Feasibility assessment for biogas and fertilizer production from mechanically separated organic fraction of municipal solid waste (MS-OFMSW) in Chinese samll city

Zili Mei[a], Dong Li[b]*, Xiaofeng Liu[b]

[a]Key Laboratory of Development and Application of Rural Renewable Energy, Ministry of Agriculture, Biogas Institute of Ministry of Agriculture, Chengdu, 610041, China

[b]Key Laboratory of Environmental and Applied Microbiology, Environmental Microbiology Key Laboratory of Sichuan Province, Chengdu Institute of Biology, Chinese Academy of Science, Chengdu 610041, China

Corresponding author. Address: No. 9 Section 4, Renmin Nan Road, Chengdu, Sichuan, P.R. China

Tel.: +86 28 82890229; Fax:+86 28 82890229

E-mail address: lidong@cib.ac.cn

Abstract:

The mechanically separation technology for municipal solid waste treatment was developed in China recently. In order to assess the feasibility for anaerobic digestion of mechanically separated organic fraction of municipal solid waste (MS-OFMSW), and to evaluate the feasibility of digested residue used as fertilizer, mesophilic anaerobic digestions and analysis of fertilizer composition and heave metals were carried out for two fractions of MS-OFMSW (MS-OFMSW$_a$: above screen, MS-OFMSW$_b$: below screen). The biodegradability of MS-OFMSW$_a$ with volatile solid (VS) / total solid (TS) of 28.6% and methane potential of 93.1 L/kgVS was higher than that of MS-OFMSW$_b$ with VS/TS of 17.1% and methane potential of 37.3 L/kgVS. There was no inhibiton by VFAs, ammonia and heavy metal for AD of MS-OFMSW. The nutrient contents in solid fraction of digested residue of MS-OFMSW all met the requirement of Chinese standards for urban solid wastes using as fertilizer. However, heavy metal contents (Cr, Cd, Pb and Ni) did not satisfy the requirement of Chinese standards.

Keywords: Municipal solid waste; Mechanically separation technology; Biogas; Fertilizer; Heavy metal

1. Introduction

Municipal solid waste (MSW) generation is rapidly increasing in China and the production of MSW in 2012 was 170.81 million tons, among which, 84.83% of MSW was treated harmlessly. Disposal capacities of sanitary landfill, incineration and other treatment including composting were 105.13, 35.84 and 3.93 million tons respectively (National Bureau of Statistics, 2013). However. the scarcity of land and uncontrolled secondary contamination are threatening the application of landfill and incineration, which were formerly the main MSW disposal method in large and medium-sized cities. The poor quality of compost make composting uncompetitive, which was a main means to deal with MSW in samll cities.

Anaerobic digestion (AD) treatment of organic fraction of municipal solid waste (OFMSW) has been considered the main commercially option for both waste treatment and energy/nutrition generation in European countries (De Baere, 2006). All kinds of organic waste come form urban area were used as substrate of AD. According to origin, the organic wastes includes: sewage sludge ((Martin et al., 2015; Razaviarani et al., 2013)),food and kitchen waste ((Ariunbaatar et al., 2014; Serrano et al., 2014; Shahriari et al., 2013)), fruit and vegetable waste ((Bouallagui et al., 2009; Namsree et al., 2012; Serrano et al., 2014)), fish waste ((Nges et al., 2012)), hydromechanically separated OFMSW (HMS-OFMSW) ((Borowski, 2015)), mechanically separated OFMSW (MS-OFMSW) ((Charles et al., 2009; Zhang et al., 2012)), source sorted organic fraction of municipal solid waste (SS-OFMSW) ((Davidsson et al., 2007; Ghanimeh et al., 2012; Hansen et al., 2007)), the mixture of MS-OFMSW and SS-OFMSW ((Bolzonella et al., 2003)) and unsorted municipal solid waste ((Silvey et al., 2000)).

In recent years, AD treatment of urban organic waste come form area was received attention in China and was considered to be the main disposal method in the future. There are a few AD plants in large-middle size cities such as Bejing, Chongqing, Xining and Suzhou, using food waste directly collected from resturant and canteen as material. Unfortunately, there is no commercial or demonstrative AD project using separated OFMSW as material. At present, it is impractical to collecte OFMSW by source sorting since the social development level is still low. Relatively, it is practical to obtain OFMSW by mechanical separation. Here are some companies to develop mechanical separation technologies such as hydromechanically separating and mechanically separating without using of water. These separating technologies were tested in small cities. The feasibility for AD of HMS-OFMSW from Boluo was assessed in the authors' previous studies ((Li et al., 2010)). The biodegradability of HMS-OFMSW with ratio of volatile solid (VS) to total solid (TS) of 61.6% and methane yield of 314 L/kgVS showed that it was suitable for AD treatment.

In this study, the feasibility for AD of MS-OFMSW was evaluated. The original mixed MSW was collected from Wuzhou, a small city with urban population of 310 thousands. In additon, the possibility of diegested residue for agricultural use was analyzed in view of the contents of nutrition and metal pollutants.

2. Methods

2.1. Material and inoculum preparation

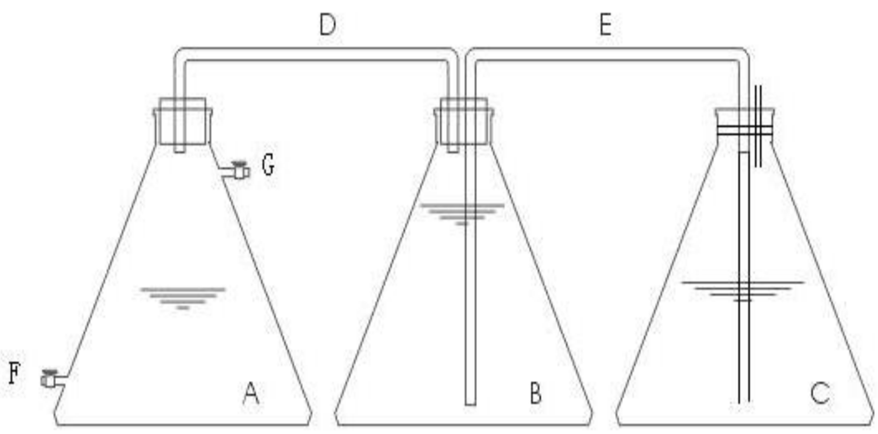
Original municipal solid waste was collected from Wuzhou urban area, Guangxi and transported to waste separation plant. Then the MS-OFMSW was obtained by mechanically separation system and divided into two parts through screen with aperture of 4 mm. The above screen fraction was defined as $MS\text{-}OFMSW_a$ and the below screen fraction was defined as $MS\text{-}OFMSW_b$. About 100 kg homogenous $MS\text{-}OFMSW_a$ and $MS\text{-}OFMSW_b$ were taken to the laboratory respectively.

In order to detailedly acquire the component of $MS\text{-}OFMSW_a$, it was manually sorted to food waste, waste paper, urban greening waste, wood and bamboo, plastics, inorganic matter. In case of the $MS\text{-}OFMSW_b$, since it was a small size homogenous particle material, the manually sorting procedure was not adopted. Before feeding, $MS\text{-}OFMSW_a$ was also ground to particles (< 4 mm).

The digested residue from bench-scale (35 L) mesophilic digester using food waste as substrate used as original inoculum in this study. An acclimation of three weeks was carried out by gradually adding $MS\text{-}OFMSW_b$. The acclimated materials was sieved to remove stone, sand, bone and other coarse matters by screen with aperture of 1 mm. The filtrate was used as inoculum of this study. The total solid (TS), volatile solid (VS), pH of inoculum were 62g/L, 17 g/L, 7.2.

2.2. Experimental reactor and procedure

The tests were conducted on batch lab-scale reactor with total volume of 1.6 L (Fig.1). All reactors were placed in the water bath and controlled at (37±1)℃. 240g homogenous substrate (based on TS) and 300 mL inoculum were feed into reactors. The total solid in reactor (TSr) was adjusted to 20% by adding tap water and the loading rate of reactor was about 73%. The headspace of reactor was filled with pure N_2 to assure the anaerobic condition. Reactor was shaken manually twice a day and the digestion time was 30 days for all reactors. The tests were conducted duplicate times.



A: Reactor B:Gas collector C:Saturated brine collector D:Gas pipe E: Saturated brine pipe F:Liquid sampling port G:Gas sampling port

Fig.1 Experimental set-up for anaerobic digestion of MS-OFMSW

The digested effluent was separated into a solid and a liquid fraction with a centrifuge (5000 rpm and 20 min). The analysis of total nitrogen (TN), total phosphorus (TP), total potassium (TK) and metal contents was carried out for both solid and liquid fractions in order to evaluate the potential of this stream as a fertilizer.

2.3. Analyzing methods

TS，VS and biochemical component compositions (sugars, starches, crude fibers, lipids, proteins, total kjeldahl nitrogen (TKN)) were determined according to Chinese Standard (GB/T 5009-2003). And the carbohydrates content was calculated based on: Carbohydrates (%) = 100- (Protein + Lipid + moisture + ash). Heat values were measured by WGR-1 heat analyzer made in Changsha. Elementary analysis was determined with Vario EL element analyzer made in Germany. Metal analysis was determined with ICP-AES (IRIS 1000 ER/S, Thermo Jarrell Ash Co. made in US). The ammonia nitrogen (NH_4^+ - N) was determined by FC-100 ammonia analyzer made in Shanghai. The pH was determined by pHS-3C pH meter made in Shanghai. The analysis of TN, TP and TK were completed according to Chinese Standard (NY 525-2002). All tests were carried out three times and the data in this paper are mean values.

Biogas production was measured by the displacement of saturated brine solutions. The percentages of CH_4 and CO_2 in headspace of reactors were determined using a gas chromatograph (Agilent 6890) equipped with a thermal conductivity detector (TCD) and a 2m stainless column packed with Porapak Q(50/80 mesh). The operational temperature at the injection port, the column oven and the detector were 100℃, 70℃ and 150℃ respectively. Argon was used as carrier gas at a flow rate of 30mL/min.

Liquid sample was centrifuged with 6000r/min at 0-4℃ and filtrated with 0.45μm cellulose acetate membranes. The concentration of volatile fatty acids (including acetate, propionate, butyrate, iso-butyrate, valerate and iso-valerate) were determined using a gas chromatograph (Agilent 6820) equipped with a flame ionization detector (FID) and a 30m × 0.25mm × 0.25μm fused-silica capillary column (DB-FFAP). Nitrogen was used as carrier gas at a flow rate of 30mL/min and split ratio was 1:50. The operational temperature at the injection port and detector were 250℃ and 300℃. The initial temperature of oven was 100℃ for 5 min, then increased to 250℃ at rate of 10℃/min and maintained for 12 min.

3. Results and discussions

3.1 Substrate characterization

Total solid (TS) of a substrate consists of volatile solids (VS) and ash. Only the biodegradable volatile solids (BVS) fraction of the VS has the potential for bioconversion, while, the refractory volatile solids (RVS) fraction which is mostly lignin and plastics can not be biologically converted to biogas. Lignin is a complex organic material which is not easily degraded by anaerobic bacteria, and normally requires a long period of time for complete degradation. In this study, the total VS of food waste, waste paper and urban greening waste was assumed to be BVS, and the total VS of wood, bamboo and plastics was RVS. The composition of MS-OFMSWa is illustrated in Fig. 2. It is clear that only 82.5% of VS can be biodegraded theoretically.

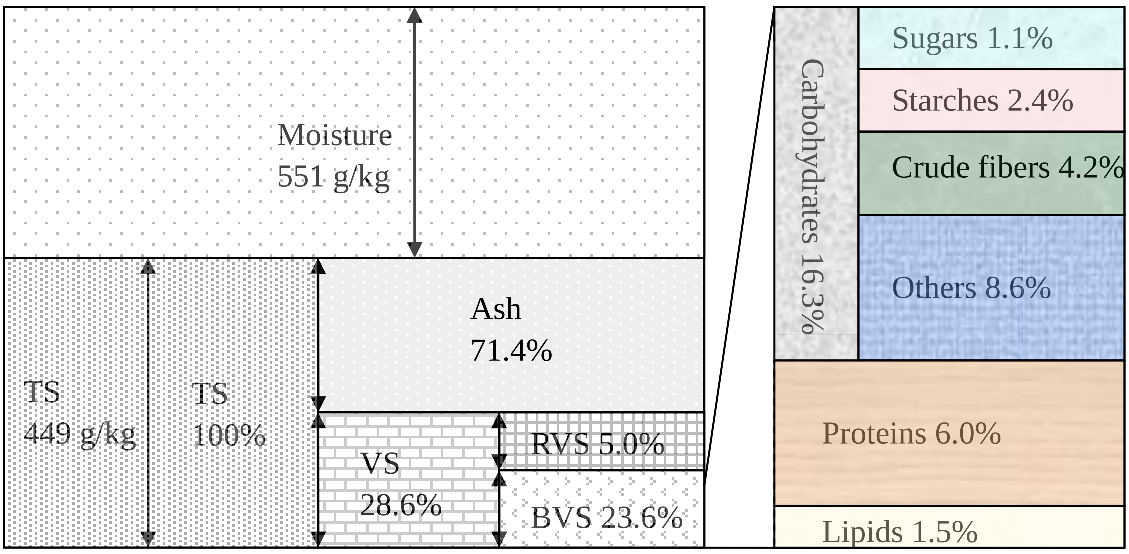


Fig.2 Component chart of $MS\text{-}OFMSW_a$

Since the $MS\text{-}OFMSW_b$ was a small size particle material, the manually sorting procedure was difficult to implement. There is no further compartmentalization of VS. The over all characteristics of MS-OFMSW are presented in Table 1. Both the $MS\text{-}OFMSW_a$ and $MS\text{-}OFMSW_b$ can be considered high-solid substrate (TS>20%). Due to the high content of ash, the heat values of two kinds of MS-OFMSW were much lower than that of SS-OFMSW. Only 28.6% and 17.1% of TS was organic matter and the residue is soil/sand, small inorganic particles. The biodegradability of MS-OFMSW in this study was not only poorer than that of SS-OFMSW from Danish cities, but also lower than that of MS-OFMSW from Spanish city. The majority of BVS is carbohydrates followed by proteins and lipids. The C: N of $MS\text{-}OFMSW_b$ was higher than that of $MS\text{-}OFMSW_a$.

Table 1 Characteristics of MS-OFMSW

Parameters	$MS\text{-}OFMSW_a$	$MS\text{-}OFMSW_b$	SS-OFMSW [a]	MS-OFMSW [b]
Particle size (mm)	≥4	≤4	-	≤30
TS (g/kg)	449	717	170-370	810
Heat value (MJ/kgTS)	6.2	2.7	19-22	-
Ash (% of TS)	38.4	82.9	8-19	47.4
VS (% of TS)	28.6	17.1	81-92	52.6
BVS (% of TS)	23.6	-	-	-
RVS (% of TS)	5.0	-	-	-
Carbohydrates (% of TS)	16.3	11.2	-	-
Sugars (% of TS)	1.1	0.8	1-10	-
Starches (% of TS)	2.4	1.6	10-19	-
Crude fibers (% of TS)	4.2	3.9	8-26	-
Proteins (% of TS)	6.0	4.9	10-18	-
TKN (% of TS)	1.0	0.8	-	-
Lipids (% of TS)	1.5	1.3	10-18	-
Carbon (% of TS)	13.1 [c]	9.8	45-52	30.5
Hydrogen (% of TS)	3.0 [c]	4.0	6.4-7.8	-
Oxygen (% of TS)	6.6 [c]	2.9	-	-
Nitrogen (% of TS)	0.6 [c]	0.2	2.2-3.1	-
Sulfur (% of TS)	0.3 [c]	0.2	0.2	-
C:N ratio	21.8	49.0	15.5-20.5	8.9
TMP (L/kg BVS) [d]	456	-	-	-
TMP (L/kg VS) [d]	376	471	495-548	-
TMP (L/kg TS) [d]	107	81	396-504	-

[a] Source sorted organic household waste from five Danish cities (Davidsson et al., 2007);

[b] Mechanically selected organic fraction of MSW from the municipal treatment plant “Calandrias” located in Jerez de la Frontera, Spain (Forster -Carneiro et al., 2008a);

[c] The corresponding fraction contained in BVS;

[d] Theoretical methane potential based on component composition (carbohydrates, proteins and lipids).

The theoretical methane potential (TMP) was used to assess the maximal methane production from complete degradation of the organic matter. The theoretical methane potential can be calculated from the component composition (carbohydrates, proteins, lipids) by the Buswell formula (Buswell and Mueller, 1952). The TMP of MS-OFMSW are lower than that of SS-OFMSW.

Table 2 lists the metal contents of MS-OFMSW. For $MS\text{-}OFMSW_a$, the rank of metal content is Ca > Fe > Al > K > Ni > Na > Mg > Cr > Mn >Zn > Cu > Pb >As > Cd > Hg. In case of $MS\text{-}OFMSW_b$, the order of metal content is Al > Ca > Fe > K > Na > Ni > Mg > Mn >Cr > Zn > Cu > Pb >As > Cd > Hg. When the anaerobic digestion is operated at 20% TSr, the contents of Al, Fe and Ni look like beyond the inhibitory level on anaerobic fermentation. However, only the metal ions are responsible for the inhibition. The inhibition of metals on anaerobic digestion will be investigated in following batch anaerobic digestion tests.

Table 2 Metal contents of MS-OFMSW

Metals	$MS\text{-}OFMSW_a$ (mg/kg TS)	$MS\text{-}OFMSW_b$ (mg/kg TS)	$MS\text{-}OFMSW_a$ (mg/L) [a]	$MS\text{-}OFMSW_b$ (mg/L) [a]	Inhibitory level (mg/L)[b]
Na	3662.5	2586.4	732.5	517.3	3500~5500
K	6803.3	4425.8	1360.7	885.2	2500~4500
Ca	29 003.9	20 320.7	5800.8	4064.1	2500~4500
Mg	2445.3	2348.4	489.1	469.7	100~1500
Al	21 251.6	23 484.4	4250.3	4696.9	1000
Fe	21 354.7	19 584.1	4270.9	3916.8	1750
Zn	157.7	455.0	31.5	91.0	160
Cu	85.6	221.0	17.1	44.2	170
Cd	4.9	7.0	1.0	1.4	180
Cr	770.7	467.2	154.1	93.4	450
Pb	43.5	177.6	8.7	35.5	-
Ni	5036.5	2549.1	1007.3	509.8	250
Mn	419.9	1233.4	84.0	246.7	-
Hg	<0.1	<0.1	<0.1	<0.1	-
As	7.9	10.8	1.6	2.2	-

[a]: Based on the anaerobic digestion at TSr 20%;

[b]: middle inhibitory level of metal ion on anaerobic digestion (Xu et al., 2006; Chen et al., 2008)

3.2. Evolution of pH, VFAs and NH_4^+-N

Fig.3 illustrates the evolution of pH, VFAs and ammonia nitrogen . The initial pH was 7.2 and 7.3 for $MS\text{-}OFMSW_a$ and $MS\text{-}OFMSW_b$. Due to the accumulation of VFAs, the pH decreased to the lowest of 6.6 and 6.9 at the day 4 and 2. Then the decreasing of VFAs concentration and the generation of ammonia yielded a increasing of pH. Then the pH was between 7.0 - 8.0.

The profiles of the total VFAs shows three stages: initially, an increase is observed from the day 0 to day 2 and 4 for $MS\text{-}OFMSW_a$ and $MS\text{-}OFMSW_b$ with the maximum value of 4461 mg/L and 2773 mg/L. Later, total VFAs dramatically decreased until the day 12 and 8 respectively. Finally, total VFAs softly decreased from 498 mg/L to 90 mg/L and 759 mg/L to 33 mg/L. The concentration of VFAs in the reactor was determined by their generation rate and consumption rate. During the first stage, hydrolysis and acidogenesis took place and the easy biodegradable fraction of organic waste was converted to volatile fatty acids (such as acetate, propionate and butyrate). At the same time, the methanogens were in adaptation period. During the second stage, aceticlastic methanogens were in exponential growth phase and the acetic acid consumption rate was superior to its generation rate even though the hydrolysis and acidogenesis were still going on. Hanaki et al. (1994) pointed out that the oxidation of propionate to acetate is more difficult than that of butyrate to acetate. Therefore, the propionate concentration is higher than others during second stage in present study. The hydrolysis of amino acids and proteins generated the accumulation of ammonia. The maximum concentrations of NH_4^+-N were 1566 mg/L and 1096 mg/L.

3.3. Biogas production

The specific biogas production rate (SBPR), volumetric biogas production rate (VBPR), methane content, cumulative biogas and methane production are used to describe the biogas production process and the results are illustrated in Fig.4.

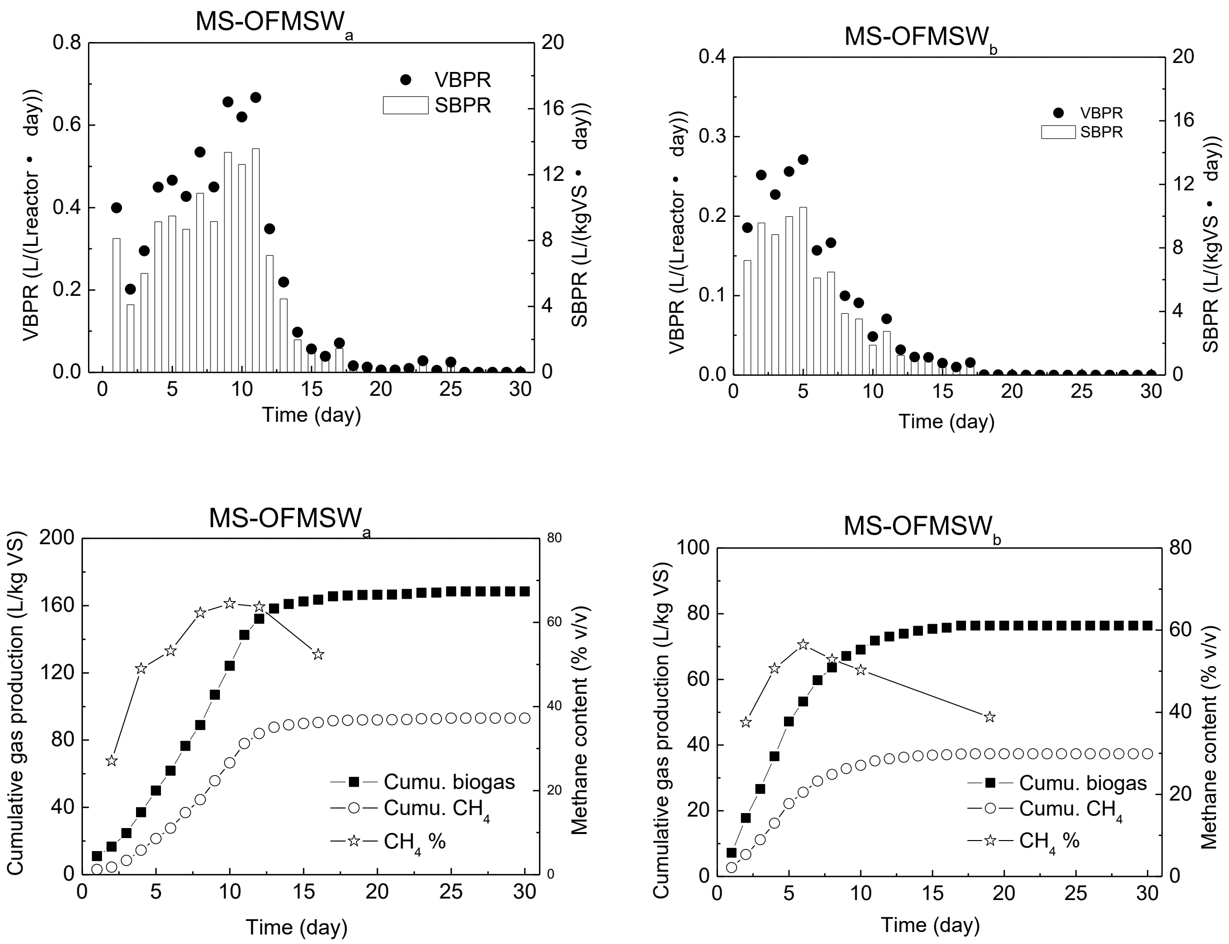


Fig4. Evaluation of the specific biogas production rate (SBPR), volumetric biogas production rate (VBPR), gas composition, cumulative biogas and methane production for MS-OFMSW

Compared to MS-OFMSW$_b$, MS-OFMSW$_a$ had better performance of biogas production. The maximum SBPR of 13.6 L/ (kgVS·day) and the maximum VBPR of 0.67 L/ (L·day) were observed at day 11 for MS-OFMSW$_a$. While, the maximum SBPR of 10.6 L/ (kgVS·day) and the maximum VBPR of 0.27 L/ (Lreactor·day) were found at day 5 for MS-OFMSW$_b$. The cumulative biogas productions at the end of day 30 were 168 and 76 L/kgVS respectively, and the cumulative methane productions were 93 and 37 L/kgVS. 90% of total biogas production was completed in the period of early 14 and 9 days for MS-OFMSW$_a$ and MS-OFMSW$_b$.

Table 3 compares the overall anaerobic digestion performance for MS-OFMSW$_a$, MS-OFMSW$_b$ and other OFMSW. The VS removal achieved 19.7% and 9.5% respectively which were much poorer than that of SS-OFMSW. The methane yields were also lower than that of SS-OFMSW. The same situation was observed on average methane content and efficiency of digestion. However, the methane yield of MS-OFMSWA was slightly higher than that of MS-OFMSW from Forster-Carneiro et al. ((Forster-Carneiro et al., 2008)). It is worth mentioning that the results of SS-OFMSW and MS-OFMSW were come from the thermophilic (55 ℃) anaerobic digestion. Since the high temperature condition is favorable for hydrolysis rate and degree of organic matters, the thermophilic anaerobic digestion may be a feasible method for increasing methane yield and VS removal.

Table 3 Comparison of anaerobic digestion performance

Parameters	MS-OFMSW$_a$	MS-OFMSW$_b$	SS-OFMSW [a]	MS-OFMSW [b]
Feed (gTS)	240	240	-	-
Feed (gVS)	68.6	41.1	-	-
TS removal (%)	5.7	1.6	-	-
VS removal (%)	19.7	9.5	74-89	-

VBPR ($L/(L_{reactor}\cdot d)$) [c]	0.67	0.27	-	-
SBPR ($L/(kg\ VS\cdot d)$) [d]	13.6	10.6	-	-
Biogas yield (L/kg TS)	48.8	13.1	-	-
Biogas yield (L/kg VS)	168.4	76.4	-	-
CH_4 yield (L/kg TS)	27.0	6.4	-	-
CH_4 yield (L/kg VS)	93.1	37.3	275-410	80
CH_4 yield (L/kg BVS)	113	-	-	-
Average CH_4 (%) [e]	55	49	58-64	-
E_{AD} (%) [f]	53	19	50-75	-

[a] Source sorted organic household waste from five Danish cities (Davidsson et al., 2007), thermophilic anaerobic digestion;

[b] Mechanically selected organic fraction of MSW from the municipal treatment plant “Calandrias” located in Jerez de la Frontera, Spain (Forster-Carneiro et al., 2008a) , thermophilic anaerobic digestion ;

[c] VBPR: the maximum volumetric biogas production rate;

[d] SBPR: the maximum specific biogas production rate;

[e] Average CH_4: cumulative methane production / cumulative biogas production;

[f] EAD: efficiency of anaerobic digestion, EAD = methane yield / theoretical methane potential based on component composition.

Optimum C/N ratios in anaerobic digesters are between 20 and 30. High C/N ratio is an indication of rapid consumption of nitrogen by methanogenesis and results in lower gas production. While, a low C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogens. In this study, the C/N ratio of MS-$OFMSW_a$ was 21.8, while the C/N ratio of MS-$OFMSW_b$ was 49.0. Therefore, this may be one reason why the methane yield of MS-$OFMSW_b$ was lower than that of MS-$OFMSW_a$. Optimum C/N ratios can be achieved by mixing of high and low C/N ratio material, such as OFMSW mixed with sewage sludge.

Fig.4 also indicates that there was no obvious inhibition of metals on anaerobic digestion for both MS-$OFMSW_a$ and MS-$OFMSW_b$. The ion concentrations of Al, Fe and Ni in liquid fraction of digested residue were all below the inhibition level (Table4). Compared with SS-OFMSW, the MS-OFMSW in this study showed the poor biodegradability and methane yield due to the presence of a large number of inorganic and inert matters. It is indicated that the current mechanically separation technology need to be improved.

Table 4 Nutrients and metal contents of digested residue of MS-OFMSW

Parameters	MS-$OFMSW_a$		MS-$OFMSW_b$		Criterion [a] (mg/kgTS)
	Solid (mg/kgTS)	Liquid (mg/L)	Solid (mg/kgTS)	Liquid (mg/L)	
pH	7.6	7.8	7.3	7.4	6.5~8.5
TN (N)	5680	530	5520	352	⩾5000
TP (P_2O_5)	9420	158	9840	120	⩾3000
TK (K_2O)	12 180	1970	12 130	1634	⩾10 000
Na	2858.9	706.6	4058.6	863.1	—
K	5785.7	1049.0	6606.4	1098.0	—
Ca	30 483.9	74.9	40 503.9	52.9	—
Mg	2833.5	100.4	3731.2	120.6	—
Al	30 710.1	1.3	38 229.7	<0.1	—
Fe	13 262.5	20.1	15 335.1	14.2	—
Zn	298.3	<0.1	444.8	<0.1	⩽500
Cu	118.3	0.1	189.4	<0.1	⩽250
Cd	5.5	<0.1	7.4	<0.1	⩽3
Cr	887.4	0.2	895.1	<0.1	⩽300

Pb	66.2	<0.1	136.9	<0.1	≤100
Ni	6467.2	99.7	7541.9	123.2	≤100
Mn	462.6	0.2	942.4	<0.1	—
Hg	<0.1	<0.1	<0.1	<0.1	≤5
As	14.5	<0.1	18.7	<0.1	≤30

a: Chinese control standards for urban solid wastes for agricultural use (GB 8172-87)

3.4. Characteristics of digested residue

Table 4 shows the nutrient and metal contents of the digested residue (including solid and liquid fractions) after 30 days digestion. This analysis was carried out for evaluating the potential of this stream as a fertilizer.

In order to reduce transportation cost, the digested residue usually was separated into a solid and a liquid fraction and the solid fraction was used as fertilizer. Separation facilitates the export of nutrients from the areas with excess of organic waste and the redistribution of nutrient to other areas in need of nutrients. For the $MS\text{-}OFMSW_a$, the separation generated 8.5%, 1.6% and 13.9% of TN, TP and TK loss which were contained in liquid fraction. In case of $MS\text{-}OFMSW_b$, the separation yielded 6.0%, 1.2% and 11.8% of TN, TP and TK loss. The nutrient contents in solid fraction for both $MS\text{-}OFMSW_a$ and $MS\text{-}OFMSW_b$ were higher than the lower value of criterion. However, four heavy metal contents (Cr, Cd, Pb and Ni) seriously exceeded the allowed levels when the solid fraction of digested residue used as fertilizer. It is necessary to determine the source of Cr, Cd, Pb and Ni and to separate source materials for using digested residue as fertilizer. Likely, these heavy metals come from dry battery which could not be seperated effectively and was crushed during the mechanically seperation process.

4. Conclusion

The biodegradability and methane production potential of $MS\text{-}OFMSW_a$ was higher than that of $MS\text{-}OFMSW_b$. $MS\text{-}OFMSW_a$ is suitble for anaerobic digestion treatment, while $MS\text{-}OFMSW_b$ is not. There was no inhibiton by VFAs, ammonia and heavy metal for AD of $MS\text{-}OFMSW_a$. The nutrient contents in solid fraction of digested residue of $MS\text{-}OFMSW_a$ and $MS\text{-}OFMSW_b$ all met the requirement of Chinese standards for urban solid wastes using as fertilizer. However, heavy metal contents (Cr, Cd, Pb and Ni) did not satisfy the requirement of Chinese standards. Current mechanically separation technology need to be improved for increasing biodegradability and reducing heavy metals

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