O_2/Fe ratios. But the results were not consistent with the findings by Lu *et al.*[6]. They found that the higher Fe/H_2O_2 ratio, the higher the filterability efficiency. This difference was possibly attributed to the low H_2O_2/Fe^{2+} ratios in their experiments. As shown in Fig. 4b, the

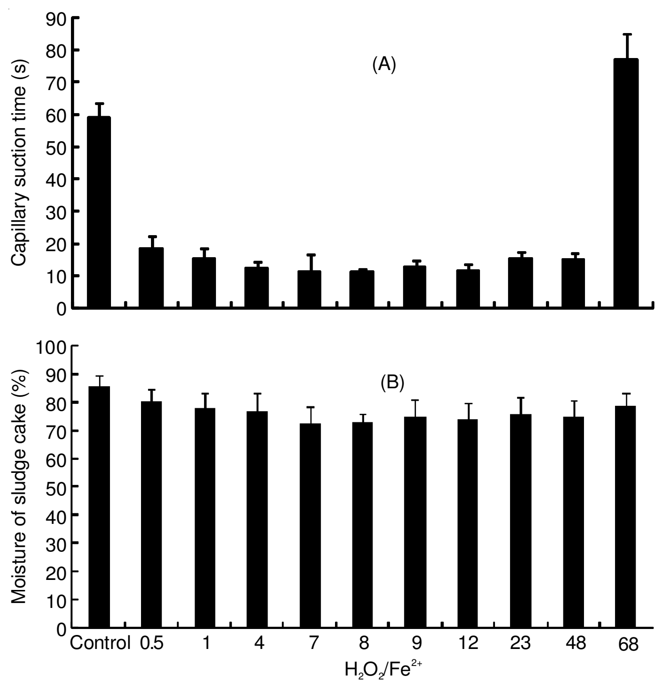

Fig. 4. Effects of H_2O_2/Fe^{2+} ratio on the filterability and dewaterability. (Experimental conditions: Fe^{2+} = 3.0 g/L; reaction time of 2.5 h; pH = 2.5; 68 °C)

moisture of the sludge cake decreased after Fenton's reagent pretreatment, the sludge dewaterability increased by 12% when the H_2O_2/Fe^{2+} ratio was 8, compared with the untreated sludge. Similarly, no significant difference in the sludge dewaterability was observed among different H_2O_2/Fe^{2+} ratios. However, the improvement degree of the filterability was greater than that of the dewaterability after Fenton's oxidation. It is not surprising that the capillary suction time is a parameter indicating dewatering rate of the activated sludge, but the moisture or dry solids content of sludge cake indicates the dewatering extent of the activated sludge. Even if the water passes through the filter cake quickly, the water content inside small pores and capillaries, as well as water bound inside the floc matrix, may remain high. Therefore, the capillary suction time may be strongly related to the "free" water in the activated sludge, whereas the moisture of sludge cake may be related to the firmly fixed water in the sludge flocs.

Effect of H_2O_2/Fe^{2+} ratio on EPS: The LB-EPS and TB-EPS contents reduced by 59-76 % and 50-87 %, respectively, after the sludge was pretreated by Fenton's reagent. When the sludge was treated by heat alone at 68 °C, the LB-EPS and TB-EPS contents only were reduced by 42% and 30%, respectively (Fig. 5). The LB-EPS and TB-EPS contents were lowest at H_2O_2/Fe^{2+} ratio of 9-12. However, when the H_2O_2/Fe^{2+} ratio increased further to 23 and even 48, the LB-EPS and TB-EPS contents both increased slightly.

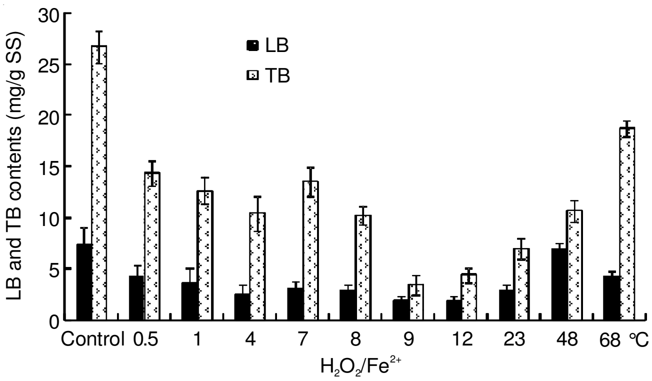

Fig. 5. Effects of H_2O_2/Fe^{2+} ratio on LB-EPS and TB-EPS contents of the sludge. (Experimental conditions: Fe^{2+} = 3.0 g/L; reaction time of 2.5 h; pH = 2.5; 68 °C)

Polysaccharide contents in LB-EPS and TB-EPS decreased after Fenton's reagent and heat pretreatment. However, there was no significant difference in PS contents in LB-EPS and TB-EPS among different H_2O_2/Fe^{2+} ratios. The reduction extent of PS content with Fenton's pretreatment was greater than that with heat pretreatment, regardless of LB-EPS or TB-EPS (Fig. 6a). In LB-EPS, proteins content increased greatly after Fenton's oxidation, whereas decreased sharply in TB-EPS. Proteins content increased approximately 3.5 times and decreased about 12 times in LB-EPS and TB-EPS, respectively, after the sludge was pretreated by Fenton's reagent with H_2O_2/Fe^{2+} ratio of 8. Similarly, there was no significant difference in proteins contents in LB-EPS and TB-EPS among different H_2O_2/Fe^{2+} ratios (Fig. 6b). Neyens *et al.*[4] also observed that the thermal and peroxidation pretreatment caused an effective reduction of proteins and polysaccharides contents of the sludge and a larger destruction for proteins than of polysaccharides.

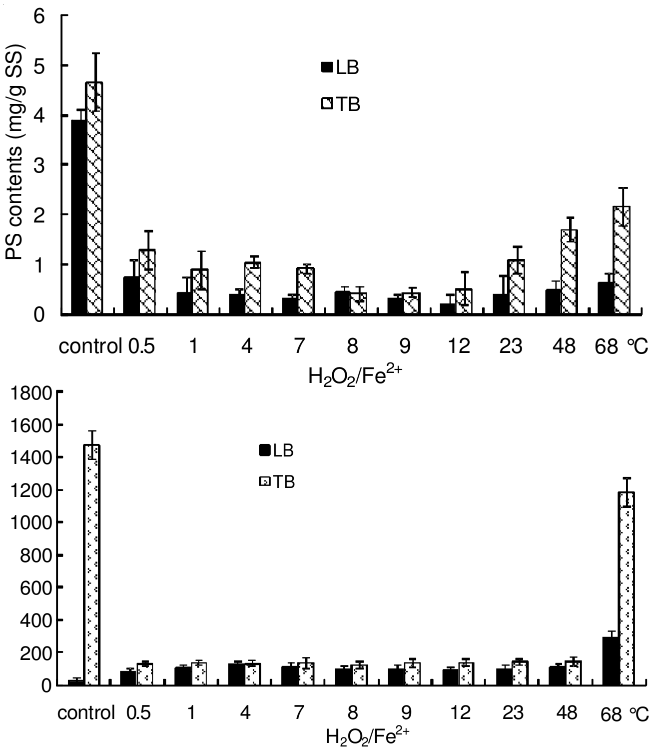

Fig. 6. Effects of H_2O_2/Fe^{2+} ratio on PS and proteins contents in LB-EPS and TB-EPS of the slud ge. (Experimental conditions: Fe^{2+} = 3.0 g/L; reaction time of 2.5 h; pH = 2.5; 68 °C)

Based on above results, the great reduction of the LB-EPS and TB-EPS (Fig. 5) concentration made by Fenton's oxidation might explain the observed favorable impact of the sludge filterability measured by capillary suction time. Degradation of EPS reduced their water retention properties, thereby released the EPS-bound water and increased the dewatering efficiency of the sludge. However, after heat pretreatment, the LB-EPS and TB-EPS contents also decreased significantly, but on the contrary, capillary suction time value increased. EPS have a high affinity for water and thus are highly hydrated. High EPS concentrations therefore increased the viscosity of sludge and decreased its filterability. But the small sludge particle might clog the filter paper, resulting in reduction of the filterability in spite of EPS reduction. The reduced sludge size is not offset by the degradation of the hygroscopic EPS (data not shown).

Table-2 shows that proteins in TB-EPS were strongly correlated with capillary suction time and moisture of sludge cake. There were weak correlations between LB-EPS, TB-EPS, PS in TB-EPS and capillary suction time, as well as moisture of sludge cake. It was surprised to find that the reduction of EPS, especially TB-EPS and its protein component, would favor the filterability and dewaterability. The results are not in agreement with our previous works and other works[4,13]. It may be explained that the TB-EPS content was significantly higher than the LB-EPS content and proteins content was also higher than PS content. The reduction of TB-EPS and proteins might make the sludge release more bound water. It was previously observed that, when EPS concentration increased to a sufficient level, there was a direct impact on sludge dewaterability that was unrelated to the sludge particle size distribution[14]. Therefore, EPS concentration was deemed more influential with respect to dewaterability of the sludge.

TABLE-2
SUMMARY OF PEARSON'S CORRELATION COEFFICIENT (R_p) AND *p*-VALUE BETWEEN THE CHARACTERISTICS OF THE SLUDGE AND CAPILLARY SUCTION TIME AND MOISTURE OF SLUDGE CAKE

Parameters	Capillary suction time (s)		Moisture of sludge cake (%)	
	R_p	P	R_p	P
LB-EPS (mg/g suspended solid)	0.563	0.03	0.794	0.04
TB-EPS (mg/g suspended solid)	0.617	0.05	0.677	0.03
Polysaccharide in LB (mg/g suspended solid)	0.011	0.02	0.714	0.04
Protein in LB (mg/g suspended solid)	-0.243	0.02	-0.005	0.06
Polysaccharide in TB (mg/g suspended solid)	0.588	0.04	0.881	0.02
Protein in TB (mg/g suspended solid)	0.893	0.05	0.946	0.01
LB/TB	0.135	0.01	0.001	0.08

Conclusion

The suitable conditions of Fenton oxidation pretreatment on the sludge filterability were as following: pH 2.5-3.0; 60-70 °C; treatment time of 2-3 h. The filterability and dewaterability of the sludge increased by 81 and 12 %, respectively, when the sludge was treated by Fenton reagent with H_2O_2/Fe^{2+} ratio of 8 at pH 2.5 under 68 °C for 2.5 h reaction time. There was no significant difference in the filterability and dewaterability after Fenton pretreatment with different H_2O_2/Fe^{2+} ratios. The greatly reduction of EPS concentration was the major reason for the observed changes in the sludge filterability and dewaterability.

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