Effects of potassium ferrate-walnut shell pretreatment on dehydration performance of residual sludge

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Abstract
Sludge dehydration is not only the first process of sludge reduction but also difficult for sludge treatment and disposal, while the high moisture content of sludge would also limit its resource utilization. In this paper, the residual sludge was treated by the strong oxidizing property of potassium ferrate (PF), and walnut shells were used as a skeleton builder to obtain the recycling dehydrated sludge. It also provides a new solution for the poor stability of PF in the treatment of sludge and waste walnut shells. The experiment results showed that the optimum dosage of PF and walnut shell was 60 mg/gDS and 0.8 g/gDS, respectively, and the water content of the combined PF and walnut shell treatment decreased by 5.2% and 3.7% compared to that of PF conditioning alone and walnut shell conditioning alone, respectively. In addition, scanning electron microscopy and three-dimensional fluorescence spectroscopy revealed a large number of cracks on the sludge surface after the combined treatment, and the sludge floc structure became more loose and dispersed, and the hydrophobic substances humic acid and fulvic acid increased, indicating that the dewatering performance of the sludge was effectively improved, further confirming that the combined PF and walnut shells treatment provides a new idea and method for sludge dewatering.

Keywords Joint processing · Walnut shell · Dewaterability · Residual sludge

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 need 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 et al. 2020). The composition of residual sludge is complex; the main composition is about 99% moisture and 1% solid composition, consisting mainly of inorganic and organic matter and a wide variety of micro-organisms, and containing some pathogens and heavy metals (Wang et al. 2018; Qi et al. 2020). 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. In addition, if the heavy metals in the sludge are not properly treated, there is a high risk of serious secondary contamination (Yin et al. 2019; Antonkiewicz et al. 2022). Therefore, sludge dehydration is an important part of sludge treatment, which can achieve the purpose of sludge reduction and is of great significance for the subsequent disposal of sludge (Mowla et al. 2013).

Potassium ferrate (PF) oxidation is an advanced oxidation process due to its good oxidizing and flocculating properties and the fact that it does not produce harmful or polluting by-products during the treatment process. It also generates coagulants during the mixing process, which can flocculate tiny particles, improve the settling and dewatering properties of the sludge, and reduce the sludge volume, and is often used as an oxidizing agent in advanced oxidation methods.
(Ye et al. 2012; Qi et al. 2017). Currently, PF has four functions in the sludge treatment process: dewatering, mini-
mination, anaerobic fermentation, and contaminant removal. For sludge dewatering, PF can decompose the flocculent structure and internal microbial cells, oxidize carbohydrate lipid-protein and other substances composed of the cell wall, break the cell wall, and release organic matter, which has a strong promotion effect on sludge dewatering performance (Hu et al. 2020; Zhang 2021). Its effect on sludge dewatering performance is influenced by the amount of PF and sludge pH. According to Wu et al., when the dosage is 500 mg/L, the maximum sludge cracking can reach 69%, the supernatant organic matter concentration is significantly increased, the increase in polysaccharide content is higher than that of protein, and the dewatering performance is significantly improved (Wu et al. 2015). However, a low dosage or high dosage of potassium ferrate will have a significant negative effect on the rehydration performance of sludge (Ye et al. 2012; Wang et al. 2021). At the initial pH = 3 of the sludge, PF 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 et al. 2012). In addition to reducing the water content of the sludge, PF also effectively reduced the capillary suction time (CTS) and specific resistance to filtration (SRF), increasing the dewatering rate of the sludge. Guo et al. used PF to reduce the specific resistance of sludge by approximately 96%, while the CTS was effectively reduced during the conditioning process, showing that the dewatering capacity of sludge was greatly improved and the dewatering rate was also increased (Guo et al. 2013). PF has proven to be extremely capable of sludge dewatering but inevitably has certain shortcomings. Firstly, PF is less stable in the treatment process, and therefore, there is a certain amount of loss in the treatment process, which increases the cost input (Hu et al. 2020). Secondly, when physically compressing the sludge after PF treatment, it was found that a sludge cake with a high solids concentration could not be obtained due to the higher compressibility in the sludge. This resulted in the sludge cake being very susceptible to deformation, which in turn caused blockage of the sludge cake pores and reduced the filtration performance of the sludge.

Walnuts, one of the world’s most famous dried fruit foods, are very popular among consumers due to their rich nutrient content. China is not only the number one consumer of walnuts but also has the largest production and cultivation area in the world (Zhao et al. 2014). However, the processing and consumption of walnut products generate a large number of walnut shells, of which only some are treated and reused, while most are discarded or burned, resulting in a large number of wasted resources and a significant environmental hazard. Currently, since the walnut shell is composed of biological macromolecules such as lignin cellulose and hemicellulose, and has a huge specific surface area, most studies use the walnut shell to prepare activated carbon for the adsorption of heavy metals in wastewater (Guo et al. 2021; Liu 2020). Lekan prepared activated carbon from walnut shell and rice shell to remove Cd\(^{2+}\) in the solution. The results showed that the adsorption efficiency of Cd\(^{2+}\) achieved 78.58% under the optimum conditions (Popoola et al. 2019). In addition, the biochar using walnut shell also has corresponding requirements on pH. Mohamed et al. used it to remove heavy metal ions such as Pb\(^{2+}\), Cu\(^{2+}\), and Cr\(^{3+}\) in the solution, the strongest adsorption capacity of biochar was found when the pH was 5–6, and the adsorption capacity of heavy metal ions such as Pb\(^{2+}\), Cu\(^{2+}\), and Cr\(^{3+}\) reached 792, 638, and 574 mg/g (Zbair et al. 2019). Xiao made a similar study on the adsorption capacity and mechanism of Hg\(^{2+}\) in wastewater (Xiao 2021). Secondly, the extraction and properties of brown pigments from walnut shells have also been studied by some authors. Li et al. used walnut shells as a raw material to extract brown pigments and purified them using a macroporous resin method and found that the purified pigments were more heat resistant and stable under non-alkaline conditions, and that light, oxidants, and some metal ions had some effect on them (Tao et al. 2021). Cai found that when added to the sludge it not only provided support but also formed many pore channels, which facilitated the removal of water from the sludge. In addition, the water content of the sludge gradually decreased with increasing doses of walnut shells, and the smaller the particle size of walnut shells, the better the dewatering performance of the sludge cake (Cai 2014).

The combined treatment method can reduce or eliminate the limitations of a single treatment method, and also fully utilize the advantages of each treatment method to better improve the dewatering effect of sludge (Qiao et al. 2020). At present, there is no research on the combined treatment of residual sludge with PF and walnut shells to explore the dewatering properties of sludge. To fill the gap, and also to address the aforementioned shortcomings of PF in the process and after treatment of sludge, as well as to explore new forms of walnut shell utilization, reduce waste walnut shell resources, and improve the environment. Firstly, the degree of cracking and dewatering of sludge by walnut shells and PF was investigated through single-factor experiments, and secondly, the advantages of walnut shells as a skeleton builder combined with the strongly oxidizing properties of PF were used together to investigate the effects of both on sludge dewatering performance. The dewatering performance of the sludge was compared with that of the PF oxidation method and walnut shell skeleton builder alone, followed by the analysis of the dewatering mechanism of wastewater by subjecting sludge samples and supernatants from different treatments to electron microscopy scanning.
and 3D fluorescence spectroscopy to provide a new approach to sludge dewatering and a new pathway to improve the environment.

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.

A total of 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.

A total of 200 mL of sludge samples were taken and then 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.

A total of 200 mL 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 300 r/min, and after a certain time, different dosages of walnut shells with the abovementioned 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 abovementioned sludge indicators after treatment were measured respectively.

To investigate the sludge dewatering performance and microscopic morphological changes, the sludge mixture treated with different treatment methods was further analyzed using scanning electron microscopy (SEM) with reference to the study of Wang et al. (Wang et al. 2007), and the samples were dried in an oven at a temperature of 40°C for 12 h to a constant weight, then sprayed with gold after cooling. The microscopic morphology of the sludge samples was observed using FEI Q45 environmental scanning electron microscope. In addition, to further analyze the distribution of organic matter in the sludge, three-dimensional fluorescence measurements were performed on the supernatant of the sludge samples using an FS-5 fluorescence spectrometer. The excitation wavelength EX was set to 235–400 nm and the emission wavelength Em was set to 345–550 nm with a step size of 1 nm (Li et al. 2006).

Results and discussion

Effects of potassium ferrate pretreatment on sludge performance

Dosages of potassium ferrate

The experimental results of the effects of PF dosages on the degree of sludge disintegration and sludge dehydration performance are shown in Fig. 1 and Fig. 2. When the dosage of PF is within 10 mg/g-40 mg/gDS, the values of polysaccharide, protein, and SCOD of the supernatant, protein, and polysaccharide contents were determined respectively.

A total of 200 mL 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 300 r/min, and after a certain time, different dosages of walnut shells with the abovementioned 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 abovementioned sludge indicators after treatment were measured respectively.

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

Abb: TS, dry matter content; VS, volatile substance content; SRF, specific resistance to filtration
hydrolysis of sludge as a whole, so it also indicates that the sludge hydrolysis is best at this concentration. (Qiu et al. 2016; Li et al. 2018). However, when the dosage of PF is continually increased, both polysaccharide and SCOD concentrations showed a decreasing trend. This is because PF, as a strong oxidant, can oxidize and disintegrate the gelatinous structure of the sludge EPS and bridging substances, releasing organic substances. Therefore, the decrease in polysaccharide concentration may be due to the oxidation of the released polysaccharides into small molecules by PF, which in turn also leads to a decrease in SCOD concentration (Luo et al. 2018). In addition, PF can also destroy the microbial cell membrane and release cytoplasm and intracellular substances into the water. When the dosage of PF 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 PF dosage. When PF was added at 40 mg/gDS, the water content and SRF of the sludge showed a decreasing trend to reach the lowest value, and the lowest values of water content and SRF were 75.4% and, respectively, and the lowest SRF was $3.609 \times 10^{11}$ m/kg. Compared with the original sludge cake, the moisture content is decreased by 7.2%, and the SRF is decreased by 35.3%. This indicates that when PF is added to the sludge, the extracellular polymer EPS and cell membrane of the sludge are destroyed, organic matter such as proteins and polysaccharides are released, and the bound water inside the cells is converted to other forms of water, thus reducing the water content and SRF value of the sludge. 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. It is the excessive oxidation that will produce excessive cellular debris, which will lead to clogging of the filter membrane and deteriorate the dewatering performance. In addition, the OH- produced by oxidation will lead to an increase in the number of negative charges in the sludge, which will increase the repulsion between the sludge particles. Therefore, the optimal dosage of PF is chosen to be 40 mg/gDS.

**Reaction time**

The experimental results to investigate the effect of reaction time on the degree of sludge cracking and sludge dewatering performance are shown in Fig. 1 and Fig. 2 of the Supplementary Information (SI). 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 protein, polysaccharide, and SCOD reached the maximum value, which increased 12.37 times, 6.11 times, and 2.43 times compared with the original sludge. As the reaction time goes on, all three concentrations begin to decrease. This is because PF has strong oxidizing properties under acidic conditions, which can oxidize and disintegrate the EPS of the sludge and release a large amount of dissolved organic matter, polysaccharide, protein, and so on. However, as the reaction continues, the oxidizing ability of PF is gradually decreased, and the ability to disintegrate EPS is gradually decreased, too. Similar results were demonstrated by Zhang et al. (Zhang et al. 2019b). According to the Fig. 2 of the SI, 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 \(3.35 \times 10^{11}\) 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. 1 of SI, this indicates that the oxidation of the sludge by PF is basically completed when the reaction time is 20 min, so it is determined that the optimal reaction time is 20 min.

**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. 3 of SI. The initial pH has a great influence on the reaction of PF. When the initial pH was 2, the release of protein and polysaccharide reached the maximum value, which increased 16.35 times and 8.93 times, respectively, compared with the original sludge. 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. PF has a higher redox potential under both acidic and basic conditions. The oxidation potential of 2.2 V under acidic conditions is higher than that of 0.72 V under basic conditions. Therefore, PF has a higher degree of sludge disintegration under the acidic condition.

From Fig. 3, 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, PF 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 PF 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 PF are as follows. The dosage of PF 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 \(3.35 \times 10^{11}\) m/kg, respectively.

**Effects of walnut shell pretreatment on the sludge dehydration performance**

**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. 4. When the particle sizes of the walnut shells are the same, the moisture content and SRF of the walnut shells with the dosage of 0.5 g/gDS are lower than those with the dosage of 0.1 g/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 \(2.77 \times 10^{11}\) m/kg respectively. The decrease of water content is mainly due to the uniform mixing of walnut shell and sludge floc, forming a skeleton.

![Fig. 3 Effects of the initial pH on the sludge dehydration performance](image-url)
support in the sludge, which makes the filter cake layer thicken continuously under high pressure also ensures the smooth passage of water and improves the sludge permeability and compressibility. However, as the particle size of walnut shells continues to decrease, the moisture content and SRF of the sludge are gradually increased. 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. Cai and Dong et al. concluded that the smaller the particle size of walnut shells, the larger the specific surface area, and the greater the number of particles at the same mass, the easier it is to distribute evenly in the sludge cake, aligning closely with the sludge particles and forming more pores within the cake to release water, making the water content of the cake lower (Cai 2014; Dong et al. 2016). Compared with other studies, the range of walnut shell particle size considered in this paper is larger and more effective to illustrate the effect of walnut shell particle size on sludge dewatering performance. Therefore,
the optimal particle size of the sludge dehydration pretreated with walnut shells is 30–50 meshes.

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. 5. 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, 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 $3.05 \times 10^{11}$ 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 and 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 $2.99 \times 10^{11}$ m/kg, respectively.

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

The experimental results of the effects of the combined treatment of PF-walnut shell on sludge dehydration performance are shown in Fig. 6. The larger the initial dosage of PF is, the higher the protein and polysaccharide concentrations in the supernatant are. When the initial dosage of PF 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 PF 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 supernatant are both increased compared to their individual treatment, which further indicates that PF 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. 7, 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 PF 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 × 10¹¹ m/kg. When the sludge is treated with PF 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 PF and walnut shells are combinedly treated. When sludge is treated with PF alone, the strong oxidation of PF will destroy EPS and release some of the bound water. After adding walnut shell, the walnut shell can play the role of framing, and also neutralize sludge charge and adsorption bridging, improving the structure of flocs, and play a certain flocculation effect. It can form porous dewatering channels in the mud cake and improve the compressibility of the cake. The separation of sludge and water is further improved, thus improving the dehydration performance of the sludge.

As shown in Fig. 8, 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 PF is treated, while the contents of protein and polysaccharide in TB-EPS are decreased compared with those of the original sludge, which indicates that PF can disintegrate the EPS structure. This indicates that PF can disintegrate the EPS structure, and hydrolyze and release macromolecular organic matter such as proteins and polysaccharides from the sludge. When PF and walnut shells are combinedly treated, the contents of protein and polysaccharides in S-EPS and LB-EPS are significantly increased, while the contents of protein and polysaccharides in TB-EPS are decreased. This indicates that more proteins are present in the raw sludge in TB-EPS, which protects the integrity of microbial cells and hinders floc and cell dewatering performance (Hui et al. 2021). In addition, under acidic conditions, PF is highly oxidizing and can oxidize part of LB-EPS and TB-EPS and convert them to S-EPS, increasing the concentration of S-EPS. According to the research of Zhang and Li et al., this conversion is beneficial to sludge dehydration, thus indicating that the PF-walnut shell can effectively improve the sludge dehydration performance (Zhang et al. 2012; Li

![Fig. 7 Effects of the combined treatment of potassium ferrate-walnut shell on the sludge dehydration performance with a moisture content; b SRF](image-url)
et al. 2019). The combined treatment of PF and walnut shells was more favorable to the release of protein from the solid phase to the liquid phase and the release of water in EPS compared to the single method. 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: PF-walnut shell > PF > walnut shell > original sludge.

To have an in-depth study of sludge, the sludge samples from the original sludge, the sludge treated with PF, 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. 9.

Figure 9 shows the changes in the microscopic morphology of the sludge under the conditions of different pretreatments. From 9(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 PF is added, the microstructure is shown in Fig. 9(b), 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. 9(c), and the pores at the junction of the 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 PF and walnut shells are added simultaneously, the microstructure of the sludge is shown in Fig. 9(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. To further analyze the distribution of the organic matter in the sludge, the supernatants from the original sludge, and the sludges treated with PF and the sludges treated with the combined treatment of PF and walnut shell are measured by three-dimensional fluorescence spectroscopy, and the results are shown in Fig. 10.

As can be seen from Fig. 10(a), there is only a very weak fluorescence peak of humic acid in the original sludge; From Fig. 10(b) after PF 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. 10 (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. 10(d), the sludge treated with the combined treatment of PF-walnut shell has 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 PF is shifted to the right by about 25 nm, while the tryptophan-like proteins appear. Because the oxidative disintegration of PF leads to the increase of macromolecular 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 et al. 2019a). 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

Fig. 8 Variations of a protein and b polysaccharide in the supernatant before and after sludge treatments
compared to the sludge treated with PF alone, indicating that PF has the strongest oxidizing ability and can oxidize and disintegrate the organic matter in the supernatant.

Figure 11 shows the dehydration mechanism of the sludge treated with the combined treatment of PF-walnut shell. As can be seen from Fig. 10, when PF is added to the sludge, PF can destroy the cell structure of the sludge through 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.

**Conclusions**

To solve the defects of poor stability of PF in sludge treatment and easy deformation of treated sludge cake, and to explore new forms of waste walnut shell utilization, this paper combined PF and walnut shell to treat sludge together to improve the dewatering performance of sludge. However, this paper only studied the organic matter in the supernatant of pretreated sludge, and did not study other substances in the supernatant, such as total nitrogen, total phosphorus, and other organic matter that are difficult to degrade, which can be used as a research direction in future studies, and also the application of walnut shell and potassium percarbonate treated sludge in agriculture or reclamation to make a better evaluation of the sludge pretreated with potassium percarbonate-walnut shell. In this paper, a combination of PF as oxidant and walnut shell as skeleton builder was chosen to treat the residual sludge, which has very important theoretical and practical implications for environmental improvement. According to the experimental results of this thesis, the water content of the combined treatment of PF and walnut shell decreased by 5.2% and 3.7% under optimal conditions compared to PF alone and walnut shell alone, respectively, and the two together had a strong dewatering effect than acting alone when used for sludge dewatering. TB-EPS and LB-EPS could be converted to S-EPS after conditioning, and the combined treated sludge A large number of cracks appeared on the surface, the sludge flocculent structure became more loose and dispersed, and the hydrophobic substances humic acid and acid richness increased, all confirming that the dewatering performance of the sludge was improved.
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Author contribution  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.

Fig. 10  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.

Fig. 11  Schematic diagram of the sludge dehydration mechanism.

Fig. 12  Schematic diagram of the sludge dehydration mechanism.

Declarations

Ethics approval  No ethical approval was necessary for this study.

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

Consent for publication  All authors consent to this publication.

Competing interests  The authors declare no competing interests.
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