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Comprehensive role of thermal combined ultrasonic pre-treatment in sewage sludge disposal

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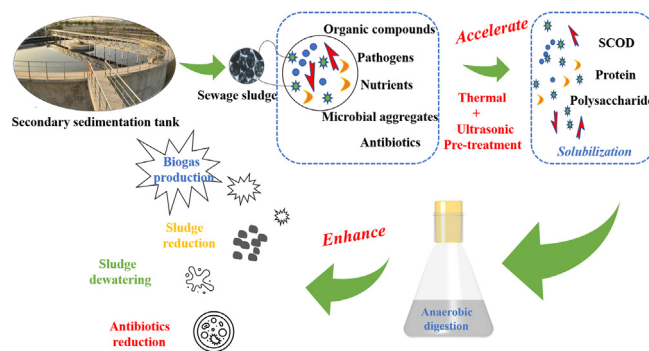
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HIGHLIGHTS

- Combined thermal and ultrasonic pre-treatment was proposed to enhance AD performance.
- The combined method significantly enhanced the dissolution of DOMs in SS.
- The combined method increased biogas production and degradation of antibiotics.
- The correlation between DOMs and the degradation of antibiotics was discussed.
- The comprehensive role of this combined method in SS disposal has been elucidated.

GRAPHICAL ABSTRACT



ABSTRACT

Thermal/ultrasonic pre-treatment of sludge has been proven to break the hydrolysis barriers of sewage sludge (SS) and improve the performance of anaerobic digestion (AD). In this study, the objective was to investigate whether the combination of two pre-treatment methods can achieve better results on the AD of SS. The results indicated that, compared with the control group and separate pre-treatment groups, the thermal combined ultrasonic pre-treatment presented more obvious solubilization of soluble proteins, polysaccharides, and other organic matters in SS. The combined method promoted the dissolution of protein-like substances more effectively, with biogas production increased by 19% and the volatile solid (VS) removal rate improved to above 50% compared with the control group. The capillary suction time is reduced by about 85%, which greatly improved the dewatering performance of SS. In addition, the combined method has advantages in degrading sulfonamide antibiotics, roxithromycin and tetracycline. Particularly, by analyzing the interaction between the degradation of different antibiotics and the composition of dissolved organic matters (DOMs), it was found that the composition of DOMs could affect the degradability of different antibiotics. Among them, the high content of tyrosine-like and tryptophan-like was conducive to the degradation of sulfamethoxazole, and the high content of fulvic acid-like and humic acid-like was conducive to the degradation of roxithromycin and tetracycline. This work evaluated the comprehensive effect of thermal combined ultrasonic pre-treatment on SS disposal and provided useful information for its engineering.

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Keywords:
 Sewage sludge
 Antibiotics
 Thermal pre-treatment
 Ultrasonic pre-treatment
 Dissolved organic matters

Abbreviations: SS, sewage sludge; AD, anaerobic digestion; WWTPs, wastewater treatment plants; DOMs, dissolved organic matters; COD, chemical oxygen demand; SCOD, soluble chemical oxygen demand; TS, total solid; VS, volatile solid; CT, control; NH_4^+-N , ammonia nitrogen; STN, soluble total nitrogen; STP, soluble total phosphorus; CST, capillary suction time.

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1. Introduction

Sewage sludge (SS) is the residue produced by centralized wastewater treatment plants (WWTPs) after waste treatment from various sources. Its composition of pollutants is characterized by solid and organic compounds, pathogens, microbial aggregates, filamentous bacteria, nutrients, and heavy metals (Harrison et al., 2006; Buaisha et al., 2020). In addition, about 70% of the undegradable antibiotics in the WWTPs are present in the digested sludge, which could be transferred to the soil and aquatic environment during disposal processes such as landfill and land use (Zhang and Li, 2018). However, management and treatment of SS are expensive and account for nearly half of the total sewage treatment cost (Khanh Nguyen et al., 2021). As a result, development and upgradation of more effective SS treatment and/or disposal technologies is in urgent need under the framework of circular economy.

Current technologies for SS disposal include anaerobic digestion (AD), dewatering, thermal drying, incineration and landfill disposal (Ding et al., 2021). Internationally, AD technology is the mainstream technology of SS disposal in EU, USA, Canada and Japan (Raheem et al., 2018). AD can not only treat organic waste including SS, but also recover energy from it, providing an environmentally friendly strategy. According to China's overall situation, "thickening-anaerobic digestion-dewatering-land application" is the priority technical route of sludge treatment and disposal (Yang et al., 2015). But at present, the low hydrolysis ratio of SS has been recognized as a severe challenge to AD, which limits its application and development in WWTPs (Liao et al., 2014). Khanh Nguyen et al. pointed out that pre-treatment of SS is a prerequisite for accelerating hydrolysis and improving AD efficiency (Khanh Nguyen et al., 2021). A large number of studies have shown that pre-treatment methods including photocatalysis, thermal hydrolysis, sonication, enzymatic hydrolysis, alkaline hydrolysis, freeze-thaw and mechanical disintegration have positive effects in the AD process of SS (Scharnberg et al., 2020; Anjum et al., 2016; Memon and Memon, 2020). The main pre-treatment effects are reducing particle size, solubilization, enhancement of biodegradability, the formation of insoluble compounds, and degradation of organic substances (Carlsson et al., 2012). Thermal pre-treatment is considered as the most effective technique to improve digestibility of SS in sewage treatment plants. This is mainly reflected in the fact that thermal pre-treatment can change the rheological properties of SS, improve digestion load rate, increase biogas production, and promote biodegradability and dehydration (Barber, 2016). Kumar Biswal et al. studied the AD of low-thermal pre-treatment (60–120 °C) of saline waste activated sludge and found that pre-treatment enhanced methane yield (13.7–29.6%), and improved organics hydrolysis and volatile solid reduction (maximum 24.6%) (Kumar Biswal et al., 2020). Similarly, thermal pre-treatment could reduce total solid (TS) by 54.7%, volatile solid (VS) by 60.4%, and the chemical oxygen demand (COD) by 59.2% (Han et al., 2017). Thermal hydrolysis pre-treatment could also improve the dewaterability of sludge ($4.6 \pm 0.5\%$) (Zhang et al., 2018). In addition, levels of antibiotics such as kanamycin, tetracycline, macrolide and lincosamide could also be reduced by thermal pre-treatments. When the thermal treatment was performed at 200 °C and 180 °C for 8 h, antibacterial activity of Kanamycin was reduced 97.9% and 96.4% respectively (Tang et al., 2020); on the other hand, the total concentration of tetracycline, oxytetracycline, chlortetracycline and azithromycin decreased by 57.9–90.2% after thermal hydrolysis pre-treatments (Li et al., 2015; Sun et al., 2019; Tang et al., 2020; Zhang and Li, 2018).

Ultrasonic pre-treatment is another common practice for SS disposal, which could effectively destroy the bacterial cell wall of sludge (Tyagi et al., 2014). The sonication efficiency is explained by high pressure on cells, generation of free radicals such as hydroxyl radical ($\bullet\text{OH}$), hydrogen radical ($\bullet\text{H}$), nitrogen radical ($\bullet\text{N}$) and oxygen radical ($\bullet\text{O}$), and hydro-mechanical shear forces produced by ultrasonic cavitation at low frequencies (Tiehm et al., 2001). Ultrasonic could effectively

accelerate hydrolysis of SS, complete disintegration of biomass within 5–10 min and improve the reduction rate of volatile solid (Nguyen et al., 2017). As a result biogas production of SS could be increased by 50% with the ultrasonic pre-treatment (Pilli et al., 2011). In addition, after the combined ultrasonic and bio-leaching treatment, the absolute abundance of 16s rRNA, sul gene, and tet gene decreased by 1.81, 1.56–1.58, and 0.34–1.23 log units respectively (Huang et al., 2020).

Although both thermal pre-treatment and ultrasonic pre-treatment technologies have been confirmed improving AD performance of SS, they have basically reached the bottleneck for further improvement; the combination application of both thermal pre-treatment and ultrasonic pre-treatment could very likely produce synergistic effects breaking this barrier. Currently, there are only a few studies that combine these two pre-treatment methods (Hassan et al., 2020; Şahinkaya and Sevimli, 2013). Specifically, in the study of Hassan et al., the effects of thermal combined ultrasonic pre-treatment on the increase of methane (40.76%), the removal rate of COD (63.06%) and the removal rate of VS (60–66%) were discussed. In the study of Sahinkaya & Sevimli, the thermal combined ultrasonic pre-treatment could quickly promote the decomposition of SS, increase the methane production (13.6%), and improve the dewaterability of SS after AD. However, the removal of antibiotics by thermal combined ultrasonic pre-treatment is rarely investigated. On the other hand, there is barely any study linking the concentration of DOMs with the degradation of antibiotics.

In this study, we analyzed and compared thermal pre-treatment, ultrasonic pre-treatment and thermal combined ultrasonic pre-treatment methods treating SS efficiently. The changing profiles of various DOMs before AD were firstly investigated in detail, and then the biogas production efficiency, sludge dewatering performance, and antibiotics degradation after AD were evaluated, the relationship between the concentration of DOMs and the degradation of antibiotics was finally analyzed.

2. Materials and methods

2.1. Research plan

The research plan of the current work entails preparation of samples, pre-treatment of SS using thermal pre-treatment, ultrasonic pre-treatment, and thermal combined ultrasonic pre-treatment, the analysis of various DOMs in the SS, followed by AD of both treated and control samples of SS and their subsequent investigation. Supplementary materials Fig. 1 reflected the specific process of our work in the form of a flowchart, and the materials and test methods used in the process were expanded below.

2.2. Sludge samples

The SS was sampled in the secondary sedimentation tank of a sewage treatment plant in Suzhou City, placed in a sealed container, and stored at 4 °C for later use within 48 h. The basic properties of SS under investigation were listed in Table 1.

2.3. Pre-treatments

We investigated the following pre-treatments of the SS in terms of the solubilization of DOMs and the reduction of ammonia nitrogen ($\text{NH}_4^+\text{-N}$): control (CT, without treatment); 1 h heating at 60 °C, 70 °C, 80 °C, 90 °C or 100 °C; 1 h sonication 1 h 40 kHz (S); 1 h heating at 100 °C then 1 h sonication at 40 kHz (S 100 °C). Eight replicate samples of 250 mL of pretreated sludge were centrifugated 10 min at 10,000 rpm to separate the sludge residue from the supernatant. The supernatant was stored at 4 °C for determination of soluble protein, polysaccharide, COD and $\text{NH}_4^+\text{-N}$.

Table 1
Characteristics of the SS under investigation.

Parameters	Value
pH	6.48 ± 0.01
Total solids (TS, w%)	3.42 ± 0.08
Volatile solids (VS, w%)	2.43 ± 0.04
VS/TS (w%)	71.05 ± 2.90
Total chemical oxygen demand (TCOD, mg/L)	57,133.00 ± 57.00
Soluble chemical oxygen demand (SCOD, mg/L)	108.00 ± 5.50
SCOD/TCOD (w%)	0.20 ± 0.01
Ammonia nitrogen (NH ₄ ⁺ -N, mg/L)	706.30 ± 3.53
Soluble polysaccharides (SPS, mg/L)	14.01 ± 0.70
Soluble proteins (SPN, mg/L)	4.80 ± 0.24
Total nitrogen (TN, mg/L)	3214.42 ± 5.63
Total phosphorus (TP, mg/L)	30.70 ± 0.51

2.4. Effect of pre-treatments on performance of AD

This part explored the effects of pre-treatments on TS, VS, soluble total nitrogen (STN), and phosphorus (STP), soluble chemical oxygen demand (SCOD), capillary suction time (CST) and antibiotics of the SS. Four pre-treatment investigations were carried out: control (CT, without treatment); 1 h heating at 100 °C (T); 1 h sonication 1 h 40 kHz (S); 1 h heating at 100 °C then 1 h sonication at 40 kHz (S 100 °C). 150 mL of above SS were mixed with 50 mL of inoculated sludge (taken from a kitchen waste fermenter in Suzhou, which has strong biological activity and could be used to accelerate the initial stage of the biological process) in 250 mL serum bottles. Nitrogen gas (N₂) flush were used to remove oxygen (O₂) from SS before it was incubated for 20 days in a digital constant-temperature oscillator under the conditions of running temperature of 55 °C and shaking speed of 120 rpm. The initial pH was 7.20 ± 0.02. The biogas produced was collected in 2 L airbags before analyzed. 10 mL samples were taken for TS, VS, and CST tests on day 3 and day 18 respectively. Samples were also centrifuged for 10 min at 10,000 rpm to harvest the supernatant to analysis SCOD, STN, STP and the mud to analysis antibiotics.

2.5. Analysis methods

The amount of biogas was measured by a graduated syringe. NH₄⁺-N, SCOD, TS, VS, TN and TP were determined with standard methods (Public and Association, 1998). Protein content in SS was determined by the Folin-phenol reagent colorimetry and polysaccharide content in SS was determined by the phenol sulfuric acid method.

According to the fluorescence area integration (FRI) method proposed by (Wen, 2003), we used a Hitachi F-7000 (Hitachi Analog Company, Japan) three-dimensional fluorescence spectrometer to measure DOMs in supernatant of the pretreated sludge. The light source is a 150 W excitation arc lamp, and the photomultiplier tube (photomultiplier tube, PMT) voltage is 700 V. The excitation spectrum range is 200–500 nm, and the scanning step length is 5 nm; the emission spectrum range is 250–550 nm, and the scanning speed is 12,000 nm/min. In order to calibrate the influence of instrument conditions and Raman scattering on the fluorescence spectrum, ultrapure water (18.25 MΩ·cm) was used as blank (In order to ensure that it is within the measurement range, we diluted all the samples by 500 times).

After centrifugation, the samples were filtered with a 0.45 μm filter membrane. The sludge samples were taken in a material tray, pre-frozen at -20 °C for 4–6 h with a freeze-drier of model SJIA-10N-50A (Shuangjia, China), then passed through an 80-mesh sieve after grinding. We used the shaking-ultrasonic-centrifugation method to extract pollutants from solid samples: weighed 0.05 g sludge sample, added 7 mL extractant (3.5 mL methanol + 3.5 mL EDTA-McIlvaine solution); after fully shaking, sonicated for 10 min, then centrifuged at 4000 r/min to collect the supernatant. Repeated this procedure twice, mixed the supernatants, and diluted to 500 mL with ultra-pure water to ensure that the methanol content was 2%. The diluted extract was further purified

by solid-phase extraction. The specific steps were as follows: firstly, added 0.5 g of Na₂EDTA into each bottle to precipitate metal ions in the water and avoid clogging after suction filtration of the extract; activated the extraction cartridge with 5 mL methanol and 5 mL ultra-pure water in turn; then loaded the sample at a speed of 5 mL/min; after loading, rinsed the cartridge with 5 mL ultra-pure water 3 times and then subject the extraction liquid to air-drying for 15 min. The residue extract enriched was then eluted with 6 mL methanol/dichloromethane/acetone (2:2:1) solution. Blew the eluent on a nitrogen dryer at 40 °C to nearly dryness, then diluted the volume to 1 mL with methanol solution; added 0.1 μg of internal standard sulfamethoxazole-D4 before passing the solution through a 0.22 μm polyethersulfone needle type filter. Finally, the samples were injected and analyzed by a UHPLC-MS/MS. The ultra-high pressure liquid chromatography-mass spectrometer used in the experiment is Waters Acquity™ Ultra Performance LC in series Quattro Premier Micromass (Waters, USA); the chromatography column is Waters Acquity™ UPLC BEH C18 (50mmx2.1 mm, 1.7 μm); the ionization source is Electrospray ionization source (ESI), and the detector is Quattro Premier Micromass, MRM detection mode, Masslynx 4.0 workstation (Waters, USA).

3. Results and discussion

3.1. Solubilization characteristics of SS after pre-treatments

We tested the effect of thermal pre-treatment on COD solubilization characteristics of SS from 60 °C to 100 °C, with or without the combination of sonication (Fig. 1a). Results showed that the COD-based solubilization of the sludge mixture increased with temperature, which was consistent with previous studies (Liu et al., 2020; Razavi et al., 2019). Fig. 1a indicated that pre-treatments increased SCOD of the control from 108 ± 5 mg/L to 876–3516 mg/L, while SCOD increased from 1364 ± 68 mg/L at 60 °C to 2635 ± 132 mg/L at 100 °C by the thermal pre-treatment alone. Thermal pre-treatment at 100 °C combined with 40 kHz ultrasonic pre-treatment reached the maximum SCOD (3516 ± 176 mg/L), representing about 32 times of the control. This was higher than the study by Dhar et al., which showed a five-fold increase in SCOD compared to the control by ultrasound-thermal pre-treatment (90 °C) (Dhar et al., 2012). The ratio of soluble versus total COD (SCOD/TCOD) reached 6.15% at 100 °C (Fig. 1b), much lower than the study of Dhar et al. (2012), where the same specific energy input (10,000 kJ/kg TSS) increased the SCOD/TCOD ratio from 6% to 33%. The results implied that the SS used in this study was much more difficult to disintegrate than the study of Dhar et al. (2012).

We can see from Fig. 2(a) and (b) that thermal pre-treatment and ultrasonic pre-treatment could increase dissolution of polysaccharides and proteins particularly, which is comparable to the previous results (Dhar et al., 2012; Neumann et al., 2017; Zhang et al., 2019). Moreover, compared with the control, the thermal combined ultrasonic pre-treatment achieved the maximum dissolution of soluble protein (473.0 VS 4.8 mg/L) and the maximum dissolution of soluble polysaccharide (478.0 VS 24.0 mg/L). This was higher than Neumann et al.'s study that the soluble concentration of protein was increased by 252–674% after the ultrasound and low temperature (55 °C) pre-treatments (Neumann et al., 2017). It was noteworthy that the content of soluble proteins increased rapidly from 90 °C to 100 °C. The higher solubilization of polysaccharides versus proteins below 90 °C might be caused by higher energy required to break proteins into oligomers and monomers (Fig. 2b). The phenomenon was well explained by the higher solubility and smaller size of polysaccharide oligomers and monomers (Chen et al., 2017). Fig. 2c showed the change of NH₄⁺-N concentration under different pre-treatments, which was mainly reflected in the decrease of its concentration with increasing temperature. This phenomenon may be caused by the coagulation process that could entrap NH₄⁺ groups and/or react with the solid matrix to form new, relatively stable bonds to alleviate ammonium inhibition of the subsequent AD process

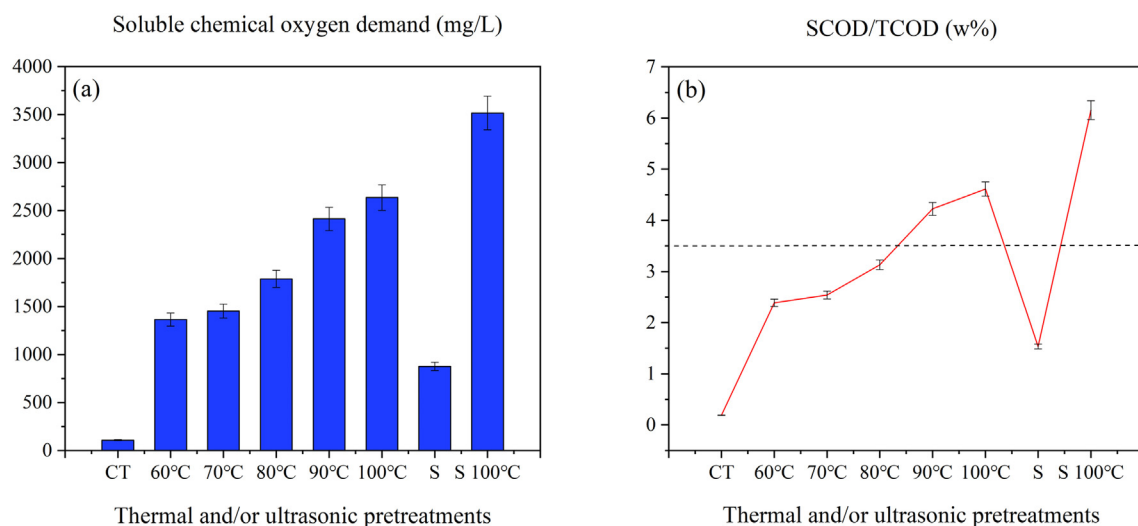


Fig. 1. Effect of thermal and/or ultrasonic pre-treatments on soluble chemical oxygen demand (a), and the difference in the ratio of soluble chemical oxygen demand to total chemical oxygen demand (b). Error bars in all figures below represent the standard deviation of triplicate samples.

(Rajagopal et al., 2013). It was found that ultrasonic pre-treatment increased the concentration of NH_4^+-N in SS due to the dissolution of a large amount of organic matter. However, the NH_4^+-N concentration (994 mg/L) in this study did not reach the highest value (3500 mg/L) mentioned by Liu et al. that can significantly inhibit the AD process (Liu et al., 2021b).

The mechanism of how thermal pre-treatment and ultrasonic pre-treatment improve AD performances is proposed in Fig. 2d. Firstly the thermal pre-treatment is to put the sludge flocculent and the bacterial micelles bulk under the heating condition of a water bath; the extracellular polymers and macromolecular organic matter in the sludge are then hydrolyzed and the cell wall of the microorganisms is destroyed; while the process strengthens the biodegradability of the material and improves the fluidity of the material (Kor-Bicakci and Eskicioglu, 2019). The contributing factors of ultrasonic sludge disintegration include sonochemical effects, high mechanical forces, and thermal effects (Pilli et al., 2011). Sonication leads to the formation of cavitation bubbles in the liquid phase; these bubbles grow and explode violently, causing high shearing forces in the surrounding liquid phase of the waste and radicals' formation (Lizama et al., 2017; Luo et al., 2014; Pilli et al., 2011). Therefore, it could be inferred that the thermal combined ultrasonic pre-treatment was simultaneously affected and strengthened by the above two mechanisms, which had also been verified in our work. Overall, our results on pre-treatments showed a notable increase of soluble chemical oxygen demand, soluble polysaccharide and soluble proteins with temperature and sonication. While the combination of thermal and ultrasonic pre-treatment could greatly enhance the above effects. As far as the concentration of NH_4^+-N was concerned, most pre-treatments would reduce NH_4^+-N in the supernatant except the ultrasonic pre-treatment; nevertheless, the increase of NH_4^+-N in supernatant after ultrasonic pre-treatment was not high enough to cause obvious inhibition on performances of the the subsequent AD process.

3.2. Change of DOMs composition and reduction of typical antibiotics

Fig. 3 demonstrated effects of thermal and sonication pre-treatments on DOMs composition of SS supernatants. The identifiable central fluorescence positions of commonly DOMs were shown in Supplementary materials (Table S1). The results indicated that the main organic component was soluble microbial products in the control group, appearing as an inclined green line in zone IV (Fig. 3a). The 100 °C thermal pre-treatment induced an increase of green spots in zones I, II, and IV (Fig. 3b), which were ascribed to tyrosine-like, tryptophan-like, and

soluble microbial products, respectively. These results were consistent with the changes in the fluorescence peaks of the I and IV regions of food waste after short-term thermal treatment reported by (Li et al., 2014), indicating that the metabolites were mainly composed of biodegradable DOMs and slightly hard-biodegradable DOMs. The sonication pre-treatment showed a similar change, albeit less intense (Fig. 3c). This was in line with the previous study by Chen et al. that ultrasonic pre-treatment could destroy extracellular polymers and help dissolve insoluble organic matter (Chen et al., 2017). Thermal combined ultrasonic pre-treatment showed in addition green, yellow and red spots in zone III, fulvic acid-like; zone V, humic acid-like (Fig. 3d). It proved that the combined method had an important effect on the slow-biodegradable DOMs such as fulvic acids and humic acids. Combined treatments in this study showed better performance than separate pre-treatments (Li et al., 2014; Wang et al., 2018). Overall, in terms of promoting the dissolution of DOMs in SS, performances of the pre-treatment strategies lined in the following descending order: 100 °C thermal combined with ultrasonic pre-treatment > 100 °C thermal pre-treatment > ultrasound pre-treatment > the control group.

The effect of pre-treatments on effluent antibiotic levels were shown in Fig. 4, sulfamethoxazole was observed only in the control and the thermal pre-treatment after 3 days of incubation, indicating that thermal and/or ultrasonic pre-treatment could rapidly degrade sulfamethoxazole in the early stage of AD. Tetracycline presented the highest levels in the whole process, and the results did not indicate a noticeable reduction level in the soluble fraction of the treated sludge. On the contrary, in the study of Zhang & Li, tetracyclines had a relatively high removal efficiency (62.9–58.5%), but the relative dissolution rate was also high or even higher than the degradation rate, resulting in unsatisfactory effluents (Zhang and Li, 2018). This study indicated that biodegradable substances generated during the pre-treatment process was vital to reduction of antibiotics. The results could be explained with the active microbial metabolism. When the co-metabolism effect is not significant, the easily biodegradable substances would compete with the biodegradation of the target antibiotic. Compared to digestion results on day 3 and day 18, the removal of sulfamethazine after pre-treatment was more prominent, especially in the ultrasound group alone, which was better than the combined pre-treatment. However, the single ultrasonic pre-treatment would increase the content of roxithromycin. The de-conjugation might cause the negative removal efficiency of roxithromycin from the sludge during the treatment process, indicating the roxithromycin was prevalent in SS (Ni et al., 2020). There are many applications using three-dimensional fluorescence spectroscopy

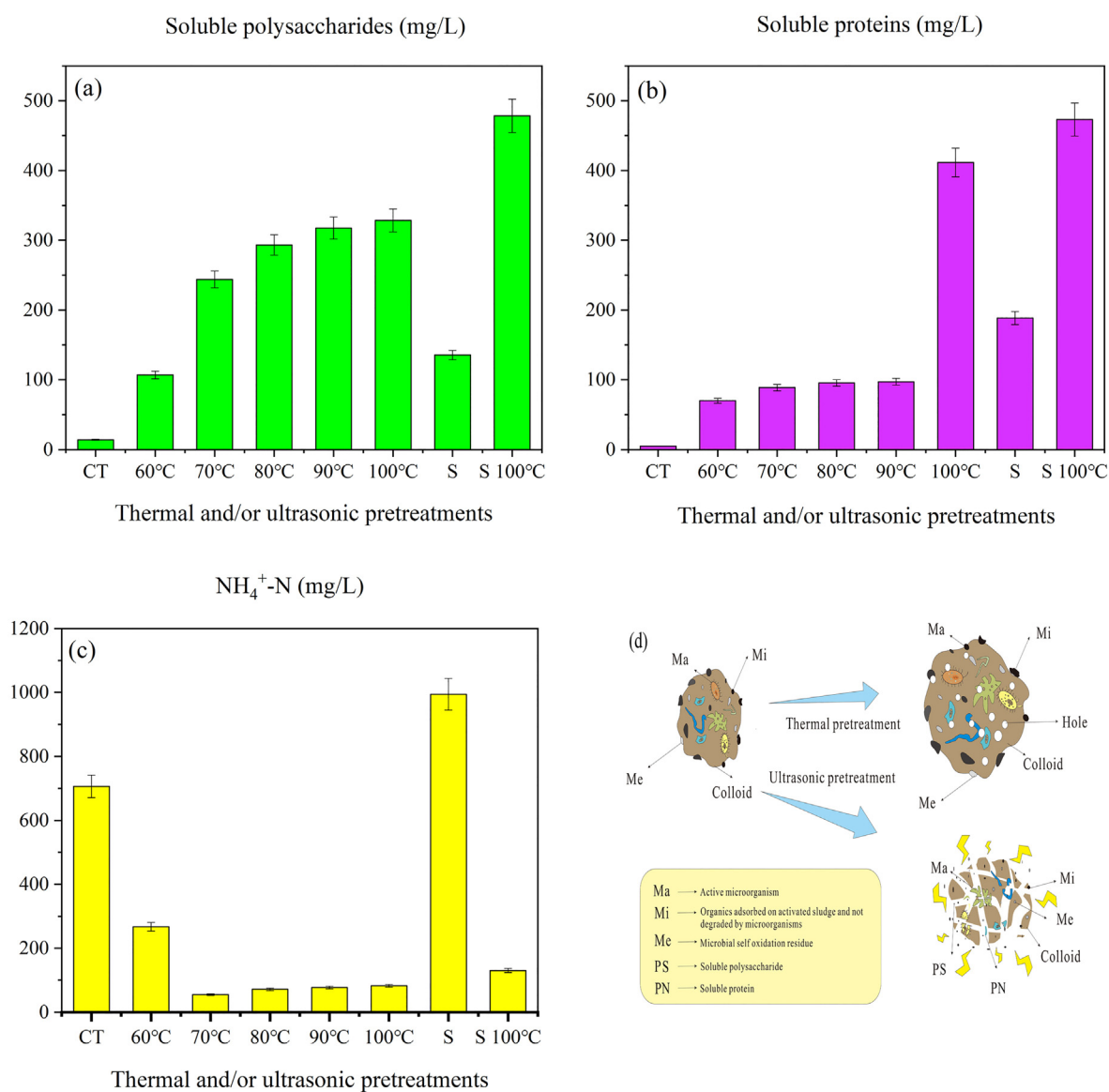


Fig. 2. Effect of thermal and/or ultrasonic pre-treatments on soluble polysaccharides (a), soluble proteins (b), ammonia nitrogen (c), and mechanisms of contributing effects (d).

to study the content of organic matter, but few studies link the content of organic matter detected by this method to the degradation of antibiotics. Combined Figs. 3 and 4, it indicated that the increase of tyrosine-like and tryptophan-like substances in the thermal pre-treatment and the thermal combined ultrasonic pre-treatment was more obvious than that of the control and the ultrasonic pre-treatment group. The corresponding thermal pre-treatment group and thermal combined ultrasonic pre-treatment group degraded sulfamethoxazole rapidly. Correspondingly, in the study of Wang et al., it was found that during AD, high concentrations of sulfa antibiotics caused a decrease in the content of tyrosine-like substances (Wang et al., 2020). It could be inferred that the content of tyrosine-like and tryptophan-like substances are positively correlated with the degradation of sulfamethoxazole. Meanwhile, the fulvic acid-like and humic acid-like substances in the thermal pre-treatment combined with ultrasonic pre-treatment group increased significantly than the other groups. After 18 days of digestion, the content of roxithromycin and tetracycline decreased to the least among the four groups. Interaction between tetracycline and extracellular polymeric substances was a dynamic process, and the interaction could be static quenching (Hou et al., 2016). It could be inferred that the content of fulvic acid-like and humic acid-like substances are positively correlated with the degradation of

roxithromycin and tetracycline. These inferences provided a new strategy for the degradation of antibiotics in sludge, such as using this dynamic interaction to selectively supplement or reduce the concentration of different organic substances in the sludge to increase the degradation of antibiotics.

3.3. Enhanced biogas production under different pre-treatments

As shown in Fig. 5a, the biogas production could be calculated according to the daily biogas production curve; four different biogas production groups were obtained through statistical calculations: 555.2 mL in the untreated group, 540.1 mL in the 100 °C pre-treatment group, 587.5 mL in the ultrasonic pre-treatment group, and 660.5 mL in the 100 °C then ultrasonic pre-treatment group. By comparison, it was found that the ultrasonic pre-treatment alone barely had any effect on biogas production. The biogas production rate increased 19.0% after the combination of sonication and 100 °C thermal pre-treatment, slightly higher than the study of Şahinkaya and Sevimli, where the total methane production in the sonothermalized reactor increased by 13.6% (Şahinkaya and Sevimli, 2013). But curiously, the biogas production decreased after 100 °C

Effect of sludge pre-treatment on organic matter composition

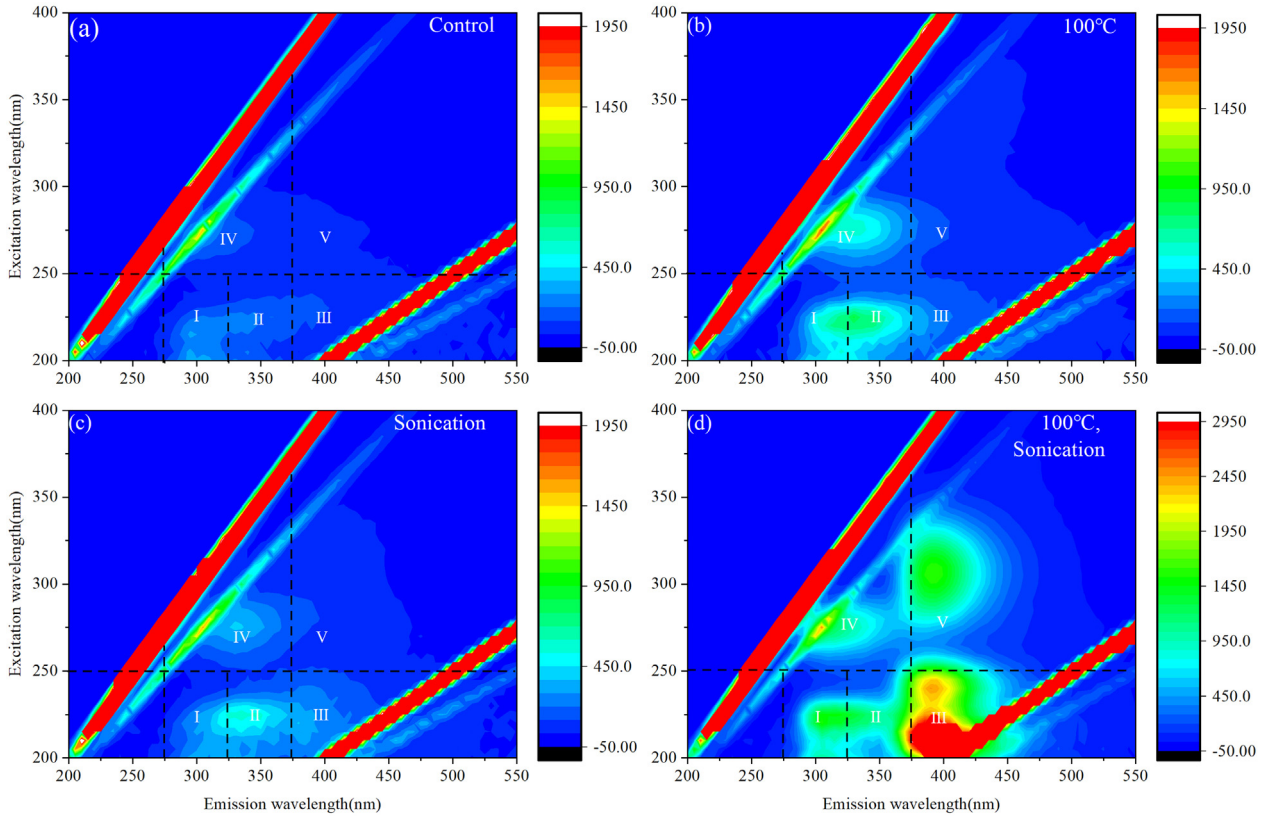


Fig. 3. Changes of dissolved organic matters in SS after thermal and/or ultrasonic pre-treatments. a) Control, b) 100 °C pre-treatment, c) ultrasonic pre-treatment, d) 100 °C then ultrasonic pre-treatments. Areas I-V refer to the main categories of organic matter: I) tyrosine-like, II) tryptophan-like, III) fulvic-acid like, IV) soluble microbial products, V) humic acid-like.

thermal pre-treatment in this study. This might be due to the theory that the thermal pre-treatment promoted the Maillard reaction and melanin production proposed by (Liu et al., 2021). In another

investigation ultrasonic pre-treatment at a moderate specific energy ratio increased biogas production by 15% (Appels et al., 2008), but ultrasound pre-treatment alone did not improve biogas production in this study, implying that although the long-term ultrasound pre-treatment released total organic carbon (TOC) from sludge continuously, 60 min of ultrasound would also cause an excessive increase in nitrogen in the water phase, which harmed the inoculum. Using the changing profiles of TOC, TN, and VS concentration with pre-treatment time to evaluate the effect of ultrasonic pre-treatment could be an option to evaluate comprehensive effects of ultrasonic pre-treatment on SS disposal (Martín et al., 2015).

Thus, the digested sludge samples on the 3rd and the 18th day were analyzed for TS, VS, SCOD, STN, STP and CST in this study. Fig. 5b indicated that the highest levels of SCOD were observed on the 3rd day of digestion with values from 4024 mg/L to 4616 mg/L, whereas only 1844–3024 mg/L SCOD were obtained after 18 days of digestion. All pre-treatments presented higher SCOD than control on day 3, whereas the reverse was observed on day 18, indicating that the thermal pre-treatment and ultrasonic pre-treatment accelerated the AD and shortened the reaction time (Khanh Nguyen et al., 2021). As shown in Fig. 5c, thermal combined with ultrasonic pre-treatment could increase the degradation rate of VS significantly compared with the control (54.4 VS 23.4%). The combined pre-treatment method presented the greatest CST reduction (85%) comparing to the control, higher than that of ultrasonic pre-treatment (75%) alone (Shao et al., 2010). Overall, both thermal and ultrasonic pre-treatment could enhance biogas production of SS, increase sludge biodegradability and improve sludge dewatering performance; the combination of the two pre-treatment methods could promote the performances of SS disposal comparing with the individual pre-treatments.

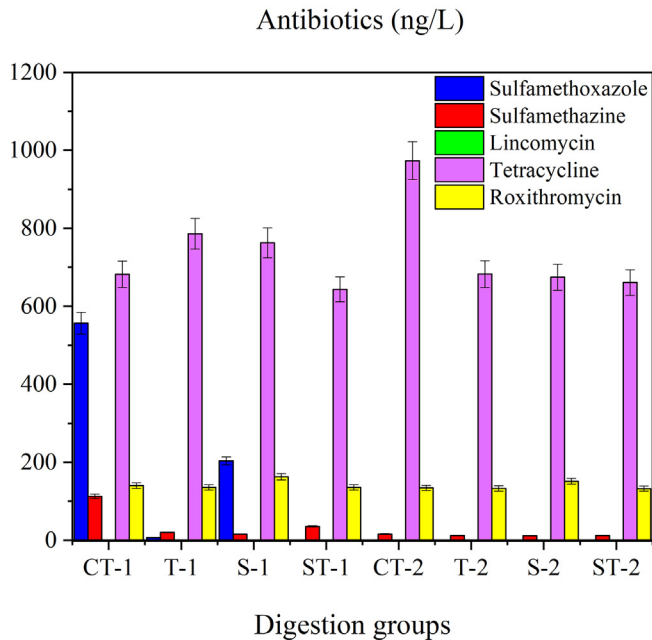
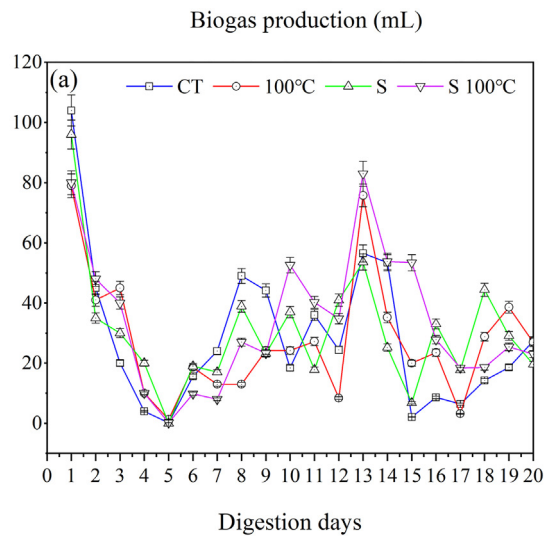
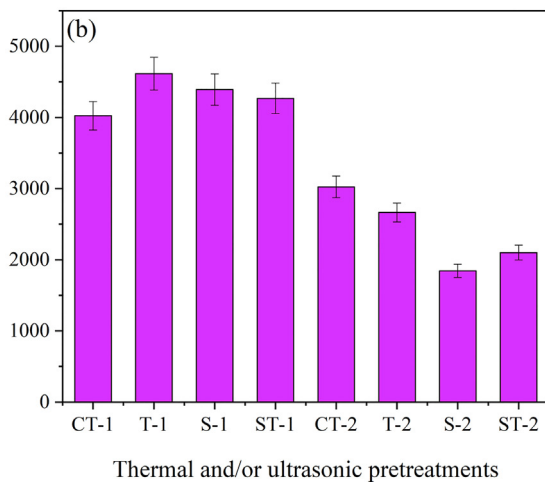


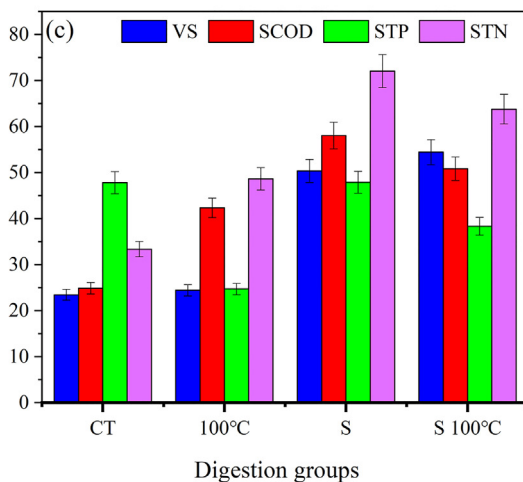
Fig. 4. Antibiotic content in different digestion groups. CT, T, S, and ST stand for control, thermal pre-treatment, ultrasonic pre-treatment and thermal combined ultrasonic pre-treatment, respectively. The suffix -1 represents results on the 3rd day, and the suffix -2 represents results on the 18th day.



Soluble chemical oxygen demand (mg/L)



Removal rates (w%)



3.4. Environmental implications

Different from other investigations, this study combines two methods of thermal pre-treatment and ultrasonic pre-treatment for AD of SS, which maximizes the dissolution of organic matter in SS and breaks the barriers in the hydrolysis stage. Compared with separate pre-treatments, this method shortens the reaction time, increases the biogas production on the one hand, and improves the dewaterability of the sludge on the other hand. Most importantly, the relationship between the migration of organic matter in the SS after pre-treatment and the degradation of antibiotics was analyzed by means of three-dimensional fluorescence, which proved that the combined pre-treatment method could effectively increase the degradation rate of antibiotics in the sludge. The research results in this article could be applied to actual medium and large AD systems. It could greatly improve reaction efficiency, increase production rate, and reduce sludge output. In addition, sludge with lower antibiotic content could be obtained, and treatment costs could be reduced. The microbial community in the process and the mechanism of increasing the degradation rate of antibiotics and resistant genes are remaining challenges for future investigations after this study.

4. Conclusions

In this study, the effects of thermal pre-treatment, ultrasonic pre-treatment, and thermal combined ultrasonic pre-treatment before and after AD of SS were comprehensively investigated. In conclusion, thermal combined ultrasonic pre-treatment is not only the best choice for solubilizing organics before AD, but also a promotion to the performance of AD. Compared with the control, thermal combined ultrasonic pre-treatment of sludge obtained the maximum SCOD concentration (3516 VS 108 mg/L), soluble protein concentration (473 VS 4.8 mg/L), and polysaccharide concentration (478 VS 24 mg/L). Thermal combined ultrasonic pre-treatment promoted the decomposition of SS better than individual pre-treatments, which could improve the efficiency of subsequent AD and shorten the reaction time. After AD, the combined pre-treatment obtained the maximum biogas increase, reduced the amount of sludge and improved the dewatering performance of the sludge, comparing to the existing separate thermal pre-treatments and ultrasonic pre-treatments. In addition, the combined method could also effectively reduce the content of antibiotics, especially the sulfa antibiotics in SS.

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CRediT authorship contribution statement

- Hongbo Liu: Conceptualization, funding acquisition, project administration, supervision, original draft.
- Xingkang Wang: Methodology, lab investigation, mechanism modelling, original draft.
- Song Qin: Lab investigation.
- Wenjia Lai: Resource, funding acquisition, review & editing.
- Xin Yang: Lab investigation.
- Suyun Xu: Supervision, original draft, review & editing.
- Eric Lichtfouse: Review & editing.

Declaration of competing interest

The authors have declared no conflict of interest.

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Fig. 5. The amount of biogas produced during digestion (a); SCOD in the digestion groups (b); the removal rates of VS, SCOD, STP, and STN in digestion groups (c). CT, T, S, and ST stand for control, thermal pre-treatment, ultrasonic pre-treatment and thermal combined ultrasonic pre-treatment, respectively. The suffix -1 represents results on the 3rd day, and the suffix -2 represents results on the 18th day.

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