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Short Communication

Anaerobic digestion performance of vinegar residue in continuously stirred tank reactor

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HIGHLIGHTS

- Anaerobic digestion of vinegar residue was investigated in continuous condition.
- CSTR showed a stable methane yield of 232.75 mL g_{vs}^{-1} at OLR of 2.5 g_{vs} L^{-1} d^{-1}.
- Effluent recirculation significantly improved the stability of the AD system.

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ABSTRACT

Anaerobic digestion (AD) of vinegar residue was investigated in continuously stirred tank reactor (CSTR). The influence of organic loading rate (OLR) and effluent recirculation on AD performance of vinegar residue was tested. Five OLRs, 1.0, 1.5, 2.0, 2.5, and 3.0 g_{vs} L^{-1} d^{-1}, were used. The highest volumetric methane productivity of 581.88 mL L^{-1} was achieved at OLR of 2.5 g_{vs} L^{-1} d^{-1}. Effluent reflux ratio was set as 50%, the results showed that effluent recirculation could effectively neutralize the acidity of vinegar residue, raise the pH of the feedstock, and enhance the buffering capacity of the AD system. Anaerobic digestion of vinegar residue could be a promising way not only for converting this waste into gas energy but also alleviating environmental pollution which might be useful for future industrial application.

1. Introduction

Vinegar residue is a by-product of vinegar production; main components are bran and rice chaff. Due to its high acidity (pH = 4) and large quantity (about 1.8–2.2 million tons per year in China) (Zhong et al., 2012), vinegar residue could cause serious environmental problem if not properly treated before discharge. It has drawn much attention on effective utilization of this waste in China. Traditional treatment methods mainly include incineration, open discharge, and land filling, however, these methods often result in land, groundwater, and air pollution. Anaerobic digestion (AD) as a means of taking advantage of solid organic waste to produce energy-rich biogas and reduce pollution has gained more and more attention. It has been proven in previous research that AD technology could be applied for vinegar residue which represents a praiseworthy solution to deal with vinegar residue and a fascinating option for producing renewable energy (Feng et al., 2013), while continuous AD of vinegar residue still rarely reported.

Organic loading rate (OLR) is one of the important parameters during AD of organic wastes. In terms of efficiency, an optimized OLR is essential for effective running of continuous anaerobic reactor. In fact, the balance of the fermentation process and biogas production can also be greatly interfered by the OLR (Luste and Luostarinen, 2010). The main problem is that at high OLR, hydrolysis and acidification rate may be higher than methane production rate, the high concentration of volatile fatty acid (VFA)

Abbreviations: AD, anaerobic digestion; C/N ratio, carbon to nitrogen ratio; CSTR, continuously stirred tank reactor; HRT, hydraulic retention time; OLR, organic loading rate; TA, total alkalinity; TMY, theoretical methane yield; TS, total solids; TVFA, total volatile fatty acids; VFA, volatile fatty acids; VS, volatile solids.

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accumulated in the process of hydrolysis and acidification will ultimately lead to irreversible acidification (Nagao et al., 2012). High organic loading could lead to collapse of the subsequent biogas production system, a long time of recovery, or complete replacement of the materials within the reactor, so reactors are usually not run in highest OLR (Lerm et al., 2012). The effects of OLR on the AD of vinegar residue remain unclear.

It is easy to cause acidification during anaerobic fermentation of acidic organic wastes. Effluent recirculation can neutralize the organic acids produced in the fermentation, avoiding excessive acid phenomenon. Especially, in the case of high organic loading of solid fermentation, effluent recirculation is an effective method to solve the problem of traditional fermentation acidification. Nordberg Å et al found that the effluent recirculation caused the increase of alkalinity and the pH value and made it feasible to increase the OLR from 2.2 to 3 g_{vs} L^{-1} d^{-1} in the premise of maintaining hydrolysis and methane production at a stable state (Nordberg et al., 2007). Considering the high acidity of vinegar residue, the high loading may cause in a low pH environment in continuous feeding process, which might decrease the efficiency of CSTR. Effluent recirculation might be beneficial for AD of vinegar residue.

The objectives of this study were (1): to evaluate the anaerobic digestibility of vinegar residue in continuous condition; (2): to determine the stable methane yield of vinegar residue in continuously stirred tank reactor (CSTR); (3): to investigate the influence of OLR and effluent recirculation on the reactor performance.

2. Methods

2.1. Substrate and inoculum

Vinegar residue was collected from a vinegar factory in Jincheng, Shanxi province, China and then air-dried at room temperature for future use. The sludge was collected from a sewage treatment plant of Beijing as inoculum. Theoretical methane yield (TMY) of vinegar residue was calculated based on reported formula (Li et al., 2013b), which was also shown in Supplementary material.

2.2. Reactor setup and operation

The experiment was carried out in an 11 L CSTR digester with a working volume of 9 L (as shown in Fig. 1) and a HRT of 45 days. The reactor was made of organic glass, with one feed inlet on the upper right, and three discharging holes in the left side of different heights respectively. The reactor temperature was kept stable at 37 °C by circulating heated water and temperature control device. The stirring intensity and frequency were 60 r/min and 2–3 min per hour, respectively.

9 L sludge and a small amount of vinegar residue were added to the reactor and AD was conducted. After biogas production became stable and parameters such as pH value located in the normal range, the continuous feeding was started. Digester was operated with semi-continuous model. 200 mL of digestate was taken from discharge hole of the reactor before feeding. A certain amount of vinegar residue was combined with water up to 200 mL and then added into the reactor every day. The initial OLR was set as 1.0 g_{vs} L^{-1} d^{-1}, and then increased by 0.5 g_{vs} L^{-1} d^{-1} each time when biogas production kept stable for 10 d during the anaerobic process. At the OLR of 2.0 g_{vs} L^{-1} d^{-1}, effluent recirculation was investigated. 200 mL of digestate was taken out of reactor before feeding every day, and then filtered. After solid–liquid separation, 100 mL liquid was mixed with a certain amount of vinegar residue and water (made up to 200 mL) and then added into the reactor.

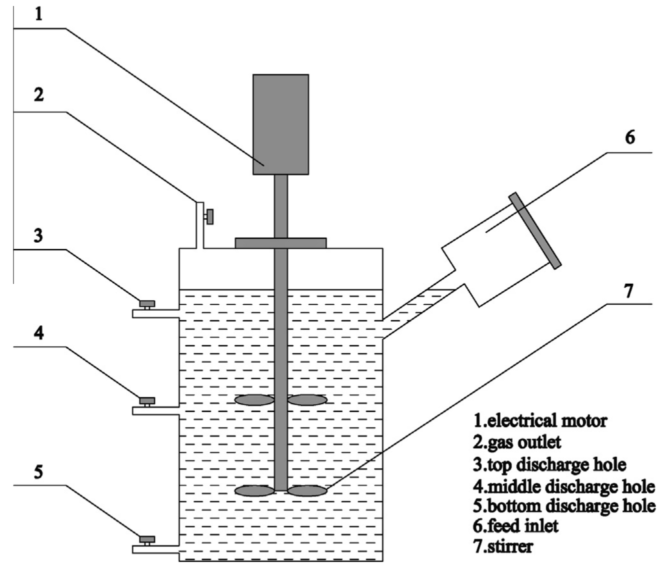

Fig. 1. Schematic diagram of CSTR anaerobic digester.

During the experimental period, the biogas production, gas components, and influent and effluent pH were chosen as the main parameters to follow-up the process stability and measured every day. Effluent samples were taken for alkalinity, VFA, TS, and VS analyses in every 3 days. The whole system ran for 128 days.

2.3. Analytical methods

The TS, VS contents of vinegar residue, sludge, and effluent, and total alkalinity were measured according to standard methods (APHA, 1998). The pH value was determined using pH meter (Mettler Toledo, USA) equipped with a le438 electrode. Elemental compositions (C, H, N, and S) were measured by an organic element analyzer (Vario EL cube, Germany). Oxygen content was determined using a 2400 II oxygen analyzer (Perkin Elmer Instruments, USA). The cellulose, hemicellulose, and lignin contents were determined according to the Van Soest method (Van Soest et al., 1991) by an A2000 fiber analyzer (ANKOM, USA). Biogas production, biogas composition, and VFA concentration were measured according to reported methods (Li et al., 2013a), which were also shown in Supplementary material.

2.4. Statistical analysis

The significant differences were determined using one way analysis of variance (ANOVA) by OriginPro 8.0 (Origin Lab, USA).

3. Results and discussion

3.1. Characteristics of feedstock

Table 1 showed characteristics of vinegar residue and inoculum. Vinegar residue had TS and VS content of 91.41% and 83.78%, respectively. The VS/TS ratio of 91.65%, indicated a relatively high organic content, was preferred by methane generation (Li et al., 2013a). Vinegar residue contained nearly 70% fiber (cellulose, hemicellulose, and lignin), lower than some widely used biomass such as corn stover, might be more suitable to be used for AD as organic substrates with high lignocelluloses content usually resulted in long digestion time and low biogas production (He et al., 2008). Vinegar residue had a carbon to nitrogen ratio (C/N ratio) of 23.06, which located in the appropriate range of

Table 1
Characteristics of substrate and inoculum.

Parameter	Vinegar residue	Sludge
TS (%)[a]	91.41 ± 0.05	3.10 ± 0.02
VS (%)[a]	83.78 ± 0.58	2.11 ± 0.02
VS/TS (%)	91.65 ± 0.71	68.14 ± 0.12
Cellulose (%)[b]	28.38 ± 0.16	NA
Hemicellulose (%)[b]	32.77 ± 0.19	NA
Lignin (%)[b]	9.58 ± 0.04	NA
C (%)[b]	43.14	31.33
H (%)[b]	6.22	4.23
O (%)[b]	39.34	NA
N (%)[b]	1.87	2.85
S (%)[b]	0.35	NA
C/N	23.06	11.00

NA: not analyzed.
[a] As total weight of sample.
[b] As TS of sample.

13.0–28.0 (Romano and Zhang, 2008), suggesting that vinegar residue might be fit for AD.

3.2. Methane production performance of different OLRs

The pH value and TS of influent at different OLRs were shown in Fig. 2a and b, respectively. The corresponding influent pH decreased from 5.65 to 4.81 and TS significantly increased from 7.37% to 14.74% as the OLR improved from 1.0 to 3.0 g_{vs} L^{-1} d^{-1}. Low pH could result in inhibition of methanogenesis and disruption of the anaerobic process (Brown and Li, 2013).

Fig. 3 showed the daily methane yield and volumetric methane productivity at different OLRs. The CSTR digester was operated for 128 days with the OLR increased gradually from 1.0 to 3.0 g_{vs} L^{-1} d^{-1}. Each OLR was conducted for about 30 days. In the anaerobic digestion of solid organic waste, methane yield is a key performance indicator to measure the efficiency of the reactor. The methane content of biogas in the whole process was basically stable at 50–60% without obvious fluctuations. With the increase of OLR from 1.0 to 3.0 g_{vs} L^{-1} d^{-1}, the corresponding average methane contents in biogas were found to be 51.34%, 50.39%, 50.12%, 53.44%, and 52.61%, respectively. The result showed that the increase of OLR may not produce obvious inhibition on methanogens in the system.

During the continuous process, the daily methane yield was fluctuated when the OLR increased and kept stable after running of 10 days. With the OLR increasing from 1.0 to 3.0 g_{vs} L^{-1} d^{-1}, daily methane yield was in the range of 150–260 mL g_{vs}^{-1}. As shown in Fig. 3b, the average daily methane yield was in the range of 214.4–232.75 mL g_{vs}^{-1} at the OLR lower than 3.0 g_{vs} L^{-1} d^{-1}. When the OLR improved to 3.0 g_{vs} L^{-1} d^{-1}, daily methane yield significantly decreased to 182.96 mL g_{vs}^{-1} ($\alpha < 0.01$). With the increase of OLR, the average volumetric methane productivity increased gradually and reached the top value of 581.88 mL L^{-1} at OLR of 2.5 g_{vs} L^{-1} d^{-1}, which had significant improvement ($\alpha < 0.01$) compared with 226.22, 312.31, and 442.92 mL L^{-1} at OLR of 1.0,

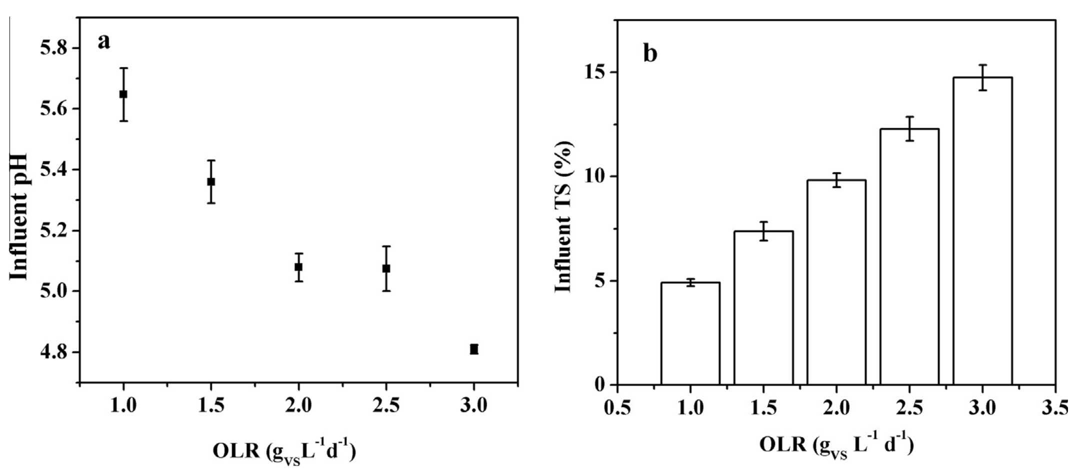

Fig. 2. Influent pH value and TS concentration at different OLRs.

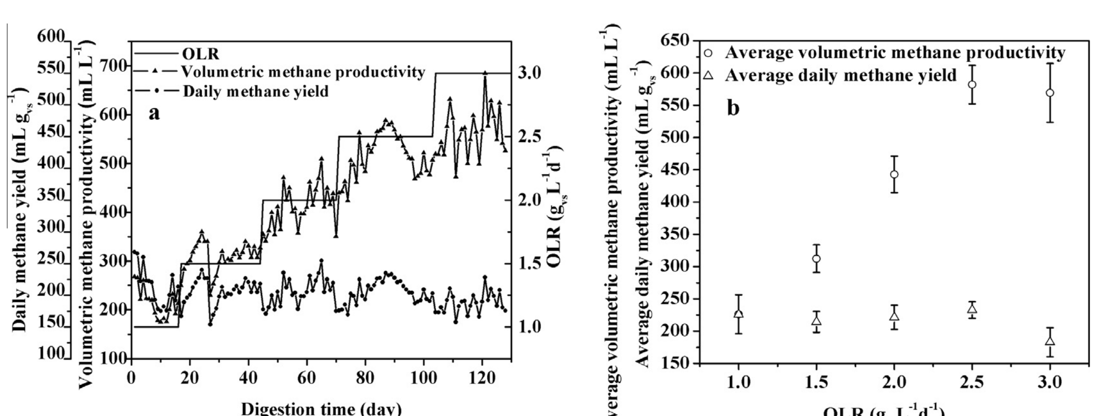

Fig. 3. Methane production in AD process. (a) Daily methane yield and volumetric methane productivity at different OLRs; (b) average methane yield and average volumetric methane productivity at different OLRs.

Table 2
The VFA concentration, pH, TA, and VFA/TA at different OLRs.

OLR (g_{vs} L^{-1} d^{-1})	VFA (mg L^{-1})	pH	TA (mg $CaCO_3$ L^{-1})	VFA/TA
1.0	114.1 ± 30.1	6.96 ± 0.18	1770.6 ± 70.3	0.06
1.5	114.6 ± 23.9	6.80 ± 0.02	1749.9 ± 95.8	0.07
2.0	232.8 ± 32.9	6.73 ± 0.01	1699.4 ± 88.7	0.14
2.5	344.6 ± 14.0	6.60 ± 0.04	1336.3 ± 307.2	0.26
3.0	622.2 ± 54.2	6.45 ± 0.03	914.9 ± 496.4	0.68

1.5, and 2.0 g_{vs} L^{-1} d^{-1}, respectively. When the OLR increased to 3.0 g_{vs} L^{-1} d^{-1}, average volumetric methane productivity declined to 569.2 mL L^{-1}, which had no significant difference ($\alpha > 0.05$) with that of 2.5 g_{vs} L^{-1} d^{-1}. In a word, both methane yield and volumetric methane productivity achieved the highest value at OLR of 2.5 g_{vs} L^{-1} d^{-1}.

3.3. Effects of OLR on VFAs

During the semi-continuously digested process, the concentration of total volatile fatty acids (TVFA) in the reactor was measured at stable stage of each OLR to determine the performance and stability of the anaerobic system. As shown in Table 2, the concentrations of TVFA were accumulated with the increase of OLR. The concentration of TVFA was rapidly improved to 622.2 mg L^{-1} at OLR of 3.0 g_{vs} L^{-1} d^{-1}, suggesting that the organic acids were not fully utilized. The high organic loading, hydraulic overload, and the presence of toxic inhibitor are the most common causes of fatty acid accumulation. Fatty acids (mainly propionate, and also acetate and butyrate) accumulation may lead to the failure of reaction (Ma et al., 2009). The result showed that at OLR of 3 g_{vs} L^{-1} d^{-1}, almost 80% of the VFAs were propionic acid, which was an undesirable terminal fermentation product. A number of studies have found that propionic acid accumulation can inhibit the activity of methanogens, which leads to the failure of methanation. (Wang et al., 2009).

3.4. Influence of OLR on pH and alkalinity

The pH value is an important index on the stability of anaerobic process. A preferred pH value generally located in the range of 6.8–8.2 (Raposo et al., 2011). The growth rate of methanogens is greatly reduced below pH 6.6 (Mosey and Fernandes, 1989). As shown in Table 2, pH showed a relatively decline with the increase of OLR which was associated with the accumulation of TVFA. The system pH decreased to 6.45 at the OLR of 3.0 g_{vs} L^{-1} d^{-1}, indicated that the condition was no longer suitable for anaerobic fermentation.

Alkalinity indicates the capacity to neutralize acids and provides protection against rapid changes in pH value (Raposo et al., 2012). The total alkalinity (TA) of a stable operation normally range from 1000 to 3000 mg $CaCO_3$ L^{-1} (Wilcox et al., 1995). The VFA/TA value is another indicator used to determine the stability of AD, and a value below 0.4 is preferred for AD (Li et al., 2014). As seen in Table 2, with the OLR increasing, alkalinity gradually declined and the VFA/TA value enhanced. The results showed that the lowest yield of 914.9 mg $CaCO_3$ L^{-1} and highest VFA/TA value of 0.68 were obtained at OLR of 3.0 g_{vs} L^{-1} d^{-1}, both indicated that the system was in a state of instability.

3.5. TS and TS removal in the effluent

The TS removal is an indicator of digestion efficiency of organic waste. As shown in Fig. 4, the effluent TS content in system showed a trend of gradual raise with the increase of OLR, suggested that TS was accumulated in the digester under the condition of high OLR. Partly because CSTR digester had been running a certain time at one loading, TS was accumulated to a certain degree and the TS removal was also reduced accordingly. When OLR reached 3.0 g_{vs} L^{-1} d^{-1}, both the effluent TS and TS removal presented substantial fluctuations, the average effluent TS was as high as 87 g L^{-1} while average TS removal was lower than 40%, suggested that the vinegar residue inside the system didnot digest completely, and it was also one of the reasons resulting in low methane production.

3.6. Influence of effluent recirculation on the digestion performance

The influence of effluent recirculation on the reaction was investigated with the OLR of 2.0 g_{vs} L^{-1} d^{-1}, maintaining for 30 days in order to compare with no effluent recirculation condition.

In the same condition of OLR, effluent recirculation condition had a slightly higher average methane content of 51.61% than no effluent recirculation condition which was 50.12%. The average daily methane yield in effluent recirculation condition and no effluent recirculation condition were 216.10 and 221.46 mL g_{vs}^{-1}, respectively. Compared with no effluent recirculation conditions, effluent recirculation did not have significantly influence ($\alpha > 0.05$) on methane content and daily methane yield. There was no significant difference ($\alpha > 0.05$) on the TVFA concentration between no effluent recirculation and effluent recirculation, which TVFA was 226.75 mg L^{-1} basically remained unchanged. The TS removal decreased from 55.90% to 50.31% after effluent recirculation, this was related to the effluent sample contained a certain amount of substrate. The pH showed a trend of rise after effluent recirculation, which had a great influence on alkalinity in the

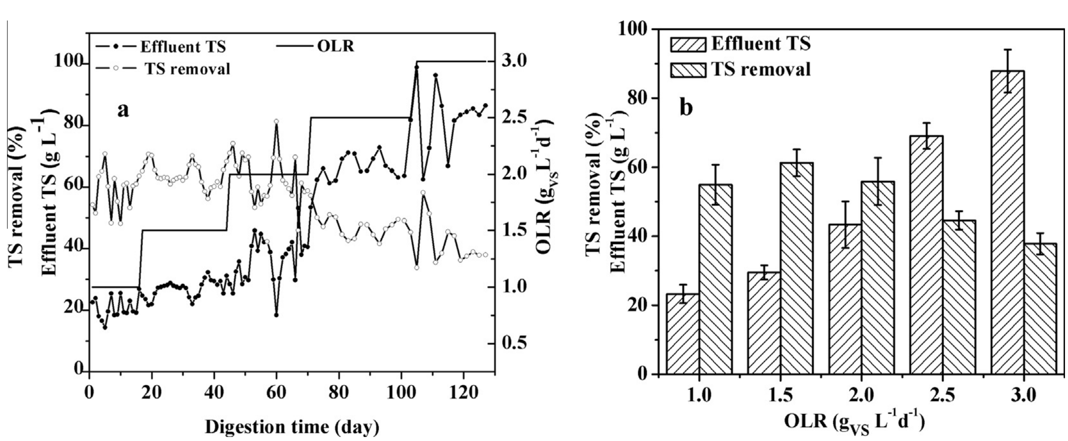

Fig. 4. TS changes at different OLRs. (a) Effluent TS and TS removal at different OLRs; (b) average effluent TS and average TS removal at different OLRs.

system. The alkalinity increased significantly ($\alpha < 0.01$) from 1699 to 2074 mg $CaCO_3$ L^{-1} after effluent recirculation, showed that system was in a relatively stable stage with the buffering capacity of pH changes. Other OLRs also achieved the similar results. Effluent recirculation significantly improved the stability of the system, and thus ensured the CSTR could maintain a relatively high processing capacity. The TMY of vinegar residue was calculated to be 472.33 mL g_{VS}^{-1}, but the highest methane yield achieved in this study was 232.75 mL g_{VS}^{-1}, indicating that more research on pretreatment of vinegar residue before AD might be necessary to improve methane production.

4. Conclusions

In this study, vinegar residue was anaerobic digested in a CSTR. At OLR of 2.5 g_{VS} L^{-1} d^{-1}, the highest methane yield and volumetric methane productivity were achieved 232.75 mL g_{VS}^{-1} and 581.88 mL L^{-1} respectively. The results showed that effluent recirculation could not only significantly improve the stability of the AD system and save water, but also remain the methane production in a high level. The results indicated that AD in CSTR is an effective and practical method for vinegar residue re-utilization and methane production. More research and industrialization is worth-while to be done in the future.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.03.086.

References

APHA, 1998. Standard Methods for the Examination of Water and Wastewater, 18th ed. American Public Health Association, Washington DC, USA.

Brown, D., Li, Y., 2013. Solid state anaerobic co-digestion of yard waste and food waste for biogas production. Bioresour. Technol. 127, 275–280.

Feng, L., Li, Y., Chen, C., Liu, X., Xiao, X., Ma, X., Zhang, R., He, Y., Liu, G., 2013. Biochemical methane potential (BMP) of vinegar residue and the influence of feed to inoculum ratios on biogas production. BioResources 8, 2487–2498.

He, Y., Pang, Y., Liu, Y., Li, X., Wang, K., 2008. Physicochemical characterization of rice straw pretreated with sodium hydroxide in the solid state for enhancing biogas production. Energy Fuels 22, 2775–2781.

Lerm, S., Kleyböcker, A., Miethling-Graff, R., Alawi, M., Kasina, M., Liebrich, M., Würdemann, H., 2012. Archaeal community composition affects the function of anaerobic co-digesters in response to organic overload. Waste Manage. 32, 389–399.

Li, Y., Feng, L., Zhang, R., He, Y., Liu, X., Xiao, X., Ma, X., Chen, C., Liu, G., 2013a. Influence of inoculum source and pre-incubation on bio-methane potential of chicken manure and corn stover. Appl. Biochem. Biotechnol. 171, 117–127.

Li, Y., Zhang, R., He, Y., Zhang, C., Liu, X., Chen, C., Liu, G., 2014. Anaerobic co-digestion of chicken manure and corn stover in batch and continuously stirred tank reactor (CSTR). Bioresour. Technol. 156, 342–347.

Li, Y., Zhang, R., Liu, G., Chen, C., He, Y., Liu, X., 2013b. Comparison of methane production potential, biodegradability, and kinetics of different organic substrates. Bioresour. Technol. 149, 565–569.

Luste, S., Luostarinen, S., 2010. Anaerobic co-digestion of meat-processing by-products and sewage sludge – Effect of hygienization and organic loading rate. Bioresour. Technol. 101, 2657–2664.

Ma, J., Mungoni, L.J., Verstraete, W., Carballa, M., 2009. Maximum removal rate of propionic acid as a sole carbon source in UASB reactors and the importance of the macro-and micro-nutrients stimulation. Bioresour. Technol. 100, 3477–3482.

Mosey, F., Fernandes, X., 1989. Patterns of hydrogen in biogas from the anaerobic digestion of milk-sugars. Water Sci. Technol. 21, 187–196.

Nagao, N., Tajima, N., Kawai, M., Niwa, C., Kurosawa, N., Matsuyama, T., Yusoff, F.M., Toda, T., 2012. Maximum organic loading rate for the single-stage wet anaerobic digestion of food waste. Bioresour. Technol. 118, 210–218.

Nordberg, Å., Jarvis, Å., Stenberg, B., Mathisen, B., Svensson, B.H., 2007. Anaerobic digestion of alfalfa silage with recirculation of process liquid. Bioresour. Technol. 98, 104–111.

Raposo, F., De la Rubia, M.A., Fernández-Cegrí, V., Borja, R., 2012. Anaerobic digestion of solid organic substrates in batch mode: an overview relating to methane yields and experimental procedures. Renew. Sustainable Energy Rev. 16, 861–877.

Raposo, F., Fernández Cegrí, V., De la Rubia, M., Borja, R., Béline, F., Cavinato, C., Demirer, G., Fernández, B., Fernández-Polanco, M., Frigon, J., 2011. Biochemical methane potential (BMP) of solid organic substrates: evaluation of anaerobic biodegradability using data from an international interlaboratory study. J. Chem. Technol. Biotechnol. 86, 1088–1098.

Romano, R.T., Zhang, R., 2008. Co-digestion of onion juice and wastewater sludge using an anaerobic mixed biofilm reactor. Bioresour. Technol. 99, 631–637.

Van Soest, P.J., Robertson, J.B., Lewis, B.A., 1991. Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition. J. Dairy Sci. 74, 3583–3597.

Wang, Y., Zhang, Y., Wang, J., Meng, L., 2009. Effects of volatile fatty acid concentrations on methane yield and methanogenic bacteria. Biomass Bioenergy 33, 848–853.

Wilcox, S., Hawkes, D., Hawkes, F., Guwy, A., 1995. A neural network, based on bicarbonate monitoring, to control anaerobic digestion. Water Res. 29, 1465–1470.

Zhong, M., Wang, Y., Yu, J., Tian, Y., Xu, G., 2012. Porous carbon from vinegar lees for phenol adsorption. Particuology 10, 35–41.