Effects of Potassium Ferrate-Walnut Shell Pretreatment on Dehydration Performance of Residual Sludge

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Abstract

Sludge dehydration is not only the primary part in sludge reduction, but also a difficult point in sludge treatment and disposal, while the high moisture content of the sludge will also limit its resource utilization. In this paper, the strong oxidizing property of potassium ferrate was used to treat the residual sludge, and walnut shells are used as a skeleton builder to obtain the dehydrated sludge that can be recycled. The disintegration degree of extracellular polymer of sludge (EPS), the moisture content of the sludge, and the specific resistance of sludge (SRF) were investigated to explo re the effects of potassium ferrate-walnut shell pretreatment on sludge dehydration performance. The experimental results show that the optimal dosages of potassium ferrate and walnut shells are 60 mg/gDS and 0.8 g/gDS, respectively, and the moisture content and SRF of the sludge after pretreatment reach the lowest values of 70.2% and 1.107×10^{11} m/kg, which greatly improves the dehydration performance compared with the individually treated potassium ferrate and walnut shells, and provides the new ideas and methods for sludge dehydration.

Introduction

With the increasing development of the economy and the improvement of the level of urbanization, the number of urban domestic sewage treatment plants has also increased. According to statistics, about 12.32 million tons of dry sludge can be produced by sewage plants in China every year, of which about 11.82 million tons of dry sludge needs to be disposed of. The massive production of sludge determines that sludge treatment accounts for an important proportion of secondary pollution control in sewage treatment plants (Wu B et al., 2020). The composition of residual sludge is complex, consisting mainly of inorganic and organic matter and a wide variety of micro-organisms, and containing some pathogens and heavy metals. At the same time(WANG Ganlin et al., 2018). At the same time ,the residual sludge in wastewater treatment plants before treatment contains a very high moisture content, which is generally greater than 99%. After gravity sedimentation, the moisture content is still above 95%. Due to the high moisture content, sludge is prone to decay and deterioration, which will have a serious impact on the subsequent treatment and disposal sites. Therefore, sludge dehydration is an important part of sludge treatment, which can chieve the purpose of sludge reduction and is of great significance for the subsequent disposal of sludge (Mowla D et al., 2013).

In recent years, chemical conditioning has become a typical and effective method of sludge treatment(Zahedi S et al., 2017). Commonly used chemical treatment methods are conventional coagulation and advanced oxidation processes (AOP), with the application of AOP receiving increasing attention (Wei H et al., 2018). Polyacrylamide (PAM) and FeC13 are two commonly used conventional coagulants in conventional coagulation methods, but neither of them can achieve satisfactory sludge dewatering performance(Yu W et al., 2018). This is mainly because PAM cannot significantly change the viscous structure of the sludge and FeCl3 cannot effectively destroy the sludge structure. In recent years, advanced oxidation processes (AOP) including Fenton oxidation, Fenton-like oxidation and potassium permalate oxidation have been shown to be effective in improving sludge dewatering performance by disrupting the floc structure and removing extracellular polymers (EPS) (Ho Y C et al., 2010; Maqbool T et al., 2019). Among them, potassium permalate oxidation is an advanced oxidation process, due to the good oxidising and flocculating properties of potassium permalate (K_2FeO_4) and the fact that no harmful or polluting by-products are produced during the treatment process. The coagulant is generated during the mixing process, which can flocculate tiny particles, improve the settling performance and dehydration properties of sludge, and reduce the volume of sludge (Ye F et al., 2012; Qi L et al., 2017). The effects of potassium ferrate pretreatment on sludge dehydration performance are mainly influenced by the amount of potassium ferrate and the pH value of the sludge. At the initial pH = 3 of the sludge, potassium ferrate pretreatment can improve the dehydration performance of the sludge, while the dehydration performance of the sludge deteriorates at the pH values from 4 to 8 (Zhang X et al., 2012). When Wu et al. Wu C et al. (2015) used potassium ferrate (K_2FeO_4) to pretreat the sludge, the results showed that when the dosage was 500 mg/L, the maximum sludge disintegration (DDSCOD) could reach 69%, the concentration of organic matter in the supernatant was significantly increased, and the increase of polysaccharide content was higher than that of protein.

After chemical conditioning, the filtration resistance of the sludge can be reduced and the filterability of the sludge can be improved. However, when the conditioned sludge is physically compressed, a sludge cake with a high solids concentration cannot be obtained due to the higher compressibility in the sludge. This results in the sludge cake being very susceptible to deformation, which in turn causes blockage of the pores of the sludge cake and reduces the filterability of the sludge. Skeleton builders, also known as sludge physical regulators, were generally inert materials, such as lime, fly ash, and gypsum. When these skeleton building materials were added into sludge, they could not only play a supporting role, but also form many pore channels, which was beneficial to the removal of moisture in the sludge. Skeleton builders are broadly divided into two categories :carbon-based materials and mineral materials (Benitez J et al., 1994). Carbon based materials are mainly coal coke, coal dust, wood chips, wheat residue, etc. Mineral materials mainly include industrial waste, such as fly ash, cement dust, lime and gypsum (Zhao Y Q et al., 2002). Among them, fly ash is one of the most widely studied skeletal materials (Chen C et al., 2010). Both carbon-based and mineral materials are used to improve sludge dewatering performance by changing the properties of sludge solids.In addition, the external physical compression had little effect on the pore structure, which could effectively avoid the problem of sludge deformation during compression and effectively improve the sludge dehydration efficiency(Cai Li et al., 2014). Luo et al.(2013) treated the residual sludge with wood chips as a skeleton builder and concluded that a skeletal structure with many pores and channels was constructed between the sludge, which promoted the formation of a permeable structure between the sludge, thereby increasing the dehydration rate of the sludge.

The main purpose of this paper was to explore the effects of the combined treatment of potassium ferrate-walnut shell on sludge dehydration performance and to compare it with the sludge dehydration performance by potassium ferrate oxidation and walnut shell skeleton construction separately. Subsequently, the sludge samples from the original sludge, the sludge treated with potassium ferrate, the sludge treated with walnut shell and the sludge treated with the combined treatment of potassium ferrate-walnut shell were scanned by an electron microscope and the supernatant was measured by a three-dimensional fluorescence spectrum, which analyzed the dehydration mechanism of the sewage and at the same time provided new methods and ideas for sludge dehydration.

Materials And Methods

The main experimental materials in this study were sludge samples and walnut shell samples. The sludge samples were selected from the sludge of the final sedimentation tank of Xi'an No. 5 Sewage Treatment Plant, and were placed in a refrigerator at 4°C to ensure the activity of the sludge, and then naturally settled for 24 h, and the supernatant was dumped. The basic properties of the concentrated sludge are shown in Table 1. The walnut shell samples were mainly purchased online. The purchased walnut shells were rinsed with tap water, crushed in a pulverizer and graded and sieved to obtain walnut shell powders with different particle sizes, and then dried at 105°C for later use.

Table 1
Basic properties of sludge with concentration

Moisture content (%)	pH	TS (g/L)	VS (g/L)	SRF (m/kg)	Protein (mg/L)	Polysa-ccharide (mg/L)	SCOD (mg/L)
97.3	6.85	25.93	12.6	5.58×10^{11}	14.95	10.50	859

200 mL of sludge samples were taken and placed in a beaker, and the pH of the sludge was adjusted with 10% dilute sulfuric acid and 10% dilute sodium hydroxide. Then, a certain amount of potassium ferrate was added, and a six-set agitator was started to stir at a rotating speed of 300 r/min for a certain time for the test. The dehydration performance of the sludge was investigated under different dosages of potassium ferrate, different reaction times and different initial pH values, and the moisture contents of the sludge, the SRF, SCOD of the supernatant, protein and polysaccharide contents were determined respectively.

200mL of sludge samples were taken and placed in a beaker, the pH of sludge was adjusted with 10% dilute sulfuric acid and 10% dilute sodium hydroxide, and then walnut shells with different dosages were added. At the same time, different particle sizes of walnut shells were set, and then a six-set agitator was started to stir at 300 r/min for 3 min and at 150 r/min for 20 min to conduct the test respectively. The effects of different particle sizes and different dosages of walnut shells on the sludge dehydration performance were explored, and the sludge indicators after treatment were determined as described above.

200mL of sludge samples were taken and placed into a beaker, the pH of sludge was adjusted with 10% dilute sulfuric acid and 10% dilute sodium hydroxide, and a certain amount of potassium ferrate was added. A six-set agitator was started to stir at 300r/min and after a certain time, different dosages of walnut shells with the above-mentioned optimal particle size were added for the experiment. The effects of the combined treatment of potassium permanganate-walnut shell on the sludge dehydration performance were investigated, and the above-mentioned sludge indicators after treatment were measured respectively.

Results And Discussion

3.1 Effects of potassium ferrate pretreatment on sludge performance

3.1.1 Dosages of potassium ferrate

The experimental results of the effects of potassium ferrate dosages on the degree of sludge disintegration and sludge dehydration performance are shown in Fig. 1 and Fig. 2. When the dosage of potassium ferrate is within 10 mg/g-40 mg/gDS, the values of polysaccharide, protein and SCOD in the sludge are gradually increased and the concentration is the highest when the dosage of potassium ferrate is 40 mg/gDS. At this time, the polysaccharide concentration, the protein concentration and the SCOD concentration are 67.57 mg/L, 331.17 mg/L and 2106 mg/L, respectively, which are increased by 6.43 times, 22.15 times and 2.45 times respectively compared with the initial sludge. When the dosage of potassium ferrate is continually increased, various indicators are trending downward, which reveals that the degree of sludge disintegration reaches the maximum when the dosage of potassium ferrate is 40 mg/gDS. This is because potassium ferrate, as a strong oxidant, can oxidize and disintegrate the gelatinous structure of the sludge EPS and bridging substances, releasing organic substances, such as proteins and polysaccharides. In addition, potassium ferrate can also destroy the microbial cell membrane and release cytoplasm and intracellular substances into water. When the dosage of potassium ferrate is too high, the organic matter released into the supernatant will be further oxidized and degraded, resulting in the decrease of the organic matter content in the supernatant.

From Fig. 2, it can be seen that the moisture content and SRF of the sludge are changed with the change of potassium ferrate dosage. When the dosage of potassium ferrate is increased from 10 mg/gDS to 40 mg/gDS, the moisture content and SRF of the sludge both show a downward trend. The lowest moisture content is 75.4%, and the minimum SRF is 3.609×10^{11}m/kg. Compared with the original sludge cake, the moisture content is decreased by 7.2%, and the SRF is decreased by 35.3%. With the continual increase of the dosage, the moisture content and the SRF of the sludge cake are both increased, of which the increase of the SRF is more obvious. This is because in the redox process of potassium ferrate, iron ions are reduced from high-valence Fe6+ to low-valence Fe3+ with different forms of charges, and the final product involved in the oxidation process is Fe(OH)3 with excellent flocculation properties, which can allow the colloidal particles in the sludge to flocculate by adsorption and bridging. Combined with Fig. 1, when potassium ferrate is added to the sludge, the extracellular polymer EPS and cell membrane of the sludge are destroyed, and organic substances, such as proteins and polysaccharides are released, and the intracellular bound water is also converted into other forms of water, thereby decreasing the moisture content and SRF value of the sludge. With the continual increase of the dosage, the dehydration performance of the sludge will deteriorate. This is because excessive oxidation will produce excessive cellular debris, which will cause the blockage of the filter membrane. In addition, the OH^- generated by oxidation will lead to an increase in the number of negative charges in the sludge, which will increase the repulsion between sludge particles and make the dehydration performance worse. Therefore, the optimal dosage of potassium ferrate is chosen to be 40 mg/gDS.

3.1.2 Reaction time

The experimental results to investigate the effects of the reaction time on the degree of sludge disintegration and sludge dehydration performance are shown in Fig. 3. Within the reaction time of 30 min, the protein concentration, the polysaccharide concentration and the SCOD concentration are maintained at a high value. When the reaction time is 20 min, the maximum values of the protein, the polysaccharide and the SCOD reach 184.95 mg/L, 64.12 mg/L and 2091 mg/L, respectively, which are increased by 12.37 times, 6.11 times and 2.43 times higher than those of the original sludge. As the reaction time goes on, all three concentrations begin to decrease. This is because potassium ferrate has strong oxidizing properties under acidic conditions, which can oxidize and disintegrate the extracellular polymer of the sludge (EPS) and release a large amount of dissolved organic matter, polysaccharide, protein and so on. However, as the reaction continues, the oxidizing ability of potassium ferrate is gradually decreased, and the ability to disintegrate EPS is gradually decreased, too. Therefore, potassium ferrate has the best disintegration effect on the sludge when the reaction time is 20 min.

The variation of moisture content and SRF of the sludge with time is shown in Fig. 4. It can be seen that when the reaction time is 20 min, the moisture content and SRF are rapidly decreased, and reach the lowest values of 75.3% and 3.35×10^{11} m/kg, respectively. Compared with the original sludge, the moisture content is decreased by 7.3% and the SRF is decreased by 39.9%. As the reaction time continues, although the moisture content and SRF of the sludge have changed, the overall trend is still upward. Combined with Fig. 3, this indicates that the oxidation of the sludge by potassium ferrate is basically completed when the reaction time is 20 min, so it is determined that the optimal reaction time is 20 min.

3.1.3 Initial pH values

The experimental results to explore the effects of the initial pH on the degree of sludge disintegration and sludge dehydration performance are shown in Fig. 5. The initial pH has a great influence on the reaction of potassium ferrate. When the initial pH is 2, the release of protein and polysaccharide reaches the maximum, which are 244.48 mg/L and 93.78 mg/L, respectively. Compared with the original sludge, they are increased by 16.35 times and 8.93 times, respectively. With the increase of pH values, the protein, polysaccharide and SCOD are first gradually decreased and then gradually increased. When the pH is from 5 to 6, the concentrations of the three substances reach the lowest value. When the pH is 10, the release of SCOD reaches the maximum of 2382 mg/L. This is because potassium ferrate has a higher redox potential under both acidic and alkaline conditions, and the oxidation potential of 2.2 V under the acidic condition is higher than that of 0.72 V under the alkaline condition. Therefore, potassium ferrate has a higher degree of sludge disintegration under the acidic condition.

The variation of the moisture content and SRF of the sludge with the initial pH is shown in Fig. 6. It can be seen that the moisture content and SRF of the sludge are gradually increased with the increase of the initial pH. When the pH is 3, the moisture content of the sludge reaches the lowest value of 75.8%. When the pH is increased to 7, the moisture content is rapidly increased and exceeds 80%, and the change of SRF is roughly the same as that of the moisture content. From Fig. 5, when pH<7, potassium ferrate has a higher degree of the sludge disintegration, which can convert more bound water into free water and reduce the sludge moisture content. In addition, H^+ can neutralize the negative charges in the sludge flocs, reduce the repulsion between the fine particles in the sludge, facilitate the aggregation of colloidal particles, thus improving the dehydration performance of the sludge. When pH>7, on the one hand, the oxidizing property of potassium ferrate is gradually decreased. On the other hand, the alkaline condition increases the number of negative charges in the sludge, and a lot of negative charges increase the repulsion between the fine particles in the sludge, which leads to the deterioration of the sludge dehydration performance.

In conclusion, the optimal conditions for the sludge dehydration pretreated with potassium ferrate are as follows. The dosage of potassium ferrate is 40 mg/gDS, the reaction time is 20 min, and the initial pH is 3. At this time, the moisture content and SRF of the sludge are 75.4% and 3.35×10^{11} m/kg, respectively.

3.2 Effects of walnut shell pretreatment on the sludge dehydration performance

3.2.1 Particle sizes of walnut shells

The experimental results to explore the effects of different particle sizes of walnut shells on the sludge dehydration performance are shown in Fig. 7. When the particle sizes of the walnut shells are the same, the moisture content and SRF of the walnut shells with the dosage of 0.5g/gDS are lower than those with the dosage of 0.1g/gDS. When the particle sizes of walnut shells are 30-50 meshes, the moisture content and SRF of the sludge reach the lowest values, which are 75.6% and 2.77×10^{11} m/kg respectively. As the particle size of walnut shells continues to decrease, the moisture content and SRF of the sludge are gradually increased. This is because the walnut shells with larger particle sizes are easy to float on the surface of the sludge due to their light mass and large size, which leads to that the walnut shells cannot be well mixed with the sludge. Because the particle sizes are too small, the walnut shells with smaller particle sizes cannot form a skeleton builder in the sludge cake and may also block the pore structure in the sludge cake, causing the deterioration of the sludge dehydration performance. Therefore, the optimal particle size of the sludge dehydration pretreated with walnut shells is 30-50 meshes.

3.2.2 Dosage of walnut shells

The experimental results to explore the effects of different walnut shell dosages on the sludge dehydration performance are shown in Fig. 8. With the increase of walnut shell dosage, the contents of protein and polysaccharide in the sludge supernatant are gradually increased. However, the range of changes is very small, in which the content of protein is increased from 16.86 mg/L to 48.29 mg/L and the content of polysaccharide is increased from 15.84 mg/L to 48.26 mg/L. This is because walnut shells do not oxidize and disintegrate EPS, so the increase of the organic matter in the supernatant may be caused by the carbon release of walnut shells in water. It can be seen that the moisture content and SRF values of the sludge are gradually decreased with the increase of the dosage of walnut shells. The moisture content of the sludge cake is significantly reduced when the dosage of walnut shells is 0.8 g/gDS. At this time, the moisture content and SRF are 73.9% and 3.05×10^{11} m/kg, respectively. Compared with the original sludge, the moisture content is decreased by 8.7%, and the SRF is decreased by 45.3%. This is because the addition of walnut shells to the sludge enables the walnut shells to form a skeleton support in the sludge, provides a water passage, so that the sludge cake can still maintain the moisture unobstructed under high pressure, and improve the dehydration performance of the sludge. With the continual increase of walnut shell dosage, the moisture content and SRF of the sludge cake have no obvious change. Due to the water absorption of the walnut shell itself, the absorbed moisture is not easily removed, so the addition of excessive walnut shells reduces the moisture that can be removed, resulting in no significant change in the moisture content.

To sum up, the addition of walnut shells to the sludge can effectively improve the dehydration performance of the sludge, and the moisture content and SRF of the sludge are gradually decreased with the increase of the walnut shell dosage. When the particle sizes of walnut shells are 30-50 meshes and the dosage of walnut shells is 0.9 g/gDS, the moisture content and SRF of the sludge are 73.6% and 2.99×10^{11} m/kg, respectively.

3.3 Effects of the combined pretreatment of potassium ferrate-walnut shell on sludge performance

The experimental results of the effects of the combined treatment of potassium ferrate-walnut shell on sludge dehydration performance are shown in Fig. 9. The larger the initial dosage of potassium ferrate is, the higher the protein and polysaccharide concentrations in the supernatant are. When the initial dosage of potassium ferrate is 60 mg/gDS and the dosage of walnut shells is 0.6 g/gDS, the protein concentration reaches the maximum of 226.4 mg/L, which is 15.14 mg/L higher than that of the original sludge. When the initial dosage of potassium ferrate is 60 mg/gDS and the dosage of walnut shells is 0.8 g/gDS, the polysaccharide concentration reaches the maximum of 155.6 mg/L, which is 14.82 times higher than that of the original sludge. The contents of the protein and the polysaccharide in the sludge supernatant are both increased compared to their individual treatment, which further indicates that potassium ferrate can release the soluble organic matter from the sludge. It is only due to the lack of water passages that the separated organic matter cannot be released smoothly, but the addition of the walnut shell as a skeleton builder provides a water channel and enables to further release the organic matter.

From Fig. 10, it can be seen that with the increase of the walnut shell content, the moisture content of the sludge is gradually decreased. When 60 mg/gDS of K2FeO4 and 0.8 g/gDS of walnut shell are combinedly treated, the moisture content of the sludge reaches the lowest value of 70.2%. Compared with the lowest moisture content of 75.4% and the lowest moisture content of 73.9% when potassium ferrate and walnut shell are treated separately, they are both decreased, which indicates that both of them have a synergistic effect in sludge dehydration. As can be seen from Fig. 10(b), the SRF is also gradually decreased with the increase of the walnut shell content. When 60 mg/gDS of K2FeO4 and 0.8 g/gDS of walnut shell are combinedly treated, the SRF reaches the lowest value of 1.107×1011 m/kg, which is decreased by 80.16% compared with the original sludge of 5.58×10^{11} m/kg. When the sludge is treated with potassium ferrate and walnut shells separately, the maximum decreases of SRF are 39.9% and 45.3%, respectively, indicating that the filterability of the sludge can be improved when potassium ferrate and walnut shells are combinedly treated. This is because, when the sludge is treated with potassium ferrate alone, the strong oxidation of potassium ferrate can destroy EPS and release part of the bound water. After walnut shells are added, the walnut shells can play a role of a skeleton builder, which can form porous dehydration channels in the sludge cake and can improve the compressibility of the sludge cake. The separation of sludge and water is further improved, thus improving the dehydration performance of the sludge.

As shown in Fig. 11, the contents of protein and polysaccharide in the dissolved state extracellular polymer (S-EPS), loose extracellular polymer (LB-EPS) and compact extracellular polymer (TB-EPS) of the sludge are all increased after walnut shells are treated. This may be because after the addition of walnut shells, the walnut shells are distributed in the flocculent substances of the sludge and combined with organic substances, such as proteins to form complexes through hydrophobic and electrostatic interactions, thereby releasing more organic matter into EPS. The contents of protein and polysaccharide in S-EPS and LB-EPS are significantly increased after potassium ferrate is treated, while the contents of protein and polysaccharide in TB-EPS are decreased compared with those of the original sludge, which indicates that potassium ferrate can disintegrate the EPS structure, and hydrolyze and release the macromolecular organic matter, such as protein and polysaccharide in the sludge. When potassium ferrate and walnut shells are combinedly treated, the contents of protein and polysaccharide in S-EPS and LB-EPS are significantly increased, while the contents of protein and polysaccharide in TB-EPS are decreased from 212.1 mg/L and 103.26 mg/L to 104.01 mg/L and 40.33 mg/L, respectively. To sum up, compared with the original sludge, the concentrations of protein and polysaccharide in the S-EPS layer treated with different methods are increased, while in the LB-EPS layer, the concentrations have relatively little change, and in the TB-EPS layer they are decreased, and the range of changes is as follows: potassium ferrate-walnut shell>potassium ferrate>walnut shell> original sludge. This indicates that TB-EPS and LB-EPS can be converted into S-EPS after treatment. Under the acidic condition, potassium ferrate has strong oxidizing properties, which can oxidize part of LB-EPS and TB-EPS and convert them into S-EPS, thus leading to the increase of the concentration of S-EPS. According to the research of Zhang et al.(2012) , this conversion is beneficial to the sludge dehydration, thus indicating that potassium ferrate-walnut shell can effectively improve the sludge dehydration performance.

In order to study the sludge more intuitively and in-depth, the sludge samples from the original sludge, the sludge treated with potassium ferrate, the sludge treated with walnut shell and the sludge treated with the combined treatment of both are analyzed by a scanning electron microscope, and the results are shown in Fig. 12.

Fig. 12 shows the changes in the microscopic morphology of the sludge under the conditions of different pretreatments. From 12(a), it can be seen that the surface of the original sludge is flat and compact, and the inter-floc structure is relatively tight, but the dehydration is poor. When potassium ferrate is added, the microstructure is shown in Fig. 12(b), and the floc structure of the sludge becomes more dispersed and a large number of cracks appear on the surface. The microstructure of the sludge treated with walnut shells alone is shown in Fig. 12(c), and the pores at the junction of walnut shell and the sludge are larger. At the same time, a large number of porous structures appear, which indicates that walnut shells have formed a skeleton structure in the sludge, and the addition of walnut shells can enhance the permeability and compressibility of the sludge. When potassium ferrate and walnut shells are added simultaneously, the microstructure of the sludge is shown in Fig. 12(d). The sludge particles are more obviously disintegrated, and the floc structure becomes looser and more dispersed, which makes it easier for the moisture in the sludge floc to pass through the sludge cake and ultimately reduces the moisture content of the sludge. In order to further analyze the distribution of the organic matter in the sludge, the supernatants from the original sludge, and the sludges treated with potassium ferrate, the sludges treated with the combined treatment of potassium ferrate and walnut shell are measured by three-dimensional fluorescence spectroscopy, and the results are shown in Fig. 13.

As can be seen from Fig. 13(a), there is only a very weak fluorescence peak of humic acid in the original sludge; From Fig. 13(b) after potassium ferrate treatment, the fluorescence peaks of humic acid and fulvic acid in the sludge have strong intensities, and there is a tryptophan fluorescence peak with weaker intensities. From Fig. 13 (c), the sludge treated with walnut shells has a stronger fluorescence peak of tryptophan-like protein and a weaker humic acid fluorescence peak. From Fig. 13(d), the sludge treated with the combined treatment of potassium ferrate-walnut shell have the stronger fluorescence peaks of tryptophan-like protein, fulvic acid, and humic acid. It can be seen that the fluorescence peak of humic acid in the sludge treated with potassium ferrate is shifted to the right by about 25 nm, while the tryptophan-like proteins appear. Because the oxidative disintegration of potassium ferrate leads to the increase of micromolecular organic matter in the sludge, the appearance of the fluorescence peak of fulvic acid as a hydrophobic substance indicates that the dehydration performance of the sludge has been improved (ZHANG Siwei et al., 2019) . After the walnut shell treatment, a strong peak of tryptophan-like fluorescence appears, indicating that more fluorescent-like proteins can be released from walnut shells. After the combined treatment, the intensities of the fluorescence peaks of humic acid and fulvic acid are enhanced compared with the original sludge and the sludge treated with walnut shell alone. However, the intensities of the fluorescence peaks of humic acid and fulvic acid are decreased compared to the sludge treated with potassium ferrate alone, indicating that potassium ferrate has the strongest oxidizing ability and can oxidize and disintegrate the organic matter in the supernatant.

Fig. 14 shows the dehydration mechanism of the sludge treated with the combined treatment of potassium ferrate-walnut shell. As can be seen from Fig. 14, when potassium ferrate is added to the sludge, potassium ferrate can destroy the cell structure of the sludge through the strong oxidation, releasing part of the internal water and the bound water from the sludge, while accelerating the release of interstitial water in the sludge. When the walnut shells are added, the walnut shells are staggered in the sludge to form a new dehydration channel, which further accelerates the separation of the sludge and the water and improves the dehydration performance of the sludge.

Conclusion

According to the experimental results of this paper, the following conclusions can be drawn. When the excess sludge is combinedly pretreated, under the optimal reaction conditions of potassium ferrate dosage of 60 mg/gDS and walnut shell dosage of 0.8 g/gDS, the minimum values of the moisture content and SRF of the sludge after pretreatment are 70.2% and 1.107×10^{11} m/kg, respectively. Compared with the sludges treated with potassium ferrate and walnut shell separately, the moisture content and SRF of the sludge are reduced. The changes of the EPS in the sludge supernatant show that potassium ferrate can effectively destroy the sludge flocs, and can release the organic matters, such as proteins and polysaccharides from the TB-EPS and LB-EPS layers into the solution to convert them into S-EPS. Therefore, the binding force between the sludge particles and the moisture is reduced, and the moisture in the sludge is easier to be removed.

It can be observed by a scanning electron microscope (SEM) that after the combined treatment of potassium ferrate and walnut shells, a large number of cracks appear on the surface of the sludge, and the structure of the sludge floc becomes dispersed. The pores at the junction of walnut shell and the sludge become larger and a skeleton structure appears. The addition of walnut shells can enhance the permeability and compressibility of the sludge.

The three-dimensional fluorescence spectra show that the combined treatment of potassium ferrate -walnut shell can disintegrate the sludge and can increase the hydrophobic substances, such as humic acid and fulvic acid in the sludge supernatant.

Declarations

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Author contributions DSL designed the experiment, SXW and ZZ performed the experiments and analyzed the data. SXW and RHJ reviewed the manuscript.

Data availability The datasets used in the current study are available from the corresponding author on reasonable request.

Ethical approval No ethical approval was necessary for this study.

Consent to participate All participants in this study consent to participation.

Consent to publish All authors consent to this publication.

Competing interests The authors declare that they have no competing interests.

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Figures

Figure 1

Effects of potassium ferrate dosages on sludge disintegration with (a) protein and polysaccharides; (b) SCOD

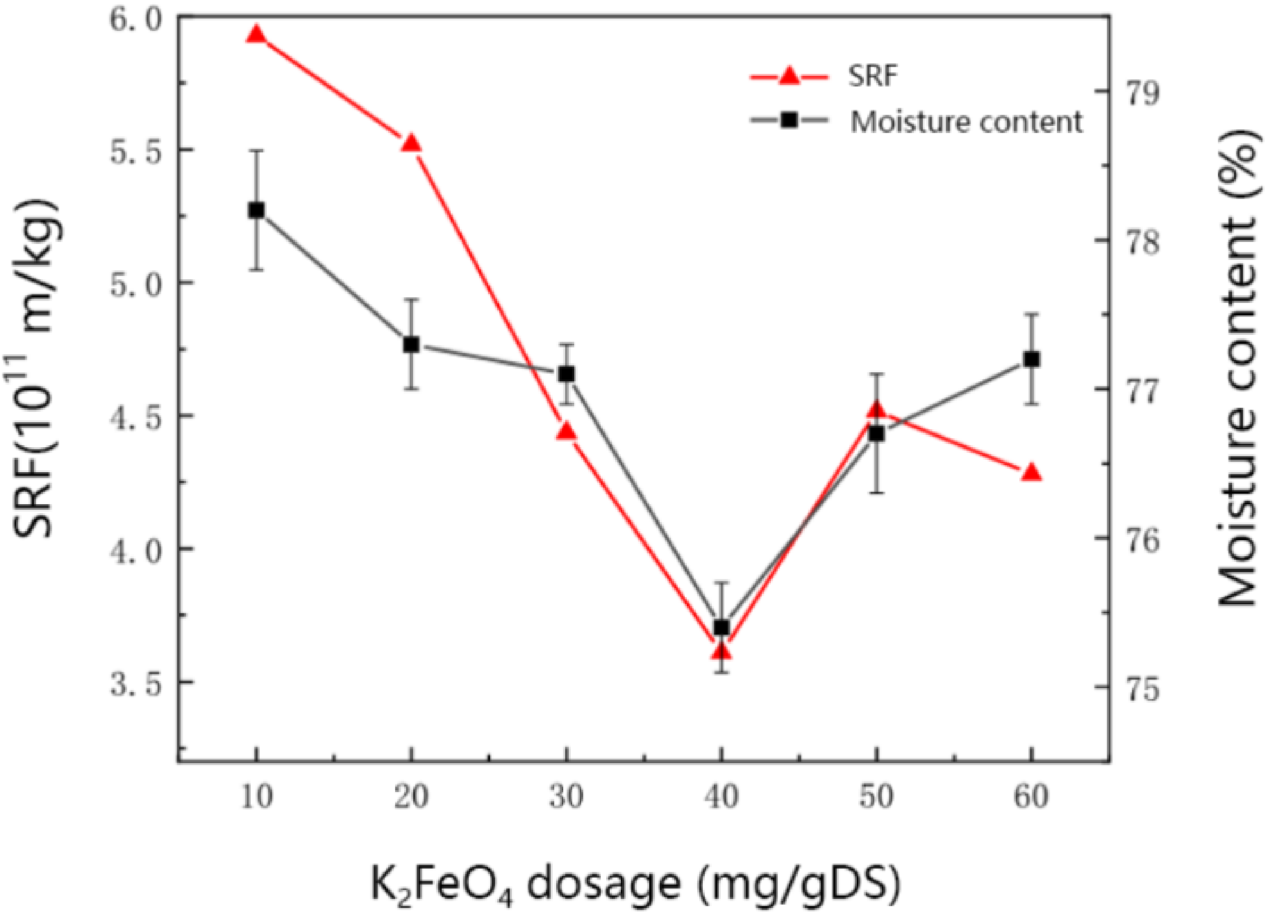

Figure 2

Effects of potassium ferrate dosages on sludge dehydration performance

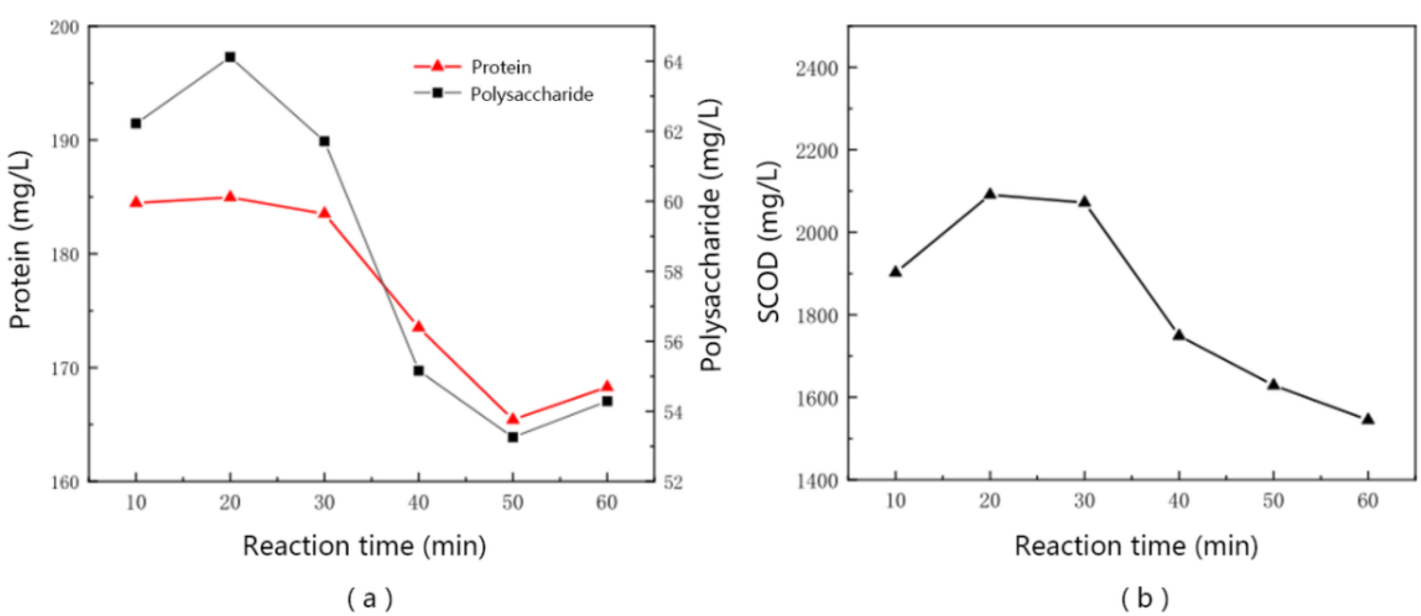

Figure 3

Effects of reaction time on sludge disintegration with (a) protein and polysaccharide; (b) SCOD

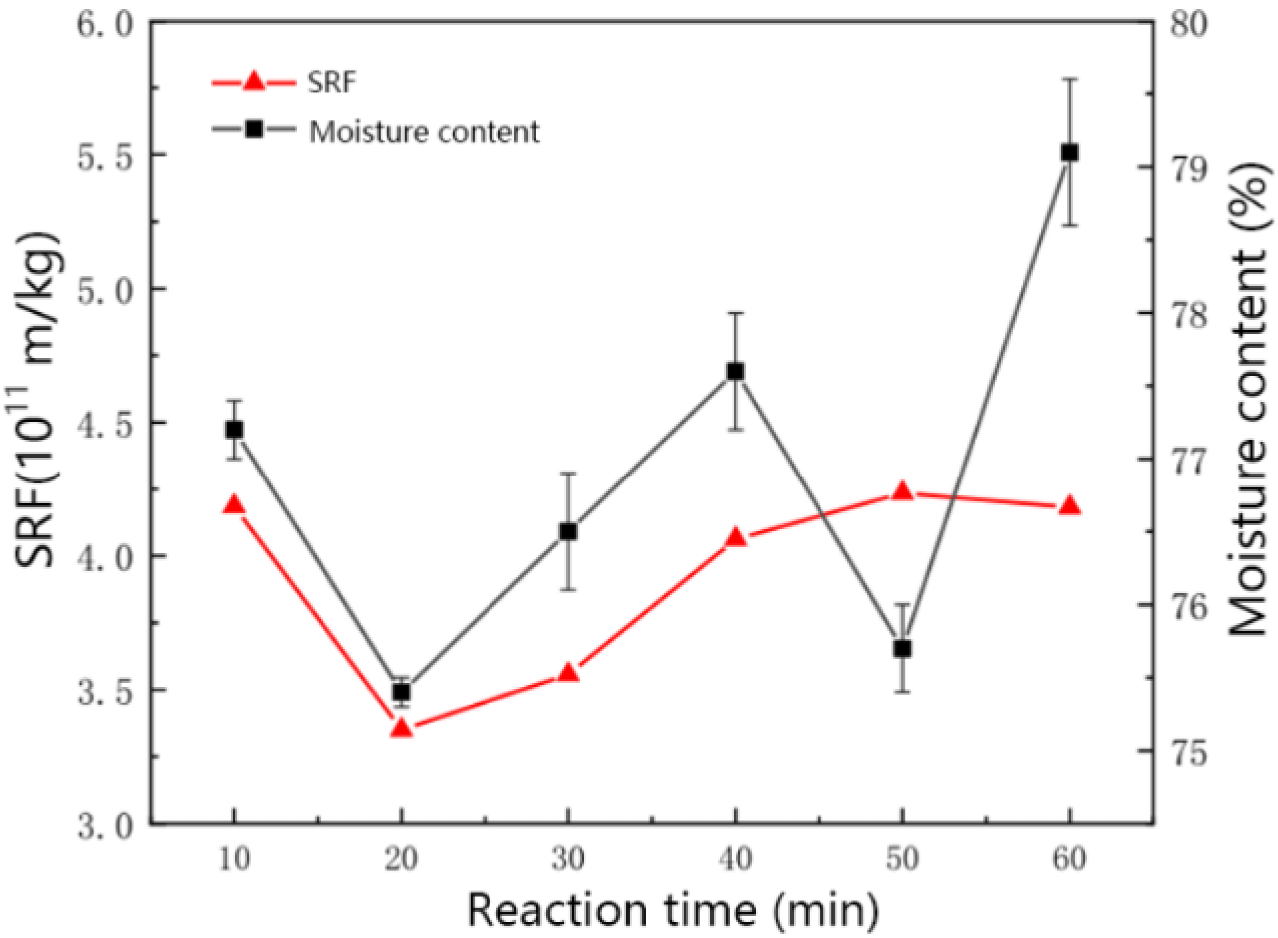

Figure 4

Effects of reaction time on sludge dehydration performance

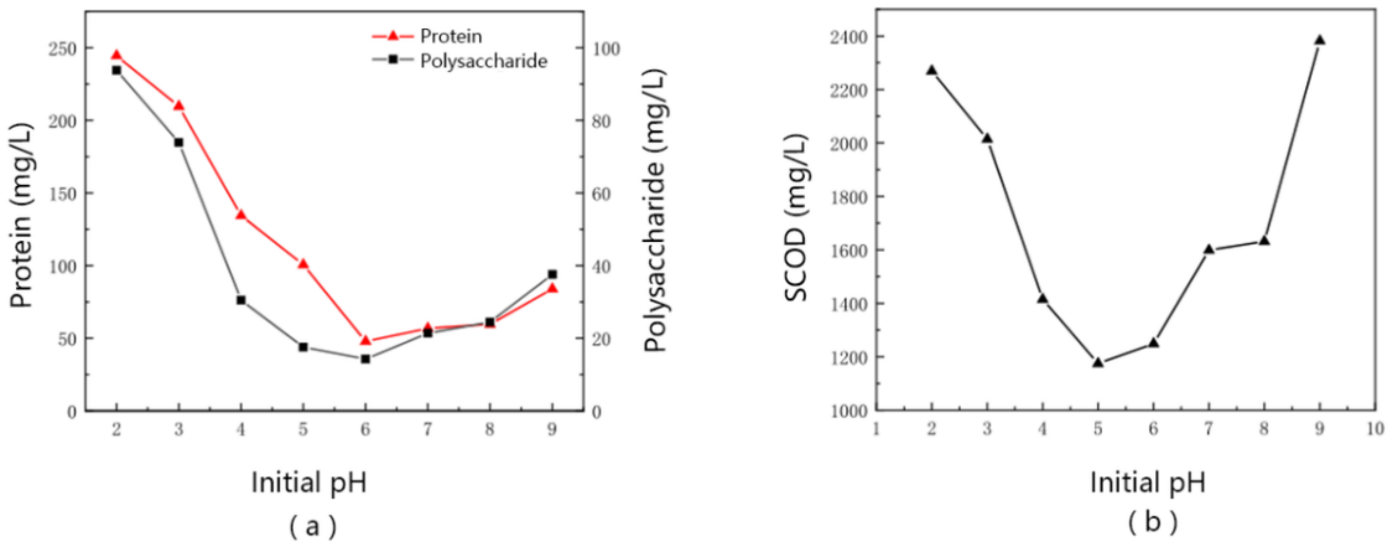

Figure 5

Effects of the initial pH on sludge disintegration with (a) protein, polysaccharide; (b) SCOD

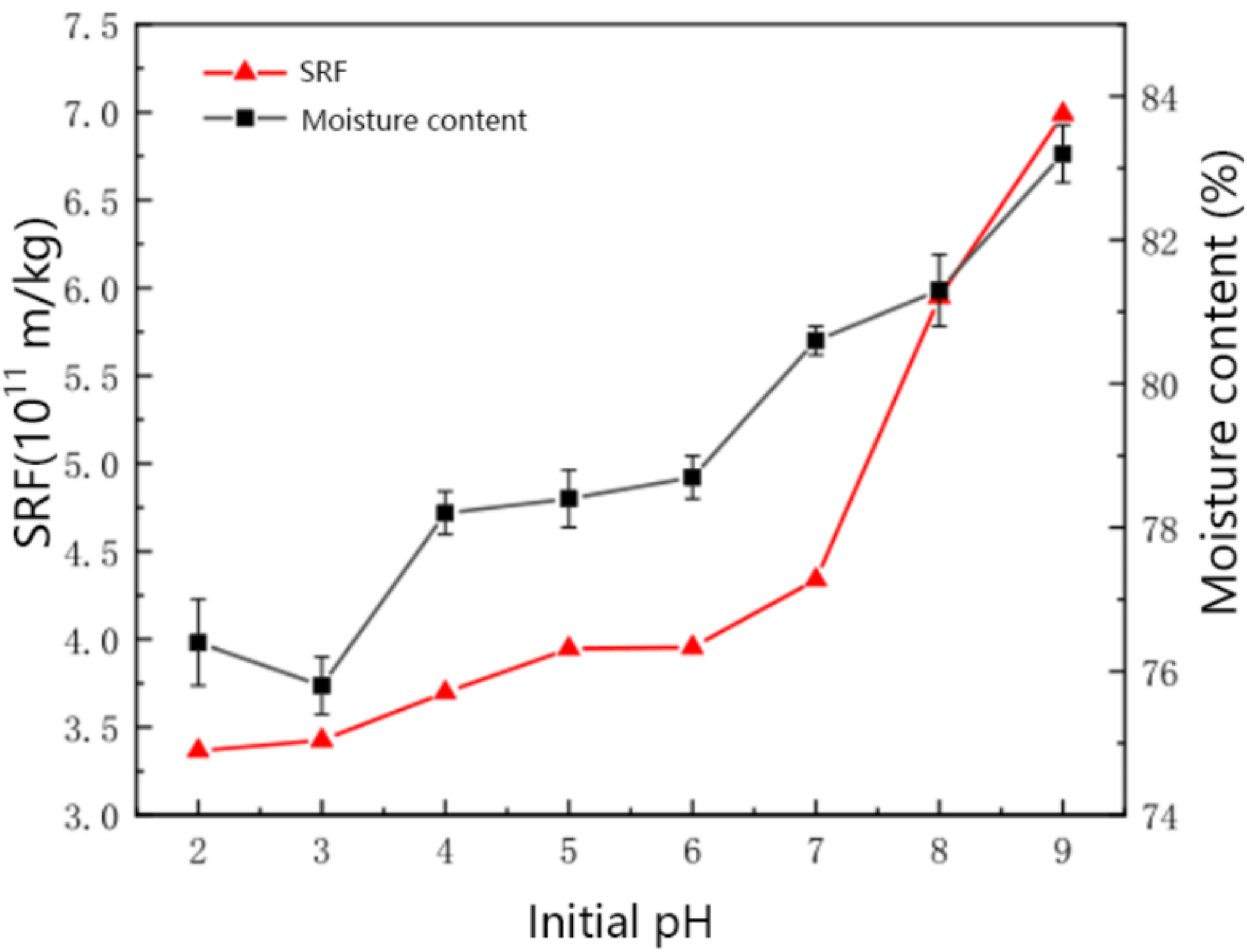

Figure 6

Effects of the initial pH on the sludge dehydration performance

Figure 7

Effects of walnut shell particle sizes on sludge dehydration performance with (a) moisture content; (b) SRF

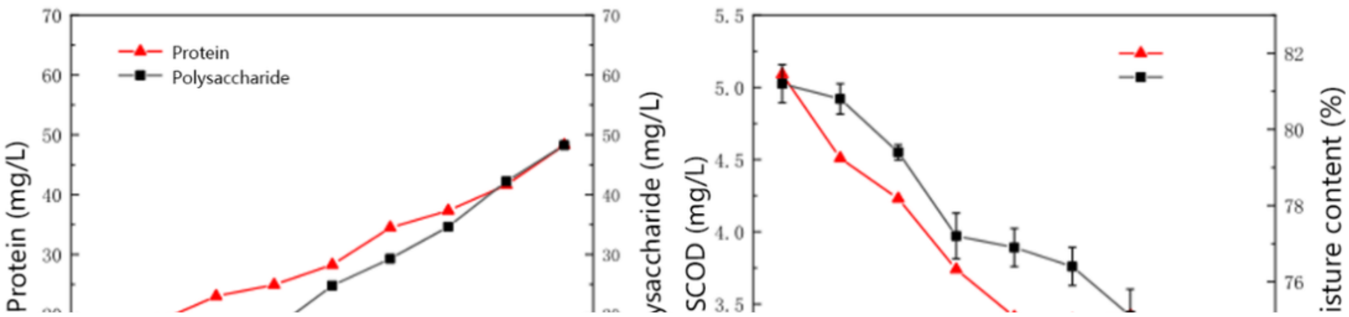

Figure 8

Effects of walnut shell dosage on sludge dehydration performance with (a) protein and polysaccharide; (b) moisture content and SRF

Figure 9

Effects of the combined treatment of potassium ferrate-walnut shell on the sludge disintegration with (a) protein; (b) polysaccharide.

Figure 10

Effects of the combined treatment of potassium ferrate-walnut shell on the sludge dehydration performance with (a) moisture content; (b) SRF

Figure 11

Variations of (a) protein and (b) polysaccharide in the supernatant before and after sludge treatments.

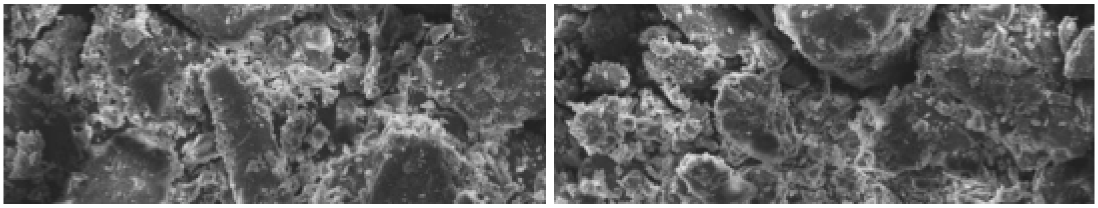

Figure 12

SEM images of the sludge under the conditions of the different pretreatments

(a) original sludge; (b) sludge treated with potassium ferrate; (c) sludge treated with walnut shell; (d) sludge treated with the combined treatment

Figure 13

Three-dimensional fluorescence spectra of the supernatants of the sludge samples: (a) Original sludge; (b) Sludge treated with potassium ferrate; (c) Sludge treated with walnut shell; (d) Sludge treated with the combined treatment

Figure 14

Schematic diagram of the sludge dehydration mechanism