Effects of acid-heat combined treatment on sludge dewatering performance at low temperature

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Abstract. The effects of different initial pH value, temperature and heating time on sludge dewatering performance were studied by treating sludge with acid-heat combination at low temperature and taking dewatering rate (amount of filtrate per unit time) and dewatering degree (moisture content of mud cake) as indexes to evaluate the sludge dewatering performance. And the mechanism of action was preliminarily discussed by analyzing the concentration of SCOD, protein and polysaccharide in sludge supernatant, Zeta potential and floc morphology of sludge. The results showed that the concentration of organic matter in sludge supernatant increased significantly when the sludge was treated by acid-heat combination, which indicated that the method promoted the fragmentation and dissolution of sludge flocs, and the internal bound water was released more, at the same time, the decrease of Zeta potential and the increase of temperature were beneficial to the flocculation of sludge, which effectively improved the degree and rate of sludge dewatering. The optimal conditioning conditions were determined as follows: pH 3, temperature 90°C and heating time 40 min. Under such condition, the sludge dewatering rate reached 21.30 ml/min and the moisture content of mud cake decreased to 63.20%.

1 Instruction

When urban sewage treatment plants adopt activated sludge method to treat sewage, a large amount of residual sludge will be generated. The moisture content of sludge is usually above 95%, and the dewatering performance is poor. The high moisture content of residual sludge is an important factor restricting its subsequent treatment and disposal, and how to effectively reduce the sludge moisture content is the key link of sludge treatment [1].

At present, organic and inorganic polymer flocculants are commonly used chemical regulators [2-3], but these agents generally can only improve the rate of dewatering, not the degree of dewatering. It is believed that EPS (extracellular polymer) in sludge is an important factor affecting sludge dewatering [4], and its main components are hydrophilic and viscous proteins and polysaccharides, which make it difficult to release the bound water wrapped in the sludge [5-6]. Therefore, relevant scholars put forward various methods to crack sludge EPS to improve dewatering performance, such as ultrasonic [7], heat treatment [8], Fenton treatment [9], acid and alkali treatment [10] etc. Among them, heat treatment and acid treatment are two cost-effective and easy to operate methods. For example, Wang [11] et al. found that when the sludge temperature exceeded the critical temperature (120-150°C), dewatering began to show a positive effect. At the temperature of 180-210°C, the water content of sludge after dewatering decreased from 52% to 20%. At the same time, studies have shown that when the sludge heating temperature is lower than the critical value, the dewatering performance decreases [12]. Raynaud et al. [13] found that under acidic conditions, sludge flocs would be decomposed, which could reduce the moisture content of filter cake, enhance the stability of flocs and improve the sludge dewatering performance. Neyens [14] et al. treated the sludge with H_2SO_4 at the temperature of 120 to 155°C, and the solids content of the mud cake increased significantly after dewatering, reaching a maximum of about 70%. Xu [15] et al. found that after acid-heat treatment of sludge at 170°C, pH 2 and heating time 60 min, the combined water decreased from 11.21 g/gDS (raw mud) to 7.07 g/gDS, and the moisture content of mud cake after centrifugation was as low as 55.65%.

To date, domestic and foreign researches on acid-heat combined treatment have mainly focused on the high temperature stage, but the high temperature hydrothermal treatment has high requirements on equipment and large energy consumption. Therefore, this paper mainly studied the effect of acid-heat combined treatment at low temperature (<100°C) on sludge cracking effect and dewatering performance, in order to reduce energy consumption while maintaining high dehydration efficiency.

2 Materials and methods

2.1 Materials

2.1.1 Sludge source

The sludge was taken from the residual sludge of a sewage treatment plant in the Jingkai district of Hefei city. After settling for several hours, the moisture content of sludge was further concentrated to about 97%, as the experimental sludge, it was stored in a refrigerator at 4°C. The initial properties of the sludge were shown in table 1.

Table.1 Initial properties of sludge

Parameter	Value
pH	6.67±0.12
Water content (%)	96.75±0.15
TSS (g/L)	33.74±1.53
VSS (g/L)	15.83±0.75
SCOD (mg/L)	47.40±10.50
Soluble protein (mg/L)	3.10±1.32
Soluble polysaccharide (mg/L)	3.45±1.20

2.1.2 Reagents

Concentrated sulfuric acid was prepared into 9 mol/L solution, coomassie brilliant blue g-250, glucose, anthrone, potassium dichromate and potassium hydrogen phthalate. All the above reagents were analytically pure, bovine serum albumin was biochemical reagent, and all water used in the experiment was deionized water.

2.2 Methods

2.2.1 Sludge pretreatment

Add 200 g of test sludge to a 500 ml stoppered conical flask, adjust the sludge to the corresponding pH value with H_2SO_4 and NaOH, and then put it into a water bath to heat the sludge to a pre-designed temperature for a certain period of time. During the period, the conical flask was shaken regularly to achieve uniformity. After the heating was completed, the sludge was taken out and cooled to room temperature.

2.2.2 Dehydration test

Sludge dewatering performance is evaluated in two ways: one is the rate of dewatering and the other is the degree of dewatering. The 80 g pretreated sludge sample was dewatered by suction filtration under a constant pressure of 0.1 MPa. The filtrate per unit time obtained after short-term (3 min) suction filtration was used as the evaluation index of the dewatering rate. The moisture content of the mud cake obtained by suction filtration after 25~40 min (without filtrate flow in 30 s) is used as an evaluation index of the degree of dewatering. The lower the moisture content of the cake, the higher the degree of dewatering.

2.2.3 Centrifugal separation

The 25 ml pretreated sludge was centrifuged in a 50 ml centrifuge tube and centrifuged at a speed of 3000 r/min for 15 min. After centrifugation, the supernatant was filtered with a 0.45 micron filter. The obtained filtrate was used to determine the concentration of SCOD, protein, polysaccharide in the sludge supernatant and Zeta potential of sludge.

2.2.4 Analysis methods

TSS, VSS and moisture content of mud cake were determined by gravimetric method. SCOD was determined by fast digestion [16]. The protein was determined by Coomassie brilliant blue method [17] with bovine serum albumin as the standard substance. Polysaccharide was determined by Sulfuric acid-anthrone method [18] with glucose as the standard substance. Zeta potential was measured by Zetasizer-ZS90 potentiometer. The structure of sludge floc was observed by optical microscope.

3 Results and discussion

3.1 Single factor experiment

3.1.1 Influence of initial pH value on sludge dewatering performance

The sludge was initially treated with acid-heat combination at the temperature of 90°C and the heating time of 40 min. The influence of different initial pH values on sludge dewatering performance was shown in figure 1.

As can be seen from the figure, at the pH of 6.67, when the sludge was heat treated alone, the dewatering rate decreased sharply, from 12.00 ml/min (raw sludge) to 7.30 ml/min. In addition, because the dewatering rates at pH values of 6.00 and 6.67 were too low, the filtration time was too long, and the error caused by water self-evaporation was relatively large, so the moisture content of mud cake of these two values was not given in the figure. It could be known that single heat treatment at low temperature would lead to deterioration of dewatering performance. Liu et al. [19] also reached a similar conclusion. When the pH value was decreased, the dewatering rate and degree of sludge began to slowly increase. At 2.06, the dewatering rate increased from 12.00 ml/min (raw sludge) to 22.00 ml/min, an increase of 83.33%, and the moisture content of mud cake decreased from 76.82% (raw sludge) to 60.53%, a decrease of 16.29%. As pH continued to decrease, the dewatering rate started to decrease, while the moisture content of mud cake did not change much. It may be that the pH was too low, which caused a large number of cracks in sludge EPS and cells, and the viscosity of sludge solution increases, leading to a decrease in the dewatering rate [20].

As can be seen from the figure, the dewatering rate and moisture content of mud cake at pH=2.06 were 22.0 ml/min and 60.53%, respectively, slightly better than 21.30 ml/min and 63.20% at pH=3.00. In order to reduce the amount of acid, choose pH 3 as the optimal value.

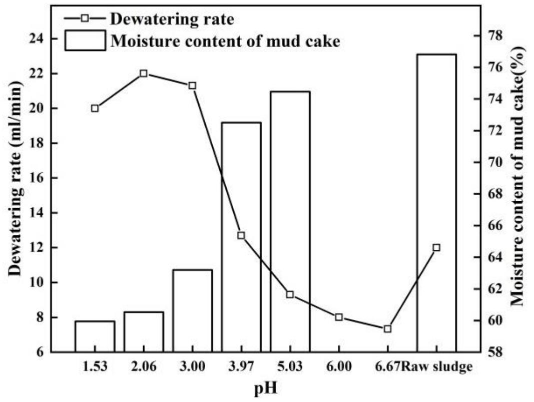

Fig. 1 Effect of pH on sludge dewatering performance

3.1.2 Influence of temperature on sludge dewatering performance

When the initial pH value was 3 and the heating time was 40 min, the sludge was treated with acid-heat combination. The influence of different temperatures on sludge dewatering performance was shown in figure 2.

As can be seen from the figure, at the temperature of 25°C, when the sludge was treated with acid alone, the dewatering rate was 13.67 ml/min and the moisture content of mud cake was 72.07%. Compared with 12.00 ml/min and 76.82% of the raw sludge, the sludge dewatering performance was improved to some extent. During the acid-heat treatment, with the increase of temperature, the sludge dewatering rate and degree showed an upward trend. When the temperature rose to 90°C, the sludge dewatering rate could reach 20.00 ml/min, and the moisture content of mud cake decreased to 63.06%. The original intention of the experiment is to save energy by lowering the pretreatment temperature below 100°C, so choose 90°C as the optimal temperature

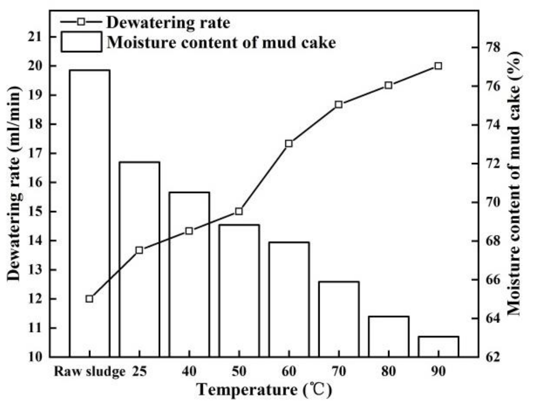

Fig. 2 Effect of temperature on sludge dewatering performance

3.1.3 Influence of time on sludge dewatering performance

When the initial pH value was 3 and the heating temperature was 90°C, the sludge was treated with acid-heat combination. The influence of different heating time on sludge dewatering performance was shown in figure 3.

As can be seen from the figure, the dewatering rate of sludge increased first, then decreased and then tended to be stable with the extension of heating time, while the moisture content of mud cake changed little. When the heating time was shorter than 40 min, the dewatering rate increased with the extension of time. At 40 min, the dewatering rate reached the maximum value of 20.67 ml/min. When the time was extended to 60 min, the dewatering rate of sludge began to decrease, and then tended to be stable with the extension of time. Therefore, choose 40 min as the optimal time.

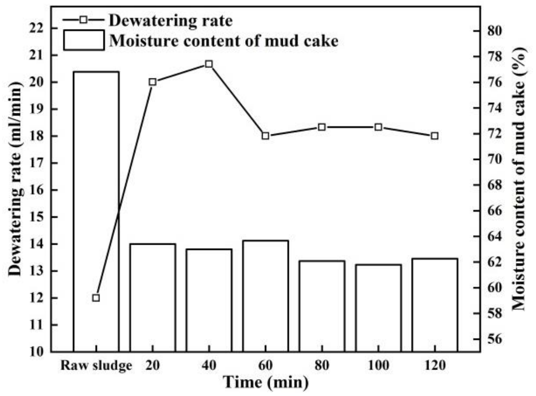

Fig. 3 Effect of time on sludge dewatering performance

3.2 Mechanism analysis

3.2.1 Content analysis of SCOD, protein and polysaccharide in supernatant solution

The concentration of SCOD, protein and polysaccharide in sludge supernatant can characterize the cracking degree of sludge EPS [21]. By cracking the sludge EPS, the internal combined water can be released, making the free water content in the sludge solution increase, thus improving the dewatering degree of sludge. However, a large number of cracking of sludge EPS and cells will not only re-loose the flocculation structure of sludge, but also increase the viscosity of sludge solution and decrease the sludge dewatering performance [22-23]. The organic matter concentration in sludge supernatant under different treatment methods was shown in table 2.

According to the determination results, the concentration of SCOD, protein and polysaccharide in the supernatant solution of the raw sludge was low, indicating that in the initial state, the content of soluble EPS in the solution was low, while the content of EPS in the sludge floc was high, and the bound water wrapped in it was difficult to release, resulting in a low degree of dewatering of the raw sludge. After the sludge was treated with acid (pH=3) alone, the concentration of SCOD, protein and polysaccharide in the supernatant solution increased, indicating that the sludge EPS and cells were cracked to a certain extent under the action of acid hydrolysis, and the sludge dewatering degree was improved. The concentration of SCOD, protein and polysaccharide in the supernatant solution increased significantly after the sludge was treated by acid-heat combination, indicating that the sludge EPS and cells were cracked to a greater extent under the combined action of acid hydrolysis and thermal hydrolysis, and the sludge dewatering degree was significantly improved. After heat treatment (T=90°C) of the sludge, the concentration of SCOD, protein and polysaccharide in the supernatant solution increased immensely, which may be due to the mutual exclusion of particles, the exposure of fine particles exposed more surface area in the water, which greatly solved the problem of sludge EPS and cells, however, the release and dissolution of excessive organic matter greatly increased the viscosity of sludge solution, which was not conducive to sludge dewatering.

Table 2 Organic matter concentration in sludge supernatant under different treatment methods

Treatment	Raw sludge	Acid	Acid-heat	Heat
SCOD (mg/L)	47.40	137.54	925.76	2882.12
Protein (mg/L)	3.10	28.81	34.32	130.40
Polysaccharide (mg/L)	3.45	28.5	203.3	268.37

3.2.2 Zeta potential and floc morphology analysis

Zeta potential is one of the important factors affecting sludge particles aggregation or dispersion, low Zeta potential absolute value means the larger the sludge particles gathered trend, in general, the greater the floc, the faster the sludge dewatering. The Zeta potential of sludge under different treatment methods was shown in figure 4, and the floc morphology of sludge under different treatment methods was shown in figure 5.

As can be seen from the figure, the potential of raw sludge was -14.10 mv, which caused a large electrostatic repulsion between the particles, and the sludge flocculation ability was poor. The treated sludge consisted of fine particles with uniform distribution, and the floc was small and the structure was loose (as shown in figure 5a), thus the dewatering rate of raw sludge was lower. After the sludge was treated with acid alone, the H^+ in the solution could neutralize the negative charge on the surface of the sludge, Zeta potential increased to 3.97 mv, so repulsive force between particles was reduced, which was helpful for sludge flocculation. The originally dispersed particles began to become compact and the floc structure became larger (as shown in figure 5c), which increased the rate of dewatering. After the sludge was treated with acid-heat combination, the Zeta potential was -3.49 mv, which was not much different from the acid treatment, but the increase of temperature accelerated the thermal motion of the particles and increased the frequency of particle collision and aggregation [24], which further enhanced sludge flocculation. The treated sludge showed a large floc, and the structure of flocs was tight (as shown in Figure 5d), and the sludge dewatering rate was greatly increased. While when the sludge was heat treated alone, the Zeta potential was reduced from -14.10 mv (raw sludge) to -17.50 mv, this is because the increase of sludge temperature promoted the rise of anionic groups (carboxyl, hydroxyl and phosphate groups) ionization, which made the surface of the sludge floc with more negative [19], although the rise of temperature was helpful for sludge accumulation, but low Zeta potential increased the electrostatic repulsion between the particles and further hindered the sludge flocculation. The treated sludge floc particles became smaller and dispersed (as shown in Figure 5b), and the presence of smaller particles will block the filter cake. Based on the analysis of the concentration of organic matter in the supernatant, it was believed that the substantial increase of EPS content in sludge supernatant and the decrease of flocs leaded to a serious decrease of sludge dewatering rate [20].

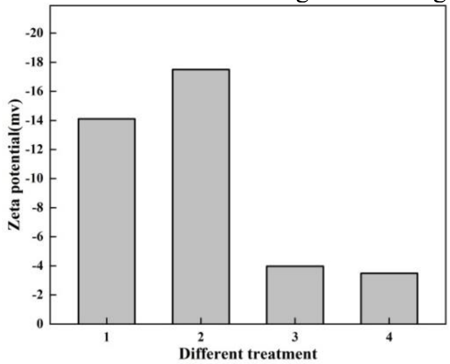

Fig.4 Zeta potential of sludge under different treatment methods (1.Raw sludge; 2.Heat treatment; 3.Acid treatment; 4.Acid-heat treatment)

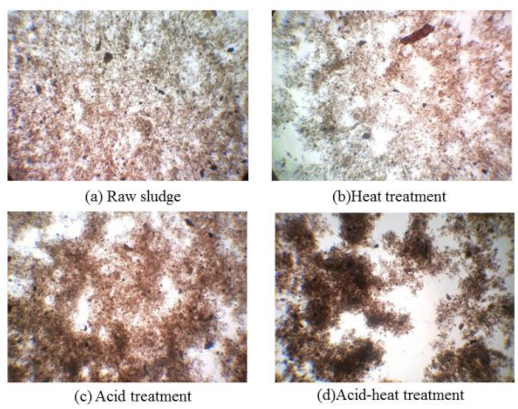

Fig.5 Floc morphology of sludge under different treatment methods

4 Conclusions

(1) The combined treatment of acid and heat can

effectively improve the sludge dewatering performance, which is obviously better than the single acid treatment or heat treatment. The experiment determined the optimal conditioning conditions: pH 3, temperature 90°C, heating time 40 min, under this condition, the sludge dewatering rate reached 21.30 ml/min, and the moisture content of mud cake decreased to 63.20%.

(2) Mechanism analysis showed that the concentration of SCOD, protein and polysaccharide in the supernatant solution increased significantly when the sludge was treated by acid-heat combination, it indicated that the sludge EPS and cells were effectively cracked, so internal bound water got more released, which effectively increased the degree of sludge dewatering. The neutralization of acidic ions in the solution and the increase of temperature promoted the flocculation of sludge, which significantly increased the rate of sludge dewatering.

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