Study on Dissolution Characteristics of Excess Sludge by Low-Temperature Thermal Hydrolysis and Acid Production by Fermentation

Zhao Penghe, Liu Yuling,* Dou Chuanchuan, and Wan Pengliang

Cite This: ACS Omega 2020, 5, 26101−26109

ABSTRACT: To investigate the dissolution characteristics of low-temperature thermal pretreatment conditions and the process of sludge fermentation to produce acid, the influence of thermal pretreatment temperature on the dissolution of excess sludge organic composition and the mechanism of cell crushing of sludge thermal pretreatment were analyzed by an experimental method, and the performance of acid production was explored by sludge fermentation after pretreatment at different temperatures. The performance of acid production by sludge fermentation after pretreatment at different temperatures was measured. The results proved that the soluble chemical oxygen demand (SCOD) shows the largest increase in dissolution rate (11.92%) at 70 °C and in dissolution quantity (6518.33 mg/L) at 90 °C. However, at 80 °C, the solubility of total organic carbon (TOC) is the highest (3224.47 mg/L), and at 70 °C, the best dissolution conditions for soluble carbohydrate (SC) and soluble protein (SP) reached 340.07 and 80.92 mg/L, respectively. The degree of sludge breaking starts to increase at 70 °C. Correlation analysis shows that dissolved organic matter is mainly derived from the cell wall and intracellular material and SP is mainly derived from intracellular material. Excitation−emission matrix spectra and parallel factor analysis (EEM-PARAFAC) divides the sludge dissolved organic matter (DOM) into five fluorescent components, including C1 (318/366) tyrosine, C2 (418/470) UVA humic acid, C3 (282/334) tryptophan substances, C4 (322/430) UVC humic acids, and C5 (314, 382, 454/526) UVA humic substances. Fermentation acid production experiment shows that the peak concentration is highest at 80 °C, the arrival time is 2 days, and the acid production type is butyric acid fermentation. Thus, it is proved that low-temperature thermal pretreatment promotes the process of acid-producing fermentation and has no effect on the type of fermentation. The optimal condition for hydrolytic dissolution and acid production under low-temperature thermal pretreatment is 80 °C.

1. INTRODUCTION

Sludge is a solid waste generated during sewage treatment, and it is a byproduct of the sewage treatment process. It has a large mass, huge volume, high water content, high organic content, and complex composition that make its treatment and disposal difficult.1 At present, the cost of excess sludge disposal accounts for 20−50% of the operating cost of the sewage treatment plant.2 From another perspective, as the excess sludge contains a large amount of organic substances (including proteins and polysaccharides), it can be fermented and utilized by anaerobic microorganisms to produce valuable substances such as volatile fatty acids (VFAs), methane and hydrogen, and simultaneously achieve volume and mass reduction. VFAs produced during the anaerobic fermentation of excess sludge are potentially used for energy recovery and producing high value-added chemicals. The recovered material can thus be used to balance the cost of operating sewage treatment plants.3

Volatile fatty acid (VFA) is an important intermediate metabolite in the process of anaerobic digestion of sludge. It not only has high added value but also can be used as an important substrate for denitrification of high-nitrogen wastewater and the operation of microbial fuel cells. It can also be further synthesized from biopolymers with a higher application value for nitrogen and phosphorus removal.4 Anaerobic fermentation of excess sludge is generally divided into three stages: hydrolysis, acid production, and methane production. Fermentation of excess sludge for acid production needs to control the fermentation process in the acid production stage.

Received: July 30, 2020
Accepted: September 18, 2020
Published: October 1, 2020
The hydrolysis stage is the speed-limiting step that affects the anaerobic digestion of excess sludge.5,6 Mechanical crushing, ultrasound, hydrothermal, alkali acid, ozone, and enzyme treatment, as well as other means have been used to crack the extracellular polymer of the sludge and release cellular material in the sludge so as to accelerate the transfer of organic matter from the solid phase to the liquid phase.7−9 After these treatment processes, the subsequent reaction rate of acid production and methane production can be improved while the reaction time can be shortened.

Some studies showed that thermal hydrolysis had certain improvement in the degradation performance, hydrolysis, and release of complex organic matter of activated sludge, as well as promoted the subsequent acid-producing fermentation process.10 Studies had shown that the release of organic matter in sludge and the effect of anaerobic digestion at temperatures between 70 and 90 °C had been significantly improved.11 Under the treatment temperature of 50−90 °C, the low-temperature hydrothermal treatment helped the organic matter to dissolve soluble carbohydrates and soluble protein, and the best thermal hydrolysis condition was 70 °C, 30 min.12 In addition, according to related studies, thermal pretreatment can cause death of microorganisms in the remaining sludge, which meets the requirements of hygiene and safety. However, most studies focused on methane production, and there were a few studies on the intermediate acid production stage. Some studies showed that cracking of excess sludge was conducive to acid production. It had been studied that anaerobic fermentation of sludge prepared by 73.79 min pretreatment was used for thermal hydrolysis treatment at 50 °C and then decreases slightly at 90 °C.

The dissolution ratio of soluble chemical oxygen demand (SCOD) in the natural state of sludge is 8.34%. Under thermal treatment conditions, from 50 to 90 °C, the dissolution ratio and SCOD amount continue to increase, and the dissolution ratio increases by 6.01, 9.13, 11.92, 12.02, and 12.17% respectively. At 90 °C, the dissolution amount increases from 2650 mg/L in the natural state to 651 mg/L. It shows that with increasing temperature in thermal pretreatment, the degree of sludge dissolution and cracking increases, and the amount of dissolution increases. But from 70 to 90 °C, the degree of cracking and dissolution changes slowly until they are consistent.

The SCOD in the excess sludge can reflect the dissolution performance, but in the subsequent recycling of sludge cracking, sludge and availability of carbon are most important. TOC needs to be tested. From Figure 1b, the solubility of TOC of the sludge in natural state is 3.8%. Under thermal pretreatment conditions, from 50 to 90 °C, the dissolution rate of soluble TOC increases by 4.6, 5.6, 7.6, 11.0, and 10.8%. The solubility of TOC increases from 849.05 to 3224.47 mg/L at 80 °C and then decreases slightly at 90 °C.

The dissolution rate and amount of organic matter in the sludge SCOD keep increasing along with the increase of temperature, showing a significantly increased dissolution rate in the initial phase, which slowed down above 70 °C. The solubility of TOC slightly decreases after reaching the maximum value at 80 °C. It may be due to the dissolution of volatile organic compounds in the sludge with increase in temperature. There are generally two reasons for this phenomenon, which are the large difference in mud quality and the increase in temperature that results in the evaporation of small molecular substances. The sludge in this experiment has been sieved to basically determine the temperature. It is caused by the volatilization of small molecules, so the organic content in the liquid phase reaches the highest value at 80 °C.

2. RESULTS AND DISCUSSION

2.1. Dissolution Characteristics of Organic Matter in Excess Sludge. 2.1.1. Dissolution Characteristics of Organic Matter. Thermal pretreatment can cause the cells in the sludge to rupture and convert some organic matter from the insoluble state to the dissolved state, thereby increasing the content of organic matter in the sludge. It can be seen from Figure 1a that...
thermal pretreatment. Figure 2 shows that under the condition of 60 min thermal pretreatment, the dissolution amount of SC increases continuously from 50 to 70 °C, then decreases to 80 °C, and slightly increases at 90 °C again. The results show that the dissolution rate of soluble carbohydrates is less than the conversion rate in the excess sludge.

Under this condition, the dissolution amount of SP is the highest at 60 °C, and gradually decreases beyond 70 °C. The dissolution amount is not much different from that in the natural state at 90 °C. It shows that the rate of protein hydrolysis and the rate of dissolution during thermal treatment are basically the same. The reason is that the secondary and tertiary conformational structures of protein molecules are destroyed under high temperatures, and the protein is hydrolyzed into peptide chains, peptides, and amino acids. Further hydrolysis of amino acids into low-molecular organic acids, ammonia, and carbon dioxide leads to a decrease in SP.  

2.2. Parallel Factor Analysis of DOM. To study the composition and fluorescence characteristics of DOM in excess sludge, based on the parallel factor model, Matlab software is used to run the DOMFluor toolkit to analyze and process the EEM data of the dissolved substances at different thermal hydrolysis temperatures. The parallel factor analysis operation determines the five-component model, which is suitable for analyzing the EEM results of sludge hydrolysis and dissolution. Therefore, a five-component model is used to model the dissolution of the thermally hydrolyzed sludge. Table 1 shows the results of the PARAFAC model for the transfer of substances from the solid state to the soluble state at different temperatures, including five fluorescent components. Figure 4 shows the fluorescence component and its location determined by the PARAFAC model. It includes two protein-like (C1 and C3) and three humus-like (C2, C4, and C5) substances. Among them, C1 (310 and 364 nm) is a metabolic protein, belonging to tyrosine-like substances, usually related to microbial products. C2 (322 and 334 nm) is a protein-like substance, belonging to tryptophan-like substance, mainly free or bound protein or amino acid, which can be used to indicate a complete protein. C3, C4, and C5 (314, 382, and 454/526 nm) are visible humic acids, usually derived from manmade sources such as sewage or agricultural waste. C4(322 and 430 nm) is soil fulvic acid, which belongs to humic acid with a high molecular weight and is terrestrial in nature. 

Figure 5 shows the distribution of maximum fluorescence intensity of each component of thermally hydrolyzed sludge at different temperatures. It can be seen that different temperatures have a significant effect on the fluorescence intensity of sludge dissolution products, and the maximum fluorescence intensities at different temperatures are different, C3, C3, C1, C3, C3, C3, respectively. This is related to the hydrolysis and dissolution characteristics of the material thermal pretreatment. During the thermal hydrolysis of sludge, the content of C3 substance increases continuously, but decreases at 60 °C. Later, with increasing temperature, it continues to produce, and drops rapidly at 90 °C. This is related to the increase of temperature and the reduction of the activity of microorganisms in the sludge. At the same time, temperature-increasing substances are converted to nonluminescent substances. The C1 substance reaches its maximum at 60 °C, and the change trend is opposite to C3. It may be due to the fact that the activities of microorganisms consume C3 substances, and certain enzymes produced by the life activities of microorganisms can promote the production of C1 substances.

After analysis, C2, C4, and C5 represent different humus-like substances. The change performance of C2 is similar to that of C1. The concentrations of C4 and C5 substances tend to stabilize after increasing. The change in performance of C4 is basically similar to that of C5, indicating that during the thermal hydrolysis process, refractory substances such as humic acid and soil humus remain basically unchanged, and the degree of hydrolysis is slightly less than the generation rate, which is shown as a slight increase in production. However, the fluorescence intensity of all substances decreases at 90 °C. From Figures 1 and 2, the amount of organic matter dissolution increases with increasing temperature. During this process, the dissolved components are involved in the hydrolysis, which is very different from the parallel factor analysis results. The reason for the analysis may be that with increasing temperature, fluorescent substances are converted into nonluminescent substances.

| Table 1. Fluorescence PARAFAC Components of DOM |
|------------------------------------------------|
| fluorescent component | Ex/Em (nm) | fluorescence type | Ex/Em (nm) |
| C1 | 318/366 | tyrosine-like substances | 310−360/370−480 |
| C2 | 418/470 | UVA humic acid | 350−440/430−510 |
| C3 | 282/334 | tryptophan | 280/330 |
| C4 | 322/430 | UVC humic acid | 320−360/420−460 |
| C5 | 314, 382, 454/526 | UVC humic acid | 250−450/380−550 |

2.3. Discussion on the Mechanism of Organic Matter Dissolution. The sludge contains a large amount of organic matter, which is distributed outside and inside the cell. The cell wall is not easy to rupture, resulting in low dissolution of...
organic matter. Cell crushing is the main factor affecting sludge dissolution. From the dissolution performance of organic matter, the TOC of solubility reached the highest value around 80 °C, predicting that sludge cell rupture and release of intracellular organic matter occurred at this temperature. The change in DNA content can test the degree of sludge wall breaking. From Figure 3, under thermal treatment conditions, the DNA content in the sludge gradually increases, reaching a...

Figure 4. Fluorescence components and positions determined by the PARAFAC model.
rupture and the release of intracellular organic matter occurred dissolved at about 70 °C. Some scholars have studied the cracking mechanism of sludge at 70–120 °C under 20 min, which showed that the sludge cell disruption, dissolution, and intracellular substances. The main components of TOC are SC, broken DNA, and other insoluble organic compounds. SP is mainly an intracellular free protein. Some studies have also confirmed that the dissolved organic matter has a similar correlation rule.

2.4. Correlation Analysis of Various Components of Excess Sludge after Pretreatment. The results of the statistical analysis of the correlation between sludge organic matter dissolution and cell wall breaking using SPSS software are shown in Table 2. The correlation analysis results show that the organic matter dissolution is significantly related to cell wall breaking. SCOD is highly related to the dissolution of TOC, SC, DNA, and very weakly related to SP, which indicates that the main organic components of SCOD are cell wall disruption, dissolution, and intracellular substances. The main components of TOC are SC, broken DNA, and other insoluble organic compounds. SP is mainly an intracellular free protein. Some studies have also confirmed that the dissolved organic matter has a similar correlation rule.

2.5. Effect of Hydrothermal Pretreatment Temperature on the Total Acid Production of Sludge Fermentation. 2.5.1. Effect of Thermal Pretreatment on Acid Production of Sludge. During anaerobic digestion, more dissolved hydrolysate will provide more nutrient substrate for acidification and produce more VFAs. As shown in Figure 6, with the progress of anaerobic fermentation acid production, the total concentration of VFAs increases with time and shows a trend of increasing first and then decreasing. The remaining sludge after thermal treatment can promote the acid production of fermentation to different degrees. In the initial stage of acid production fermentation process, compared to the substrate sludge, the acid production and the peak time of the thermal treatment sludge showed excellent effects. At 60, 70, and 80 °C, the total amount of acid produced was equivalent, but the time to reach the highest peak is different. The pretreatment reaches the peak of acid production on the 2.5th day at 60 °C and on the second day at 70, 80, and 90 °C. The amount of acid production follows the order: 80 > 70 > 90 °C. The acid production at 80 °C is slightly higher than that at 70 °C. Since the third day, the acid production fermentation has been greater than that at 70 °C. It may be because high-temperature hydrolysis causes the cell to break the wall, and small molecules are easy to provide nutrients for acid production fermentation.

2.5.2. Effect of Thermal Pretreatment on Acid Production Components of Sludge. The proportion of thermal pretreatment temperature to each single VFA changes with fermentation time. As can be seen from Figure 7, the main components of acid under the natural state of acid production peak are acetic acid, butyric acid, and valeric acid. After thermal treatment, the ratio of acetic acid to butyric acid showed an upward trend at 50 °C, and the ratio of valeric acid decreased. The reason may be that at 50 °C, valeric acid is converted to acetic acid or propionic acid. At 60 °C, acetic acid and butyric acid are still the main components, and the proportion of valeric acid has increased, which may be due to the hydrolysis of proteins, sugars, and fats during the thermal hydrolysis process. Under 70 °C, the concentration of obutyrac

### Table 2. Correlation Analysis

|                      | SCOD  | TOC   | SC    | SP    | DNA   | Dissolution Rate |
|----------------------|-------|-------|-------|-------|-------|------------------|
| **SCOD**             |       |       |       |       |       |                  |
| Pearson-related      | 1     | 0.943**| 0.900*| 0.172 | 0.817*| 1.000**          |
| distinctiveness      |       | 0.005 | 0.014 | 0.744 | 0.047 |                  |
| N                    | 6     | 6     | 6     | 6     | 6     |                  |
| **TOC**              |       |       |       |       |       |                  |
| Pearson-related      | 0.943**| 1     | 0.740 | −0.115| 0.592 | 0.943**          |
| distinctiveness      |       | 0.005 | 0.092 | 0.829 | 0.216 |                  |
| N                    | 6     | 6     | 6     | 6     | 6     |                  |
| **SC**               |       |       |       |       |       |                  |
| Pearson-related      | 0.900*| 0.740 | 1     | 0.311 | 0.895*| 0.900*           |
| distinctiveness      |       | 0.014 | 0.092 | 0.549 | 0.016 |                  |
| N                    | 6     | 6     | 6     | 6     | 6     |                  |
| **SP**               |       |       |       |       |       |                  |
| Pearson-related      | 0.172 | −0.115| 0.311 | 1     | 0.660 | 0.172            |
| distinctiveness      |       | 0.744 | 0.829 | 0.549 | 0.154 | 0.745            |
| N                    | 6     | 6     | 6     | 6     | 6     |                  |
| **DNA**              |       |       |       |       |       |                  |
| Pearson-related      | 0.817*| 0.592 | 0.895*| 0.660 | 1     | 0.817*           |
| distinctiveness      |       | 0.047 | 0.216 | 0.016 | 0.154 | 0.047            |
| N                    | 6     | 6     | 6     | 6     | 6     |                  |

**Correlation Analysis**

- **** The correlation is significant on the 0.01 level (double tail).
- * The correlation is significant on the 0.05 level (double tail).

https://dx.doi.org/10.1021/acsomega.0c03606
ACS Omega 2020, 5, 26101−26109
acid is the highest, and the proportion gradually decreases. Under the conditions of 80 and 90 °C, the proportion of acetic acid and butyric acid is the highest. From the point of view of the process of acid production by thermal treatment fermentation, after thermal pretreatment, the acid production of sludge fermentation increases with temperature, and the acid production components acetic acid and butyric acid dominate, indicating that the type of acid production is mainly butyric acid fermentation and soluble carbohydrates are involved in the reaction. Propionic acid does not change much during the entire acid production process, indicating that the propionic acid-type fermentation is relatively stable, and the rate of protein hydrolysis is roughly unchanged. Cellulose and other refractory organics are not degraded during anaerobic fermentation. Valeric acid underwent a process of decreasing first and then increasing during the fermentation process, indicating that the thermal treatment process promoted the conversion of biological macromolecules to small molecules, which was beneficial to fermentation and acid production. From the point of view of fermentation time, all fermentation acid-producing sludges can reach the peak of acid production within 3 days, and after the fourth day, they rapidly decrease and maintain a low concentration, indicating that the organic substances that are easily used by the organism are
The excess sludge for the experiments was dewatered sludge 6.58 71.52 0.65 34422.22 2650.67 74.28 36.98

Table 3. Characteristics of Sludge

| parameters       | pH  | moisture ratio (%) | VS/TS (%) | TCOD (mg/L) | SCOD (mg/L) | SC (mg/L) | SP (mg/L) |
|------------------|-----|--------------------|-----------|-------------|-------------|-----------|-----------|
| dewatered sludge | 6.58| 71.52              | 0.65      | 34422.22    | 2650.67     | 74.28     | 36.98     |
| feed sludge      | 6.76| 99.1               | 0.42      | 9200.00     | 117.33      | 4.16      |

basically consumed and the refractory substances are slowly hydrolyzed and fermented. For the untreated sludge and the sludge treated at 50, 60, and 70 °C after the fourth day, the total acid production decreased significantly more than that at 80 and 90 °C. It shows that thermal pretreatment can promote the conversion of organic macromolecules into small molecules. As the temperature continues to increase, butyric acids are hydrolyzed into small molecules such as acetic acid. Some of these materials are for microbial growth, and some remain in the liquid phase. Insoluble organic matter is converted into soluble organic matter, which can improve biochemical properties and promote fermentation. From the perspective of fermentation effect, pretreatment at 80 °C promoted not only dissolution of substances but also acid production by fermentation. After pretreatment at 80 °C for acid production by fermentation, butyric acid accounts for the highest proportion of fermentation products, which is 40.46%.

3. CONCLUSIONS

In this study, we investigated and analyzed the dissolution characteristics of excess sludge at low-temperature thermal hydrolysis and performance of fermentation acid production.

(1) Low-temperature thermal hydrolysis significantly promotes the dissolution and hydrolysis of organic matter in sludge. At 80 °C, the TOC dissolution amount is largest and theoretically the most biodegradable. Therefore, the optimal temperature for the hydrolysis and dissolution under low temperature is 80 °C.

(2) Under hydrothermal conditions, the cell walls of the microbial cells are easily cracked in 70 °C. According to the correlation analysis of the dissolved substances, combined with the dissolution mechanism, SC in the dissolved organic substances mainly comes from the cell walls and intracellular substances, SP is derived from intracellular material.

(3) Use EEM-PARAFAC to divide the sludge DOM into five fluorescent components: C1(318/366) tyrosine, C2(418/470) UVA humic acid, C3(282/334) tryptophan-like substance, C4(322/430) UVC humic acid, and C5(314,382,454/526) UVA humic acid substance.

(4) Thermal pretreatment makes the peak time of fermentation acid production higher than that of untreated sludge. Under hydrothermal treatment conditions, the peak time of fermentation acid production is higher than that of untreated sludge. On the second day after pretreatment at 80 °C, the concentration of fermentation acid production is the largest, and the type of fermentation acid production is butyric acid fermentation, and as the pretreatment temperature increases, the proportion of acetic acid and butyric acid becomes higher and higher.

4. MATERIALS AND METHODS

4.1. Materials. The excess sludge for the experiments was taken from the centrifugal dewatered sludge of a sewage treatment plant in Xi’an, which used the A2O process. After obtaining the dehydrated sludge from the sewage treatment plant, it was stored in a refrigerator at 4 °C for use. It was diluted with deionized water to a fixed solid content rate of 8% before use. The inoculated sludge used in this experiment was the sludge in the anaerobic zone of the plant. After 1 h of natural precipitation at room temperature, the supernatant was discharged as anaerobic inoculated sludge.

The properties of sludge are shown in Table 3. TCOD is the total chemical oxygen demand; SCOD is the dissolved chemical oxygen demand; VS is the volatile solids; TS is the total solids; SC is the soluble carbohydrates; and SP is the soluble protein.

4.2. Thermal Hydrolysis Experiment. Take 200 mL of the diluted excess sludge sample in batches and add it to an Erlenmeyer flask to carry out the thermal hydrolysis batch experiment. Perform a pretreatment test under the conditions of temperature gradients of 50, 60, 70, 80, and 90 °C. The mouth of the conical bottle is sealed with a double-layer plastic wrap and single-layer foil. Control the speed of the shaker to 80 r/min to ensure that the sludge in the conical flask is heated evenly. The hydrolysis time of 1 h is defined as the time to put the stored sludge at the specified temperature for thermal hydrolysis to the end of thermal hydrolysis.

4.3. Fermentation Acid Production Experiment. Take the same batch of sludge and perform thermal batch sludge acidification experiment at room temperature: 50, 60, 70, 80, and 90 °C. The ratio of hydrolyzed sludge to inoculated sludge was 4:1 (i.e., 400 mL thermally hydrolyzed sludge and 100 mL inoculated sludge), and 500 mL of mixed sludge was placed in a conical flask, sealed, and placed in a constant-temperature water bath incubator. The reaction temperature was controlled at 35 °C, the rotation speed of the constant-temperature water bath shaker was 80 rpm, and the time was 8 days. Samples were taken every 12 h, 25 mL each time.

4.4. Analysis Methods. The sludge samples were centrifuged at 9000 rpm for 10 min, and the supernatant was decanted and filtered through a 0.45 μm filter membrane for analysis. COD was determined by fast digestion spectrophotometry; TOC was determined by a total organic carbon analyzer; carbohydrate used anthracene method with glucose as the standard to determine absorbance at 625 nm; protein used the Coomassie Brilliant G250 method with bovine serum protein as the standard to determine the absorbance of the sample at 595 nm. DNA was determined by the diphenylamine method. VFAs were determined by high-performance liquid chromatography (PerkinElmer, Altus A-10). The sample was centrifuged at 9000 rpm for 15 min and passed through a 0.25 μm filter membrane. The column model was AminexHPX-87H (BioRad), and the column temperature was 35 °C. To further clarify the degree of sludge cracking, the sludge cracking degree was used to characterize the degree of sludge cracking, which can be calculated as follows:

\[
DD = \frac{\rho_{(SCOD_{\text{after}})} - \rho_{(SCOD_{0})}}{\rho_{(TCOD_{0})} - \rho_{(SCOD_{0})}} \times 100\%
\]

where \(\rho_{(SCOD_{\text{after}})}\) is the treated dissolved COD concentration, \(\rho_{(SCOD_{0})}\) is the untreated dissolved COD concen-
4.5. Parallel Factor Analysis. The parallel factor analysis model had been described in detail in previous studies, and was only briefly introduced here. PARAFAC was the promotion of bilinear principal component analysis to higher-order arrays, that is, decomposing N-way arrays into N loading matrices. In EEM data analysis, the parallel factor model equation is as follows

\[ X_{ijk} = \sum_{f=1}^{F} a_{ijf} b_{jkf} c_{ikf} + \varepsilon_{ijk} \]  

(2)

where \( X_{ijk} \) represents the fluorescence intensity of sample \( i \) measured at emission wavelength \( j \) and excitation wavelength \( k \) in EEM analysis; \( a_{ijf}, b_{jkf}, \) and \( c_{ikf} \) are the factor contributions of each component, \( F \) is the optimal number of components; and \( \varepsilon_{ijk} \) represents unexplained signals such as noise and other non-model-varying residuals. The modeling process of PARAFAC can be performed using SPSS 22.0 version software.

### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51578452) and the Key R&D Program in Shaanxi Province (2020SF-354).

### REFERENCES

1. Yang, G.; Zhang, G.; Wang, H. Current state of sludge production, management, treatment and disposal in China. Water Res. 2015, 78, 60–73.
2. Li, H.; Jin, Y. Y.; Mahar, R. B.; Wang, Z. Y.; Nie, Y. F. Effects and model of alkaline waste activated sludge treatment. Bioresour. Technol. 2008, 99, 5140–5144.
3. García-Aguirre, J.; Aymerich, E.; de Goñi, J. G. M.; Esteban-Gutiérrez, M. Myriam Esteban-Gutiérrez. Selective VFA production potential from organic waste streams: assessing temperature and pH influence. Bioresour. Technol. 2017, 99, 1081–1088.
4. Chen, Y.; Jiang, X.; Xiao, K.; et al. Enhanced volatile fatty acids (VFAs) production in a thermophilic fermenter with stepwise pH increase-Investigation on dissolved organic matter transformation and microbial community shift. Water Res. 2017, 112, 261–268.
5. Appels, L.; Baeyens, J.; Degreve, J.; Dewil, R. Principles and potential of the anaerobic digestion of waste-activated sludge. Prog. Energy Combust. Sci. 2010, 34, 755–781.
6. Kim, J.; Park, C.; Kim, T.; Lee, M.; Kim, S.; Kim, S.; Lee, J. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. J. Biosci. Bioeng. 2003, 95, 271–275.
7. Wang, X.; Jin, P. K.; Zhang, A. L.; Gao, J. L.; Zhang, B.; Hou, Y. P. Effect of mechanical elutriation on carbon source recovery from primary sludge in a novel activated primary tank. Chemosphere 2020, 240, No. 124820.
8. Guo, H.; Felz, S.; Lin, Y. M.; van Lier, J. B.; de Kreuk, M. Structural extracellular polymeric substances determine the difference in digestibility between waste activated sludge and aerobic granules. Water Res. 2020, 181, No. 115924.
9. Lei, Z.; Yang, J.; Lei, Z.; Huihun, H.; Chao, Y.; Min, L.; Lintian, M. Preparation of soybean oil factory sludge catalyst by plasma and the kinetics of selective catalytic oxidation denitration reaction. J. Cleaner Prod. 2019, 217, 317–323.
10. Chen, J.; Zhang, J. H.; Liu, J. Y.; Yao, H.; Evrendilek, F.; Buyukada, M.; Xie, W. M.; Sun, S. Y. Co-pyrolytic mechanisms, kinetics, emissions and products of biomass and sewage sludge in N\(_2\), CO\(_2\), and mixed atmospheres. Chem. Eng. J. 2020, 397, No. 125372.
11. Lu, M.-Y.; Shi, X. S.; Li, M.; Xiong, T.; Xu, D. Y.; Guo, R. B. Addition of oyster shell to enhance organic matter degradation and nitrogen conservation during anaerobic digestate composting. Environ. Sci. Pollut. Res. 2020, 27, 33732–33742.
12. Appels, L.; Degreve, J.; Van der Bruggen, B.; Van Impe, J.; Dewil, R. Influence of low temperature thermal pretreatment on sludge solubilisation, heavy metal release and anaerobic digestion. Bioresour. Technol. 2010, 101, 5743.
13. Pang, H.; Pan, X. L.; Li, L.; He, J. G.; Zheng, Y. S.; Qu, F. S.; Ma, Y. Q.; Cui, B. H.; Nan, J.; Liu, Y. An innovative alkaline protease-based pretreatment approach for enhanced short-chain fatty acids production via a short-term anaerobic fermentation of waste activated sludge. Bioresour. Technol. 2020, 312, No. 123397.
14. Liu, X.; Du, M. T.; Yang, G. N.; et al. Sulfite serving as a pretreatment method for alkaline fermentation to enhance short-chain fatty acid production from waste activated sludge. Chem. Eng. J. 2020, 385, 123991.
15. Guo, S.; Qu, F. S.; Ding, A.; He, J. G.; Yu, H. R.; Bai, L. M.; Li, G. B.; Liang, H. Effects of agricultural waste-based conditioner on ultrasonic-aided activated sludge dewatering. RSC Adv. 2015, 5, 43065–43073.
16. Tello-Andrade, A. F.; Jimenez-Moleon, M. C.; Sanchez-Galvan, G. Management of sewage sludge by composting using fermented water hyacinth. Environ. Sci. Pollut. Res. 2020, 22, 14781–14792.
17. Liu, X.; Xu, Q. X.; Wang, D. B.; et al. Unveiling the mechanisms of how cationic polyacrylamide affects short-chain fatty acids
accumulation during long-term anaerobic fermentation of waste activated sludge. *Water Res.* **2019**, *155*, 142−151.

(18) Li, H.; Li, C. C.; Liu, W. J.; Zou, S. X. Optimized alkaline pretreatment of sludge before anaerobic digestion. *Bioresour. Technol.* **2012**, *119*, 189−194.

(19) Zhang, L.; Shu, H.; Zhang, L.; Jia, Y. Gas modified pyrolysis coke for in-situ catalytic cracking of coal tar. *ACS Omega* **2020**, *5*, 14911−14923.

(20) Xing, J.; Xu, G. R.; Li, G. B. Analysis of the complexation behaviors of Cu(II) with DOM from sludge-based biochars and agricultural soil: Effect of pyrolysis temperature. *Chemosphere* **2020**, *250*, No. 126184.

(21) Bergman, U. L.; Dahlin, S.; Mesilov, V. V.; Xiao, Y.; Englund, J.; Xi, S.; Tang, C. H.; Skoglundh, M.; Pettersson, L. J.; Bernasek, S. L. In-situ studies of oxidation/reduction of copper in Cu-CHA SCR catalysts: Comparison of fresh and SO2-poisoned catalysts. *Appl. Catal., B* **2020**, *269*, No. 118722.

(22) Sciscenko, L.; Garcia-Ballesteros, S.; Sabater, C.; Castillo, M. A.; Escudero-Onato, C.; Oller, I.; Arques, A. Monitoring photolysis and (solar photo)-Fenton of enrofloxacin by a methodology involving EEM-PARAFAC and bioassays: Role of pH and water matrix. *Sci. Total. Environ.* **2020**, *719*, No. 137331.

(23) He, W.; Hur, J. Conservative behavior of fluorescence EEM-PARAFAC components in resin fraction processing and its applicability for characterizing dissolved organic matter. *Water Res.* **2015**, *83*, 217−226.

(24) Semblante, G. U.; Phan, H. V.; Hui, F. I.; Xu, Z. Q.; Price, W. E.; Nghiem, L. D. The role of microbial diversity and composition in applicability for characterizing dissolved organic matter. *Water Res.* **2015**, *83*, 217−226.

(25) Casale, M.; Pasquini, B.; Hoosharyi, M.; Orlandini, S.; Mustorgi, E.; Malegori, C.; Turrini, F.; Ortiz, M. C.; Sarabia, L. A.; Furlanetto, S. Combining excitation-emission matrix fluorescence spectroscopy, parallel factor analysis, cyclodextrin-modified micellar electrokinetic chromatography and partial least squares class-modelling for green tea characterization. *J. Pharm. Biomed. Sci.* **2018**, *159*, 311−317.

(26) Castro, J. P.; Pereira, E. R.; Bro, R. Laser-induced breakdown spectroscopy (LIBS) spectra interpretation and characterization using parallel factor analysis (PARAFAC): a new procedure for data and spectral interference processing fostering the waste electrical and electronic equipment (WEEE) recycling process. *J. Anal. Atom. Spectrom.* **2020**, *35*, 1115−1124.

(27) Li, W.-T.; Chen, S. Y.; Xu, Z. X.; Li, Y.; Shuang, C. D.; Li, A. M. Characterization of dissolved organic matter in municipal wastewater using fluorescence parafac analysis and chromatography multi-excitation/emission scan:a comparative study. *Environ. Sci. Technol.* **2014**, *48*, 2603−2609.

(28) Zhou, Z.; Qiao, W. M.; Xing, C.; Wang, C. Y.; Jiang, L. M.; Gu, Y. T.; Wang, L. C. Characterization of dissolved organic matter in the anoxic-oxic-settling-anaerobic sludge reduction process. *Chem. Eng. J.* **2015**, *259*, 357−363.

(29) Trubetskaya, O. E.; Richard, C.; Patsaeva, S. V.; Trubetskoj, O. A. Evaluation of aliphatic/aromatic compounds and fluorophores in dissolved organic matter of contrasting natural waters by SEC-HPLC with multi-wavelength absorbance and fluorescence detections. *Spectrochim. Acta, Part A* **2020**, *238*, No. 118450.

(30) Li, X. W.; Dai, X. H.; Takahashi, J.; Li, N.; Jin, J. W.; Dai, L. L.; Dong, B. New insight into chemical changes of dissolved organic matter during anaerobic digestion of dewatered sewage sludge using EEM-PARAFAC and two dimensional FTIR correlation spectroscopy. *Bioresour. Technol.* **2014**, *159*, 412−420.

(31) Lie, Z.; Yang, J.; Hao, S.; Lei, Z.; Xin, W.; Min, L.; Yusu, W.; Dan, X. Application of Surfactant-modified Cordierite-based Catalysts in Denitrification Process. *Fuel* **2020**, *268*, No. 117242.

(32) Miranda, M. L.; Osterholz, H.; Giebel, H. A.; Bruhnke, P.; Dittmar, T.; Zielinski, O. Impact of UV radiation on DOM transformation on molecular level using FT-ICR-MS and PARAFAC. *Spectrochim. Acta, Part A* **2020**, *230*, No. 118027.