

Ultrasound-assisted hydrolysis and acidogenesis of solid organic wastes in
a rotational drum fermentation system

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Abstract

The hydrolysis and acidogenesis of solid organic wastes in a rotational drum fermentation system (RDFS) were improved by direct ultrasonic irradiation (DUSI) and a modified ultrasonic treatment (MUST) composed of dilution, ultrasonic irradiation, and filtration. The effect of DUSI on VA desorption from particle surfaces was estimated. DUSI delivered few distinctions from the broth characteristics, but elevated

pH and VS degradation rate (53% higher than the control) in the subsequent acidogenesis. The results demonstrated that DUSI could dislodge VA from particle surfaces and disrupt large-size particles by hydro-mechanical shear force. To improve VA desorption and removal, a MUST process was constructed. The influences of MUST on the characteristics of the fermentation broth and the subsequent acidogenic performance were investigated. MUST raised the broth pH level from 5.1 to 5.5 and remarkably decreased VA concentration from 11.0 to 3.5 g/L. At the end of the subsequent acidogenesis, VA increasing ratios, VS degradation ratios, and surface-based hydrolysis constants of the fermentors with the control broth (CF) and the treated broth (MUSTF) were 166.7 and 732.0%, 17.0 and 26.7%, and 16.9 and $26.8 \times 10^{-6} \text{ kg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively. With the assistance of MUST, a considerably improved acidogenic performance of solid organic wastes was accomplished in terms of VA production, VS degradation, and particle hydrolysis.

Keywords: Ultrasonic irradiation; Modified ultrasonic treatment; Acidogenesis; Solid organic waste; Rotational drum fermentation system

1. Introduction

Anaerobic digestion has been considered as a favorable alternative for the volume reduction of organic wastes and energy recovery (Lettinga, 2001). It consists of a multitude of biochemical reactions in series and in parallel, in which organic compounds are mineralized to methane and carbon dioxide by diverse microorganisms. Generally, the four following steps are undertaken: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Veeken et al, 2000). In the case of particle-substrate digestion, hydrolysis has been identified as the rate-limiting step (Eastman et al., 1981; Vavilin et al., 2002). It was thought to be dependent on environmental and operational parameters such as pH, temperature, substrate, concentration of total volatile acids (VA) or undissociated volatile acids (U-VA), and process configuration (Veeken and Hamelers, 1999).

Numerous observations have suggested that the presence of, or increased VA concentrations were harmful to process performance (Zheng, and Yu, 2005; Pullammanappallil et al., 2001). It inhibited not only methanogenesis (Kroeker et al., 1979), but also hydrolysis (Llabres-Luengo and Mata-Alvarez, 1988; Veeken et al, 2000) and acidogenesis (Garcia et al., 1991). In particular, in two-phase anaerobic digestion, VA accumulated more severely in the acidogenic process due to the absence of methanogenic microorganisms which consume VA (Eastman et al, 1981). The result was

the depletion of buffering capacity and depression of pH to levels which inhibited the hydrolytic/acidogenic phase. The inhibitory pH level was reported by Babel et al. (2004) who found that a value of 2.3 g/L U-VA at pH 5 inhibited the solid waste acidification significantly. Moreover, according to the surface based kinetics (SBK) model (Sanders et al, 2000) which assumed the substrate was composed of spherical particles and degraded from the outside, the metabolic intermediaries such as VA were prone to accumulate around the particle surface. Consequently, the product films, which not only retarded the microorganisms' access to the particle-substrate but also lowered the pH levels, were formed.

To accelerate hydrolysis and acidogenesis, VA desorption and its removal from the particles is essential for the accessibility of the microorganisms to the particle-substrate. Some studies have been successful in carrying out VA removal including extraction with solvents (Mostafa, 1999; Schöller et al., 1993), electrolysis (Nomura et al., 1988; Hirata et al., 2005), leachate recirculation (Chen et al, 2007), and adsorption by ion-exchange resins or zeolite (Gluszcz et al., 2004; Aljundi et al., 2005). The excessive VA was removed by specific forces from the fermentation broth in these works. However, as for the high-total-solid substrate, VA was apt to intrude into the porous particles and was more difficult to disperse due to the poor rheological property. More violent forces need to be imposed to overcome the adsorption between VA and particles. Hydro-mechanical

shear force, which was effectively generated by ultrasound at a frequency below 100 kHz (Portenlänger, 1999), is a potential option.

The ultrasound is well-known for two cavitation phenomena, that is, sonochemical reactions and powerful hydro-mechanical shear forces. High frequency ultrasound promotes sonochemical reactions such as oxidation by radicals, whereas a low frequency promotes mechanical and physical phenomena such as pressure waves (Gonze et al., 1999). The latter has been widely applied in cleaning (Niemczewski, 2007), exhausted adsorbents regeneration (Lacin et al, 2005; Li et al, 2006; Lim and Okada, 2005), and sludge disintegration (Bougrier et al., 2005; Tiehm et al., 1997; Wang et al., 2005; Tiehm et al., 2001). It dislodged the impurities or the adsorbates from surfaces into solution or even disrupted sludge directly, depending on the power of the hydro-mechanical shear forces. Accordingly, it may potentially desorb the VA accumulated around the substrate and break up the substrate itself with the assistance of ultrasound.

In this work, ultrasound was employed to enhance the hydrolysis/acidogenesis of solid organic wastes by VA removal. The effect of direct ultrasonic irradiation (DUSI) on VA desorption from the particle surface was estimated by exploring the acidogenic performance of the fermentation broth with a rotational drum fermentation system (RDFS). Furthermore, to augment the hydro-mechanical shear forces, as well as

improve VA dispersion and removal during ultrasonic irradiation, a modified ultrasonic treatment (MUST) process composed of dilution, ultrasonic irradiation, and filtration was applied. The influences of MUST on the characteristics of the fermentation broth were investigated and its subsequent effects on acidogenic performance were evaluated via parameters such as pH, VA concentration in comparison with a control process.

2. Methods

2.1. Substrate and seeding sludge

Fermentation broths from previous acidogenic experiments (Gan et al., 2007) were employed as the substrates and their characteristics were presented in Table 1.

Table 1

Anaerobic digestion sludge from a municipal wastewater treatment plant (Gaobeidian, Beijing, China) was used as the seeding sludge.

2.2. Experimental apparatus

An ultrasonic cleaner (KQ-500B) with 10 sandwich-type transducers fixed at the bottom was used as the ultrasonic apparatus. It was worked with a fixed operating frequency of 40 kHz and a supplied power of 500 W. The temperature of the water bath

was controlled by adding ice during irradiation.

A RDFS developed by Jiang and his co-workers (2005) was used for batch experiments. It consisted of four fermentors (3.6L) which were filled with aluminum oxide milling balls (diameter: 30 mm) that took 10% volume. The system was placed in an incubator and kept at a constant mesophilic temperature ($35\pm 1^\circ\text{C}$). The semicontinuous rotation of the drum was automatically controlled at 15-min and 30-min intervals and run at a velocity of 12 rpm throughout the experiments.

2.3. Experimental procedure

2.3.1. Effect of DUSI on VA desorption from fermentation broth

A beaker (1 L) filed with 250 g fermentation broth was submerged in the ultrasonic bath for 20-min irradiation. The pH, TS and VS, VA concentration, as well as particle size distribution (PSD) of the irradiated fermentation broth, were measured. Then, the fermentation broths, both with and without DUSI, were fed to fermentors which were inoculated with anaerobic digestion sludge at a given weight ratio (1:1), respectively. As the fermentation broths were fed to the fermentors, the nitrogen was injected into the fermentors to ensure the anaerobic condition.

2.3.2. MUST to improve the acidogenic performance

To promote VA desorption and removal during irradiation, a MUST process composed of dilution, ultrasonic irradiation, and filtration was constructed. 250 g

fermentation broth was diluted with 750 g tap water in a beaker before irradiation for 20 min. After irradiation, the fermentation broth was leached through a 200-mesh stainless-steel sieve and exerted a vertical force (102.4 kPa) until 800 g filtrate weighed by an electronic balance (BL-320S, Shimadzu) was obtained. The filtrate was centrifuged at 3000 rpm for 5 min and then 750 g supernatant was wasted. The residual supernatant and the deposit were recycled to the fermentation broth. Finally, pH, TS and VS, VA concentration, VA spectrums, and PSD of the filtered fermentation broth were measured. The subsequent acidogenesis of the fermentation broths, both with and without MUST, were also performed at the same conditions described in section 2.3.1.

Both batch acidogenic experiments lasted for 10 days, and the samples were withdrawn on alternate days for analysis of pH, VA, TS and VS, and PSD. The experiments were set up in triplicate.

2.4. Measurement and analysis

The values of pH, TS and VS, and VA concentration were determined according to the sewage test procedure (Japan Sewage Association, 1997). The samples withdrawn were centrifuged at 3000 rpm for 5 min. The supernatants were passed through a 0.45 μm membrane filter for the analysis of VA spectrum by an ion chromatograph (DX600, DIONEX) with an electrochemical detector (ED50). The PSD of each sample was monitored by a laser particle size analyzer (LS-230, COULTER).

The VA production performance is evaluated by VA increasing ratio (R_{VA}) which is determined using Equation (1).

$$R_{VA} = \frac{(FVA - IVA) + PVA}{IVA} \quad (1)$$

where FVA (g) is the final VA in the fermentor; IVA (g) is the initial VA added to the fermentor; PVA (g) is the VA converted into final products by methane-producing microbes.

VA exists in solution in two principal forms, i.e., U-VA and ionized VA (I-VA), and the concentration of U-VA, which can be calculated using the following equation (Bujoczek et al., 2000).

$$UVA = VA \frac{10^{(pK_a - pH)}}{1 + 10^{(pK_a - pH)}} \quad (2)$$

where pK_a is the dissociation constant of the acids in water; $pK_a = 4.762$ for acetic acid at 35°C (Weast, 1981).

The VS degradation ratio (R_{VS} , %) can be obtained as follows:

$$R_{VS} = \frac{S_0 - S_t}{S_0} \times 100 \quad (3)$$

where S_0 (g-VS/L) is the initial substrate concentration; S_t (g-VS/L) is the substrate concentration at time t . The VS degradation rate (R'_{VS} , %/d) was derived from the ratio of VS degradation to reaction time.

The hydrolysis of the particle substrate was evaluated by the surface based kinetics

(SBK) model (Hill and Nakano, 1984; Hobson et al., 1987; Sander et al., 2000), which is described as follows:

$$\frac{dM}{dt} = -K_{sbk} A \quad (4)$$

where M (kg) is the mass of substrate; A (m²) is the surface available for hydrolysis; K_{sbk} (kg·m⁻²·d⁻¹) is the surface based hydrolysis constant. This model assumed the substrate was composed of spherical particles and completely covered with bacteria around the whole surface. The hydrolysis rate was constant per unit area available for hydrolysis. Equation (4) can be deduced into equation (5):

$$K_{sbk} = \rho \frac{\overline{R_0} - \overline{R_t}}{t} \quad (5)$$

where $\overline{R_0}$ (m) is the initial particle mean radius; $\overline{R_t}$ (m) is the particle mean radius at time t ; ρ (kg·m⁻³) is the apparent density of the particle substrate.

3. Results and discussion

3.1. Effect of DUSI on VA desorption from particle surfaces

The effect of DUSI on VA desorption from particle surfaces was evaluated by characterizing the fermentation broth after DUSI and its subsequent acidogenic performance.

The pH level and the VA concentration of the fermentation broth remained almost the same after DUSI. It implied that DUSI had little effect on VA desorption from the

substrate particle surfaces, or that the VA remained in the broth despite being desorbed by ultrasonic shear forces.

The slight decrease of TS and VS indicated that a small amount of organic solids were mechanically disrupted by shear forces or degraded by weak sonochemical reactions into ones which were small enough to dissolve under ultrasonic irradiation. There were small differences in the mean diameters between the broth, both with and without irradiation. Nevertheless, the occupied volume of the small-size particles ($\leq 850 \mu\text{m}$) in the irradiated broth increased and the larger one decreased slightly. It proved that the bigger particles were mechanically disrupted into smaller ones by the ultrasonic irradiation.

Only few distinctions on pH and VA concentration were observed between the broth with and without irradiation, so the subsequent acidogenesis was further conducted. The pH value of the irradiated broth was almost the same as the control during the first 4 days; and increased remarkably, accompanied by more biogas generation after the 4th day (data not shown). The microorganisms metabolized I-VA existing in the broth into biogas. The hydro-mechanical shear forces developed by DUSI desorbed the VA from particle surfaces into the broth and hence provided more I-VA for the microorganisms to metabolize after 4-day acclimation. It elevated the pH level, in turn, increased the I-VA portion in the broth according to equation (1).

VA concentration of the broth, both with and without DUSI, increased with fermentation time. The VA concentration of the irradiated broth was greater than the control of 4 days, while the latter exceeded the former after the 4th day. The more VA increment in the irradiated broth for the first 4 days was attributed to the VA desorption from the substrate particle surfaces or the disruption of the substrate particles during ultrasonic irradiation, both of which supplied more particle surface areas for the microorganisms to metabolize. With the pH elevation in the broth with DUSI, some VA was consumed after the 4th day, which resulted in slow VA increase in comparison to the broth without DUSI.

The VS degradation rates for the broth, both with and without DUSI, were obtained as 1.3 and 0.8%/d, respectively. The considerable elevation (53% higher than the control) of the VS degradation rate was observed under DUSI. It indicated that the DUSI process promoted the solid degradation.

The improved acidogenic performance in subsequent acidogenesis attributed to dislodging VA from the particle surface and disrupting larger particles by ultrasonic irradiation. The ultrasound waves imposed on a liquid leads to the formation of cavitation bubbles. The violent collapse of the bubbles produces intense heat, high pressure, and powerful hydro-mechanical shear forces in the liquid. However, the converted ultrasonic mechanical energy is also dissipated for the generation of flow, as

well as the generation of cavitation (Gogate et al., 2003). As for the fermentation broth with high TS content, more energy was distributed to generate flow during irradiation. Consequently, less cavitation bubbles were formed and hydro-mechanical shear forces were weakened. Furthermore, the desorbed VA remained in the broth. The VA inhibition again occurred.

3.2. MUST to promote the acidogenic performance

The MUST process consisting of dilution, ultrasonic irradiation, and filtration was employed in order to promote the positive effect of ultrasonic irradiation and remove the desorbed VA.

3.2.1. Effect of MUST on the characteristics of fermentation broth

The effect of MUST on the characteristics of fermentation broth was investigated by comparison with its control in terms of pH, TS and VS, VA concentration, VA spectrum, and PSD. The results are shown in Table 1 and Fig. 1, respectively.

As shown in Table 1, MUST increased the broth pH level from 5.1 to 5.5 and, remarkably, decreased the VA concentration from 11.0 to 3.5 g/L. The elevated pH by MUST approached optimum levels (6.0-6.5) for acidogenesis proposed by Kisaalita and Pinder (1987).

Acetic acid was predominant in both fermentation broths, followed by propionic and succinic acid, while the least was formic acid. Compared with the control, acetic, and

succinic acid contents of the broth with MUST decreased, and propionic acid content increased, with the formic acid level almost the same. The increase of propionic acid resulted from the degradation of succinic acid. As shown in Table 1, the decrease of succinic and acetic acid attributed to the feeble sonochemical reaction induced by low-frequency ultrasound (Mark et al, 1998).

Due to the dilution, MUST delivered a bigger decrease of TS and VS than DUSI. The dilution increased the violent shear forces to disrupt the particles into smaller ones and provided more medium for the small particles to dissolve. This was evidenced by the change of mean diameter and PSDs. The mean particle diameter decreased from 784.4 to 715.3 μm after MUST. Fig. 1 depicts the PSDs of the fermentation broth, both with and without MUST. For the broth with MUST, the volume occupied by particles bigger than 500 μm was apparent smaller than the control. MUST exhibited a worthwhile ability in particle size reduction owing to the dilution.

Figure 1

Compared with DUSI, the dilution improved the rheological behavior and reduced the energy dissipated for flow. More energy was converted into cavitation bubbles, and produced more violent hydro-mechanical forces. It also upgraded VA dispersion to the

broth. Eventually, the filtration removed the filtrate with desorbed VA from the fermentation broth and buffered the VA inhibition on the subsequent acidogenesis.

3.2.2. Effect of MUST on subsequent acidogenesis

MUST was more efficient than DUSI on VA removal according to the above experiment. To evaluate the effect of MUST, the fermentation broth with MUST was used as a substrate and loaded into the fermentor (MUSTF) for subsequent acidogenesis. Its acidogenic performance was compared with the control (CF) via parameters such as VA production and VS degradation.

The pH levels in both fermentors remained below 5.4 after a 2-day operation, which indicated that the acidogenesis was prevailing. The final pH value in MUSTF (5.0) was lower than that in CF (5.1), and their pH gradients were 1.1 and 0.4, respectively. The final VA concentrations (14 g/L) in the two fermentors were almost the same. The VA gradient in MUSTF (12.8 g/L) was higher than that in CF (9.2 g/L) because of the VA removal. The acidogenesis rate derived from VA formation to retention time was raised from 1.7 to 2.3 g/L·d by MUST. Correspondingly, VS content decreased from 91.1 to 66.7 g/L in MUSTF and from 93.0 to 77.2 g/L in CF. These results showed that VA inhibition on acidogenesis was buffered by MUST.

Fig. 2 exhibits the time course of VA concentration and VA increasing ratio in each

fermentor. VA concentrations in both fermentors increased with time and after 8-day reaction they were on a similar level with almost no further VA produced. These stagnancies were due to the high concentrated VA and low pH, which inhibited the activity of catabolic enzyme. In the case of no gas generation, the VA increasing ratio in MUSTF increased more rapidly than that in CF, especially during the first 2 days, due to the lower initial VA concentration of the fermentation broth with MUST. Ultimately, the final values obtained in CF and MUSTF were 166.7% and 732.0%, respectively. In fact, more gases were generated in MUSTF, which meant part of VA was metabolized into methane and carbon dioxide. The actual VA increasing ratio was higher than 732.0%. It indicated that VA inhibition was alleviated and VA production yield was augmented drastically by MUST.

Figure 2

The time course of VA spectrums is shown in Fig. 3. Acetic acid was predominant in both fermentors, followed by propionic acid during the experiment period. The occupying ratio of succinic acid diminished and finally disappeared, while that of propionic acid increased and remained at a steady level finally. The occupying ratio of acetic acid was descended at first, and then elevated gradually. These phenomena

demonstrated that succinic acid was degraded into propionic acid, which was then decomposed into acetic acid and formic acid. However, at the beginning of the experiment, more acetic acid was metabolized to CH₄ and CO₂ because of the suitable pH for methanogenic microorganisms in MUSTF. In addition, propionic acid degraded slowly and was sensitive to the hydrogen pressure. This led to the accumulation of propionic acid which was fatal for the methanogenic process. Compared with CF, an earlier disappearance of succinic acid was obtained in MUSTF, which implied that MUST assisted long-chain VA degradation.

Figure 3

Fig. 4 illustrates VS contents and VS degradation ratios of the fermentation broth during the whole experiment period. In both fermentors, VS contents decreased and VS degradation ratios increased with time. The degradation ratios were greater in MUSTF and there was a tendency to cease in CF in the last 2 days. At the shorter retention time of 4d, the reduction of VS content in MUSTF decreased facilely to 75.8 g/L as compared to 77.2 g/L obtained in CF with a residence time of 10d. Similarly, on the 4th day, VS degradation ratio in MUSTF reached 16.8%, but needed a duration time of 10d in CF. These phenomena highlighted that MUST enhanced the degradation of particles

by increasing the degradation ratio as well as shortening the residence time.

Figure 4

The PSDs of initial and final contents in each fermentor are described in Fig. 5. The PSDs of the influents to both fermentors presented a peak centered on 950 μm , but a little narrower and lower in CF. At the end of the experiment, peaks became steeper and their centers moved to 70 and 50 μm for CF and MUSTF, respectively. Particles smaller than 200 μm were predominant in both fermentors. Particles larger than 200 μm were almost undetected in MUSTF, but still existed with high occupied volume (about 30 %) in CF. The mean diameters of the broth decreased from 608.3 to 269.4 μm for CF and from 578.6 to 43.2 μm for MUSTF at the end of the experiment. Substituting them into equation (5), K_{sbk} of $16.9 \times 10^{-6} \text{ kg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ for CF and $26.8 \times 10^{-6} \text{ kg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ for MUSTF were attained. According to the SBK model, the hydrolysis rate was related to the available surface areas of the substrate. VA desorption from particle surfaces and removal from the broth, as well as direct particle disruption by MUST, provided the microorganisms more available surface areas to degrade and more favorable environments to survive. The hydrolysis was enhanced significantly with the assistance of MUST.

Figure 5

4. Conclusions

DUSI delivered few distinctions from the broth characteristics, but elevated pH and VS degradation rate (53% higher than the control) in the subsequent acidogenesis due to VA desorption from substrate particle surfaces and direct particle disruption. By strengthening the hydro-mechanical shear forces, as well as accelerating VA dispersion to the broth and ultimately removing the VA, MUST was better on VA removal than DUSI. It elevated the pH level and decreased the VA concentration of the broth. The subsequent acidogenic performance of fermentation broth in terms of VA production, VS degradation and particle hydrolysis was enhanced considerably with the help of MUST.

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Table 1

Characteristics of the fermentation broth with and without MUST

Parameter	Unit	Broth without MUST	Broth with MUST
pH	-	5.1 ± 0.2	5.5 ± 0.2
Total solids (TS)	g/L	186.1 ±10.1	183.7 ±10.7
Volatile solids (VS)	g /L	184.3 ±10.8	180.5 ±10.7
Volatile acid concentration (VA)	g/L	11.0 ± 1.7	3.5 ± 0.8
Formic acid	%	5.6 ± 1.1	5.6 ± 1.1
VA Acetic acid	%	79.9 ± 5.2	77.5 ± 5.2
spectrum Propionic acid	%	7.6 ± 3.7	11.0 ± 3.7
Succinic acid	%	6.9 ± 1.1	5.9 ± 1.1
Mean diameter	µm	784.4±27.9	715.3± 25.4

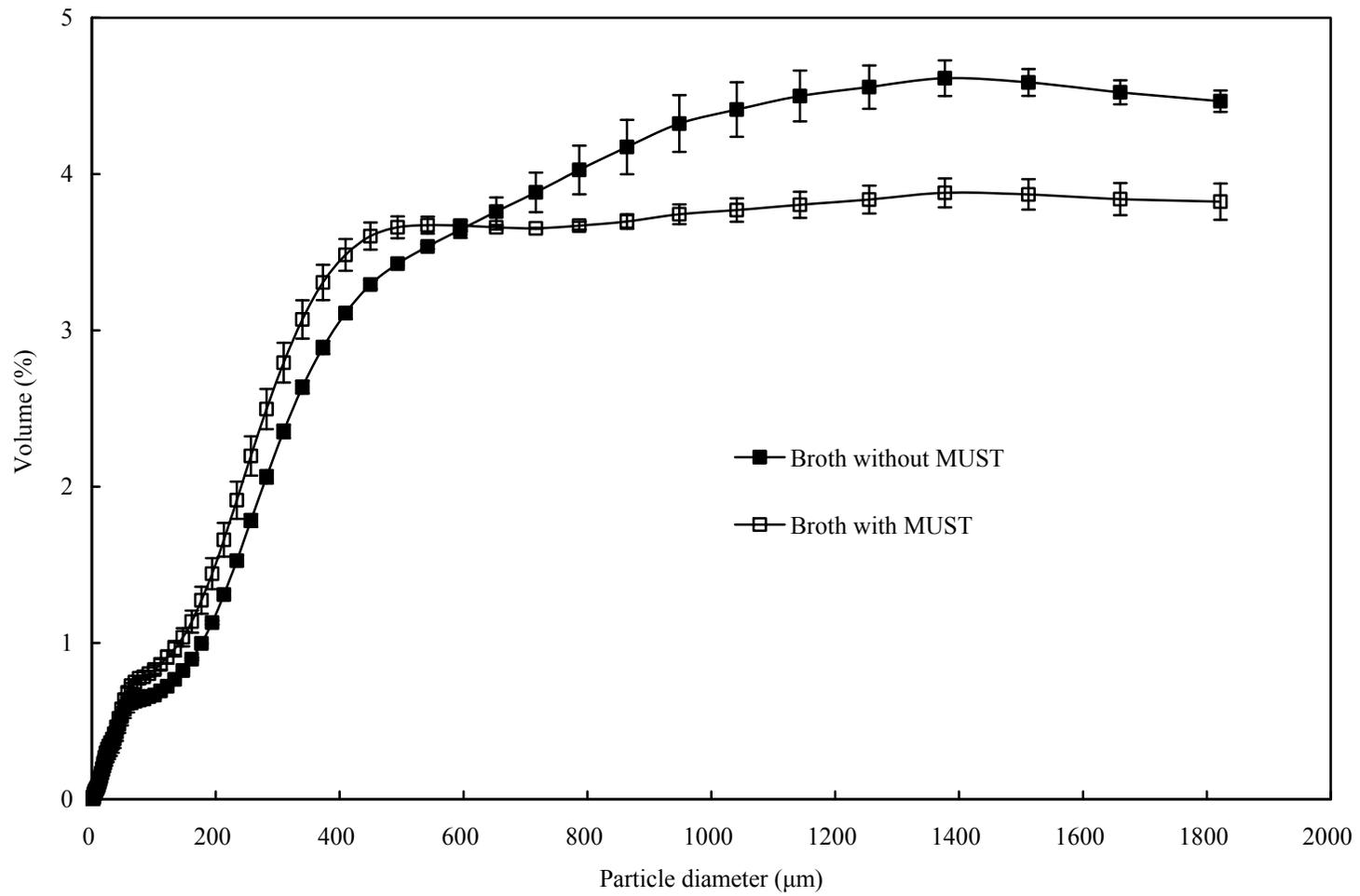


Fig. 1. Particle size distributions of the fermentation broth with and without MUST.

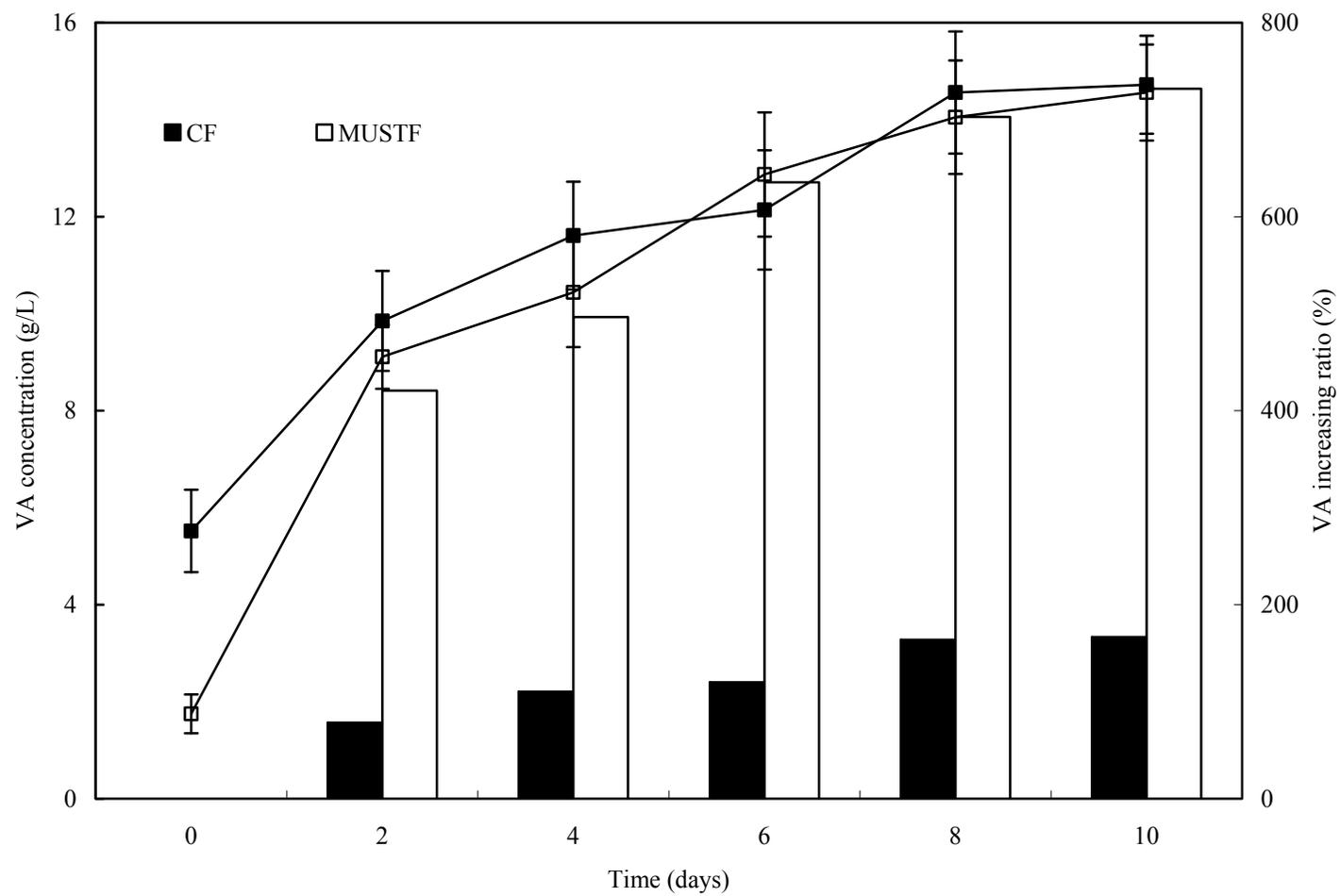


Fig. 2. VA concentrations and VA increasing ratios in the subsequent acidogenesis of the broth with and without MUST. The lines represent VA concentrations, the blocks represent VA increasing ratios.

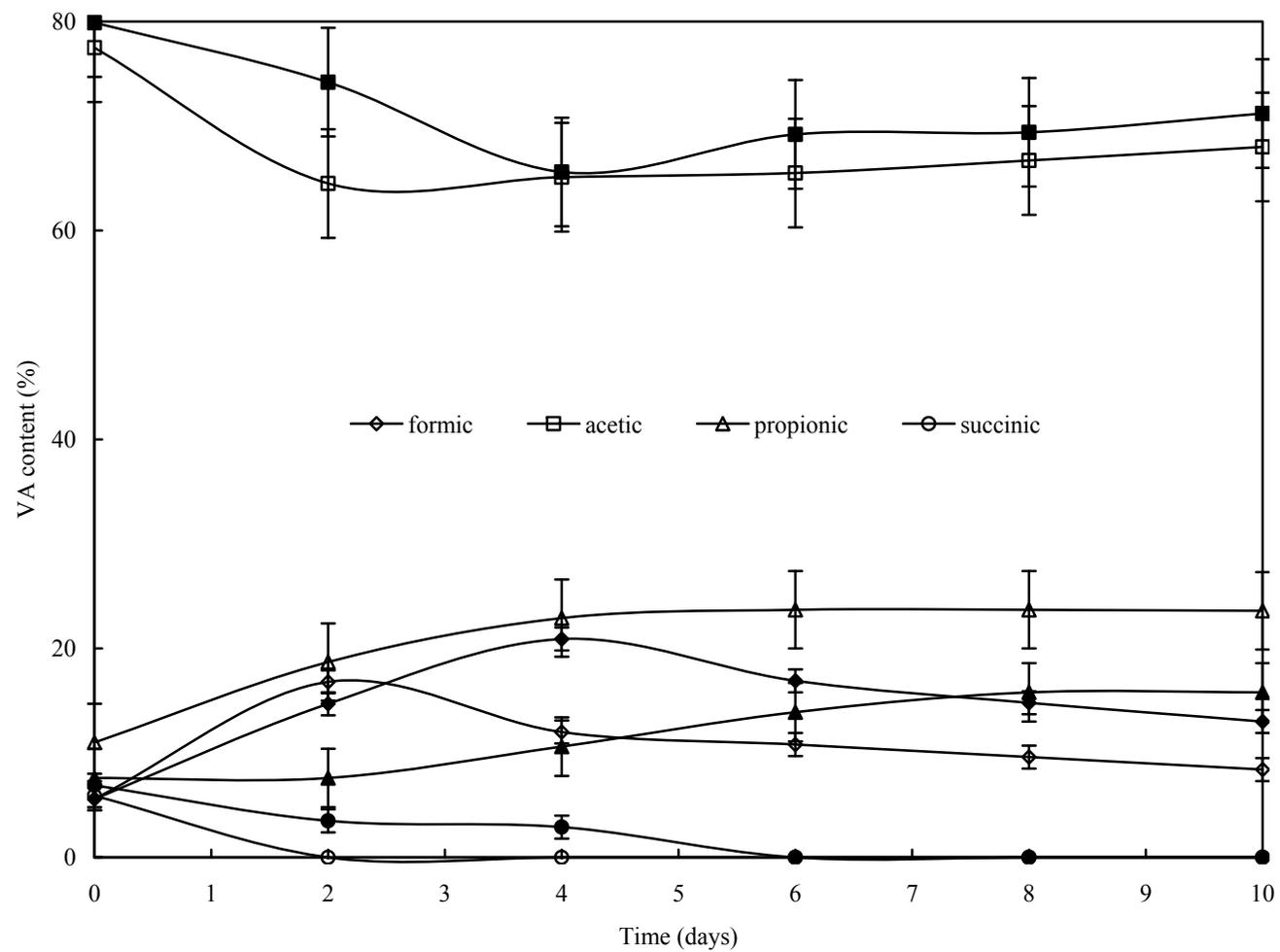


Fig. 3. VA spectrum of the fermentation broth in batch experiment. Blank symbols correspond to values in MUSTF, black symbols correspond to values in CF.

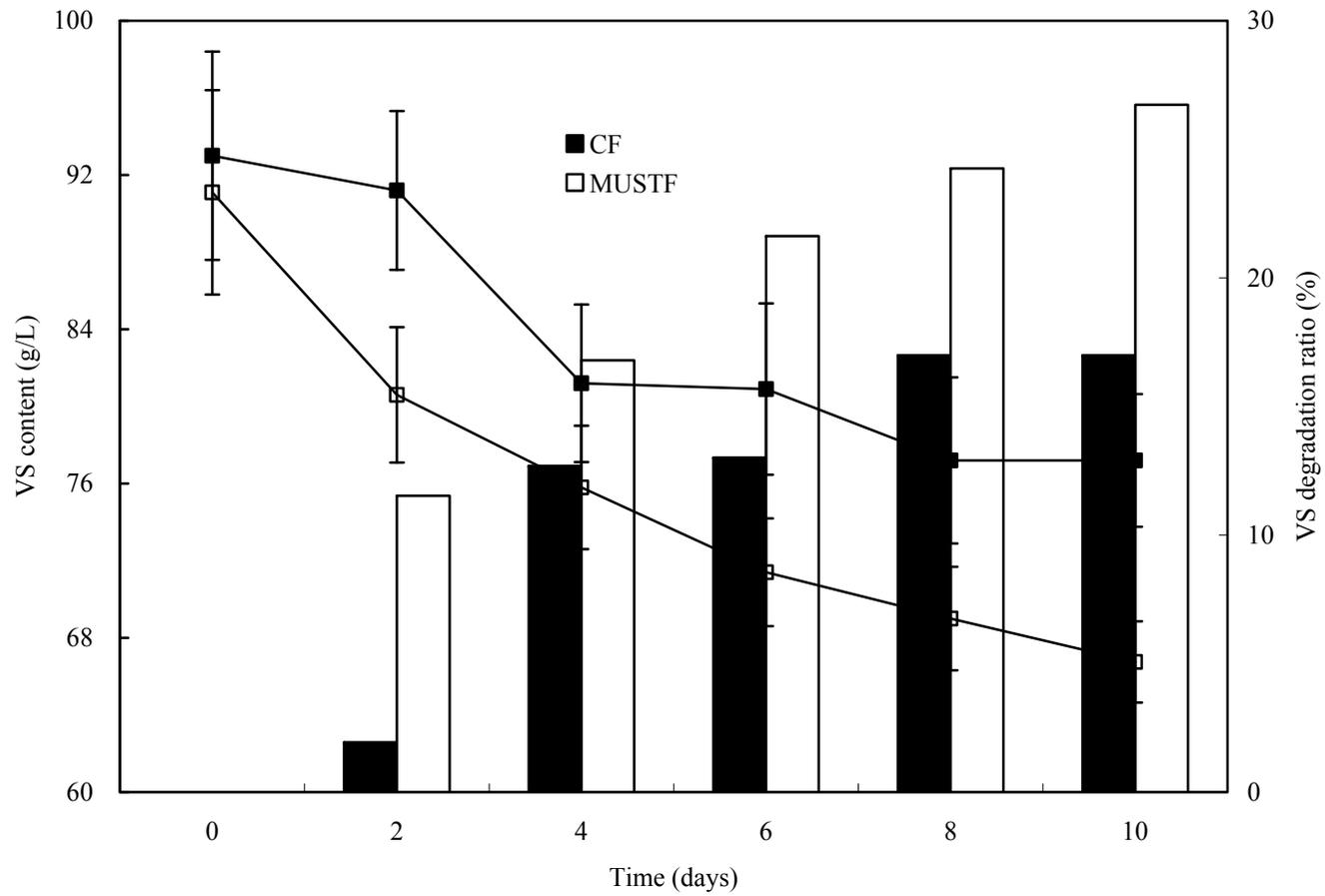


Fig. 4. VS contents and VS degradation ratios in the subsequent acidogenesis of the broth with and without MUST. The lines represent VS contents, the blocks represent VS degradation ratios.

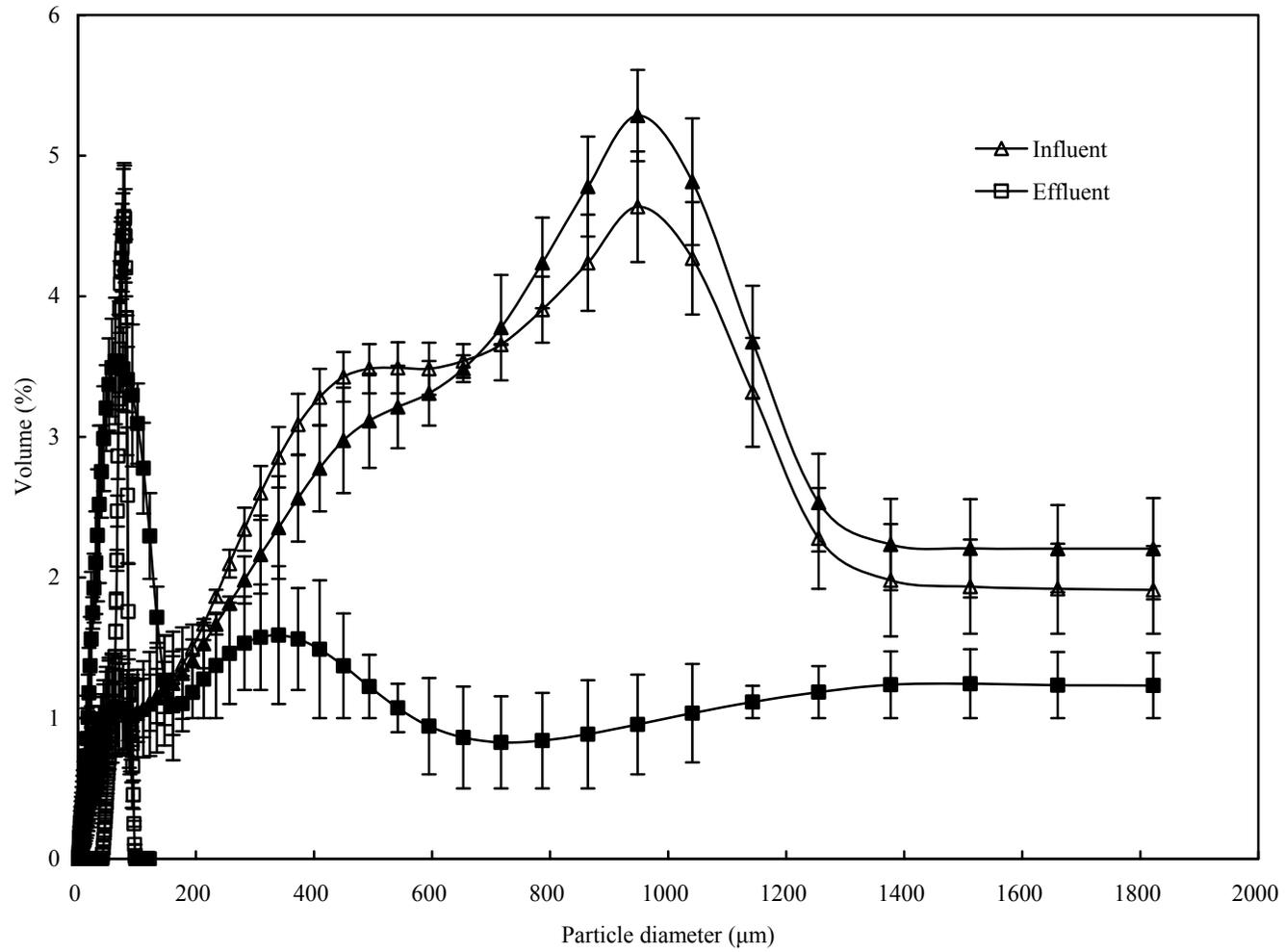


Fig. 5. PSDs of the influents and effluents in CF and MUSTF. Blank symbols correspond to values in MUSTF, black symbols correspond to values in CF.