Bioresource Technology 101 (2010) 6329–6335

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Modeling biogas production from organic fraction of MSW co-digested with MSWI ashes in anaerobic bioreactors

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A R T I C L E   I N F O

Article history:
Received 4 January 2010
Received in revised form 8 March 2010
Accepted 11 March 2010
Available online 18 April 2010

Keywords:
MSW
Modeling
MSWI ashes
Anaerobic digestion
Gompertz plot

A B S T R A C T

This study aims at investigating the effects of MSW incinerator fly ash (FA) and bottom ash (BA) on the anaerobic co-digestion of OFMSW with FA or BA. It also simulates the biogas production from various dosed and control bioreactors. Results showed that suitable ashes addition (FA/MSW 10 and 20 g L^{-1} and BA/MSW 100 g L^{-1}) could improve the MSW anaerobic digestion and enhance the biogas production rates. FA/MSW 20 g L^{-1} bioreactor had the higher biogas production and rate implying the potential option for MSW anaerobic co-digestion. Modeling studies showed that exponential plot simulated better for FA/MSW 10 g L^{-1} and control bioreactors while Gaussian plot was applicable for FA/MSW 20 g L^{-1} one. Linear and exponential plot of descending limb both simulated better for BA/MSW 100 g L^{-1} bioreactor. Modified Gompertz plot showed higher correlation of biogas accumulation than exponential rise to maximum plot for all bioreactors.

1. Introduction

Municipal solid waste (MSW) has been mainly treated by MSW incinerator (MSWI) while partly treated by landfilling, resource recovery, composting and gasification in Taiwan. The MSWI could reduce the MSW volume and generate the electricity while it also produces the residues such as bottom ash (BA) and fly ash (FA). BA and FA contain various metals and recalcitrant organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzodioxins/furans (PCDD/Fs) and they need to be carefully treated to prevent secondary pollution. In spite of their hazardous nature, both BA and FA could be used as aggregate, backfill, soil amendment and cement additives after pretreatment. However, reports of BA or FA on co-disposal or co-digestion with MSW were not many (Lo et al., 2009; Lo, 2005; Lo and Liao, 2007; Banks and Lo, 2003; Boni et al., 2007). BA and FA addition might release alkali, heavy and trace metals resulting to the potentially beneficial or detrimental effects on the MSW anaerobic digestion (Lo et al., 2009; Lo, 2005). However, beneficial facilitation of MSW biodegradation by ash addition was still not well understood. Similar investigations were also reported that metals of different levels might stimulate or inhibit the organic substrate anaerobic digestion and fermentation process (Fermoso et al., 2009; Chen et al., 2008; Yuan et al., 2009; Tan et al., 2009; Altaş, 2009; Li and Fang, 2007; Lin and Shei, 2008; Yue et al., 2007; Kuo and Genthner, 1996; Gikas, 2007; Kida et al., 2001; Ma et al., 2009; Worm et al. 2009; Kurniawan and Lo, 2009). On the other hand, PAHs and PCDD/Fs of ashes and their release were investigated by several researchers and their adsorption by adsorbents and biodegradation by microorganisms were also reported (Wyrzykowska et al., 2009; Lin et al., 2008; Yasuhara and Katami, 2007; Wang et al., 2010; Ham et al., 2008; Liu et al., 2008; Nam

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doi:10.1016/j.biortech.2010.03.048

et al., 2005; Shitamura et al., 2005; Haritash and Kaushik, 2009; Oleszczuk, 2009; Stringfellow and Alvarez-Cohen, 1999; Li et al., 2008; Antizar-Ladislao et al., 2006).

MSW anaerobic biodegradation will lead to the conversion of MSW to biogas such as methane, carbon dioxide, hydrogen and other trace volatile organic compounds. Simulations of biogas, methane and hydrogen production rate and accumulation have been reported by several reports (Altaş, 2009; Li and Fang, 2007; Lin and Shei, 2008; Bilgili et al., 2009; De Gioannis et al., 2009; Kumar et al., 2004; Tosun et al., 2008; Wang and Wan, 2009; Erses et al., 2008; Mu et al., 2007; Li et al., 2008). It is noted that modeling of biogas production were generally based on the kinetic models (De Gioannis et al., 2009; Ueno et al., 2007; Rao and Singh, 2004; Sosnowski et al., 2008; Derbal et al., 2009; Boubaker and Ridha, 2008; Gali et al., 2009), however, some were based on ADM 1 model, mass and energy conservation, fugacity and flow model, thermodynamic equilibrium model and MODUELO 2 model (Shafi et al., 2006; Pontes and Pinto, 2006; Oh and Martin, 2007; de Cortázar and Monzón, 2007). Due to the microbial role in the anaerobic process, kinetic models particularly the first order kinetics were commonly applied to simulate the anaerobic biodegradation. Like the phase of bacterial growth, biogas production rate showed a rising limb and a decreasing limb which was indicated by exponential and linear equation (De Gioannis et al., 2009; Kumar et al., 2004). In addition, biogas accumulation could be simulated by exponential rise to maximum as well as modified Gompertz equations which were commonly used in the simulation of methane and hydrogen production (Altaş, 2009; Li and Fang, 2007; Lin and Shei, 2008; Wang and Wan, 2009).

So far the investigations using BA or FA for co-digestion or co-disposal with MSW have rarely undertaken (Lo et al., 2009; Lo, 2005; Lo and Liao, 2007; Banks and Lo, 2003; Boni et al., 2007). To bridge the existing gaps in the field of study, this work investigated the effects of various dose of MSWI FA and BA on the co-digestion of MSW and MSWI ashes. For this purpose, biogas production rates in varying doses and corresponding controls were modeled using linear, exponential and the Gaussian equations. In addition, biogas production accumulation was simulated using exponential rise to maximum and modified Gompertz plots.

2. Methods

2.1. Experimental

Four anaerobic bioreactors with uniform dimensions of 1.2 m for height and 0.2 m for internal diameter were applied in this study. All anaerobic bioreactors were packed with the mixture of 22 L MSW and 12 L anaerobic sludge seeding with a total working volume of ~34 L. They were arranged in four layers with each layer containing 6.5 L of MSW and sludge seeding mixture. Except control bioreactor, the top of each layer of BA/MSW 100 g L^{-1} (2 g g^{-1} VS) and FA/MSW 10 and 20 g L^{-1} (0.2 and 0.4 g g^{-1} VS) bioreactors were placed with the designate dose (Lo et al., 2009). The four anaerobic bioreactors were placed on an oven maintained at a temperature of ~35 °C suitable for anaerobic digestion.

Characteristics of synthetic MSW, sludge seeding and MSWI ashes were similar to the reports by Lo et al. (Lo, 2005; Lo and Liao, 2007; Lo et al., 2009). Major elements of organic MSW such as C, H, O, N etc. were measured by elemental analyzer (Heraeus varioIII-NCH). C, H, O and N was measured to be about 46%, 6%, 41% and 1.4%, respectively. Thus, the formula of MSW is calculated as $C_{38.3}H_{60}O_{25.63}N$. In addition, MSW and sludge seeding were measured to have TS ~6% (VS ~5%) and ~3% (VS ~2.5%), respectively. The combined VS of MSW and anaerobic sludge seeding was measured and calculated to be 4.12%. The leachate of combined mixture had a pH, alkalinity, COD and volatile acids of ~7.7, ~208, ~4734 and ~83 mg L^{-1}, respectively. Metal constituents of the MSW, sludge seeding and MSWI ashes were also measured and reported (Lo, 2005; Lo and Liao, 2007; Lo et al., 2009). PAHs and PCDD/Fs contents and their release from FA and BA were also referred to several literatures as tabulated in Table S1 (Supplementary).

2.2. Analytical

Biogas production of the anaerobic bioreactors was measured by the water replacement method in the room temperature of ~25 °C and atmospheric pressure of ~1 atm. Parameters such as pH, electrical conductivity (EC), alkalinity, volatile solids (VS), volatile acids (VAs), chemical oxygen demand (COD) in leachates of anaerobic bioreactors were measured according to standard methods (APHA, 1995). In addition, released metals from the MSWI ashes in leachate were analyzed by ICP-OES (IRIS Intrepid II, Thermal Electron Corporation) after sampling and membrane filtration. Analytical method followed the manual of manufacturer. Briefly speaking, ICP-OES was set at the required operational conditions. Incident energy was 1100 W and reflective energy was <5 W. Observational mode of plasma was side on and the plasma height was 14 mm. Argon was used to produce the desired high temperature with RF power (1150 W). Nebulizer flow (25 PSI) and auxiliary flow were set at 0.75 and 0.5 L min^{-1}, respectively. Data acquisition was obtained with TEVA software (Thermo Elemental). All analytical methods followed the standard method for the examination of water and wastewater (APHA, 1995).

2.3. Biogas production simulation

Biogas production rates of MSW anaerobic digestion was simulated using linear, exponential and Gaussian plots. The linear equation of the two stages in ascending and descending limbs could be expressed in Eq. (1) (Kumar et al., 2004). Presumably biogas production rate would improve linearly with an increasing time, and after a climax it would decrease linearly to zero as time continuously increases

$$y = a + bt \tag{1}$$

where y is the biogas production rate (L kg^{-1} d^{-1}) at time t (day), t is the time (day) over the digestion period. a is intercept (L kg^{-1} d^{-1}) and b is slope (L kg^{-1} d^{-2}). For rising limb, b is positive whereas b is negative for falling limb.

Assuming that biogas production rate would improve exponentially with an increasing period of time and after the climax, it then decrease exponentially to zero as the time continuously increases, the exponential plot for the ascending and descending limbs could be presented in Eq. (2) (De Gioannis et al., 2009):

$$y = a + b\exp(ct) \tag{2}$$

where y is the biogas production rate (L kg^{-1} d^{-1}) at time t (day), t is the time (day) over the digestion period. a and b are constants (L kg^{-1} d^{-1}) and c is also a constant having different unit (d^{-1}). For rising limb, c is positive whereas c is negative for falling limb.

Assuming that biogas production rates and microbial kinetic growth and its decay would follow the normal distribution over the course of digestion period, the Gaussian equation, presented in Eq. (3), could be applied to simulate biogas production rates including ascending and descending limb

$$y = a\exp(-0.5((t - t_0)/b)^2) \tag{3}$$

In this equation, y is the biogas production rate (L kg^{-1} d^{-1}) at time t (day), t is the time (day) over the digestion period. a (L kg^{-1} d^{-1}) and b (day) are constants and t_0 is the time (day) where the peak (maximal) biogas production rates occurred.

In addition, biogas accumulation was simulated using exponential rise to maximum and modified Gompertz equations. Exponential rise to maximum equation is presented in Eq. (4) based on Bilgili et al. (2009) and De Gioannis et al. (2009):

$$y = A(1 - \exp(-kt)) \tag{4}$$

where y is the biogas accumulation (L kg^{-1}) at time t (day), t is the time (day) over the digestion period. A is the biogas production potential (L kg^{-1}) and k is the first order kinetic constant (d^{-1}).

Another equation for simulation is modified Gompertz equation. This equation was modified via Gompertz equation. Gompertz equation is expressed as follow:

$$y = A\exp[-\exp(b - ct)] \tag{5}$$

where y is the biogas accumulation (L kg^{-1}) at time t (day), t is the time (day) over the digestion period. A is the biogas production potential (L kg^{-1}). c is a constant (d^{-1}) and b is also a constant (no unit). Gompertz equation is modified to be modified Gompertz equation which is commonly used to simulate the biogas accumulation.

For the modified Gompertz equation (Altaş, 2009; Lin and Shei, 2008; Li and Fang, 2007; Mu et al., 2007; Li et al., 2008), it could be presented as follow:

$$y = A\exp\left\{-\exp\left[\frac{\mu_m e}{A}(\lambda - t) + 1\right]\right\} \tag{6}$$

where y is the biogas accumulation (L kg^{-1}) at time t (day), t is the time (day) over the digestion period. A is the biogas production potential (L kg^{-1}). μ_m is the maximal biogas production rate (L kg^{-1} d^{-1}) while λ is the lag phase (day) and e is equal to 2.718282. All regression models were completed by SigmaPlot 10 version.

2.4. Statistical

The ANOVA test of various ashes dose and control on the biogas accumulation and biogas production rate of experimental data over time were analyzed with SPSS 15 version. Differences were considered statistically significant when $p \leqslant 0.05$ for statistical tests.

In addition, skewness and kurtosis of the biogas production rates pertaining to curves distribution in the four anaerobic bioreactors were investigated. Coefficient of skewness is expressed as follow:

$$\beta = \frac{n}{(n-1)(n-2)}\sum_{i=1}^{n}\left(\frac{X - \bar{X}}{S}\right)^3 \tag{7}$$

where β is coefficient of skewness (no unit), n is sample number and S is standard deviation (L kg^{-1} d^{-1}). X and $\bar{X}$ are biogas production rates and average biogas production rate (L kg^{-1} d^{-1}) over the digestion period, respectively. If β is equal to 0, it is normal distribution (symmetrical distribution). β grater than zero represents right skewness (distribution curve sift to right) while β less than zero represents left skewness (distribution curve shift to left). Coefficient of kurtosis is expressed as follow:

$$\gamma = \left\{\frac{n(n+1)}{(n-1)(n-2)(n-3)}\sum_{i=1}^{n}\left(\frac{X - \bar{X}}{S}\right)^4\right\} - \frac{3(n-1)^2}{(n-2)(n-3)} \tag{8}$$

where γ is coefficient of kurtosis (no unit), n is sample number and S is standard deviation (L kg^{-1} d^{-1}). X and $\bar{X}$ are biogas production rate and average biogas production rate (L kg^{-1} d^{-1}), respectively. If $\gamma = 0$, it is called Mesokurtotic (normal kurtosis) while $\gamma > 0$ or $\gamma < 0$ represents Leptokurtotic (high kurtosis) or Platykurtotic (low kurtosis), respectively.

3. Results and discussion

3.1. Biogas production rate and accumulation

Biogas production rate and accumulation were presented in Fig. 1(a) and (b). Experimental results showed that the whole complete digestion period was ~40, ~70, ~120 and ~175 days for BA/MSW 100 g L^{-1}, FA/MSW 10, 20 g L^{-1} dosed and control bioreactors, respectively. Ashes dosed bioreactors appeared to have shorter digestion period and higher biogas production rates than control one. The peak biogas production rate occurred at about day 25, 35, 30 and 30 for BA/MSW 100 g L^{-1}, FA/MSW 10, 20 g L^{-1} dosed and control bioreactors, respectively. Peak (maximal) biogas production rates were found to be in the order of FA/MSW (20 g L^{-1}; ~6.5 L d^{-1} kg^{-1} VS) ≈ FA/MSW (10 g L^{-1}; ~6.5 L d^{-1} kg^{-1} VS) > BA/MSW (100 g L^{-1}; ~5.5 L d^{-1} kg^{-1} VS) > control (~3.5 L d^{-1} kg^{-1} VS). It is obviously observed that maximal biogas production rates were enhanced by the designate ashes dose. On the other hand, total biogas production was found in the order of FA/MSW (20 g L^{-1}; ~222 L kg^{-1} VS) > control (~209 L kg^{-1} VS) > FA/MSW (10 g L^{-1}; ~166 L kg^{-1} VS) > BA/MSW (100 g L^{-1}; ~124 L kg^{-1} VS), respectively. The FA/MSW 20 g L^{-1} dosed bioreactor appeared to have the experimental highest peak biogas production rate and total biogas production among the four bioreactors. On the other hand, control bioreactor had the lowest peak biogas production rate, however, it produced total biogas production only slightly less than FA/MSW 20 g L^{-1} dosed bioreactor. Biogas production rates in the control bioreactor over the digestion period were comparatively lower compared to those in the ashes dosed bioreactors. However, biogas production rates in the control bioreactor lasted a comparatively longer period over the whole digestion period leading to a comparatively higher total biogas production only slightly less than that of FA/MSW 20 g L^{-1} dosed bioreactor.

3.2. Anaerobic parameters

Key parameters of pH, EC, COD, alkalinity, VS and VAs for MSW anaerobic digestion in the four bioreactors were measured (Supplementary Fig. S1). Results showed that most pH, EC, COD, alkalinity, VS and VAs were found in the range of ~6.3–7.1, ~4.1–18.8 ms cm^{-1}, ~198–5226 mg L^{-1}, ~738–3193 mg L^{-1}, ~0.2–0.67% and ~0.8–245 mg L^{-1}, respectively. Most pHs in all bioreactors were found to be suitable for anaerobic digestion (pH 6.5–7.5). pH, COD, alkalinity and VAs were found to have similar values. However, EC were observed to be higher in FA dosed bioreactors than BA dosed and control ones due to potential higher release of alkali metals and anions from MSWI FA. VS was also found higher in ashes dosed bioreactor compared to those in control one indicating the potential enhanced microbial activity in ashes dosed bioreactors.

Apart from anaerobic parameters, released metals such as alkali metals, heavy metals and trace metals in leachate from ashes dosed and control bioreactors were analyzed. Alkali metals of Ca, Mg, K and Na were found to have higher released amounts particularly found in the FA/MSW 20 g L^{-1} dosed bioreactor (Supplementary Fig. S2). This phenomenon reflected the facts that higher FA dose could release higher amount of alkali metals and anions leading to a potential higher EC values. Released heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) and trace metals (Co, Mo, W and Fe) concentrations showed to have similar ranges in all bioreactors with some found higher in the ashes dosed bioreactors (Supplementary Figs. S3 and S4). Suitable levels of alkali metals, heavy metals and trace metals were reported to have the potential to enhance the microbial activity and stimulate the anaerobic digestion and fermentation process (Lo et al., 2009; Fermoso et al., 2009; Chen et al., 2008; Yuan et al., 2009; Tan et al., 2009; Altaş, 2009; Li

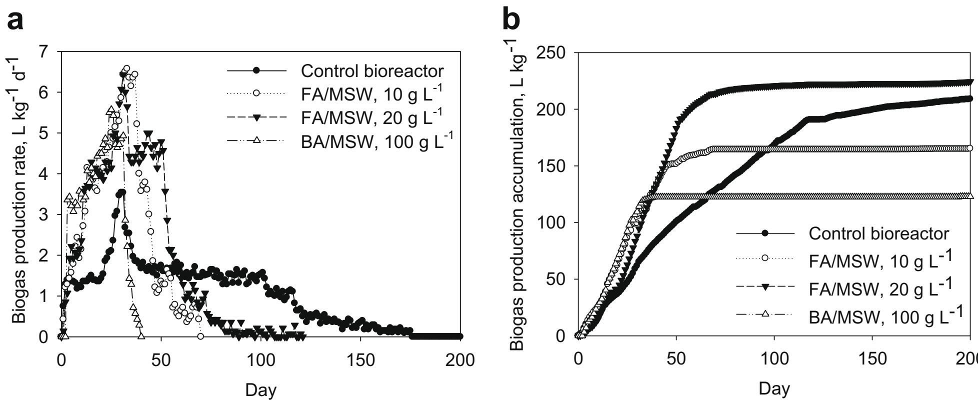

Fig. 1. Biogas production rates (a) and biogas accumulation (b) in control and three different ashes dosed bioreactors (●: control bioreactor without ash addition; ○: FA/MSW 10 g L^{-1} dosed bioreactor; ▼: FA/MSW 20 g L^{-1} dosed bioreactor; △: BA/MSW 100 g L^{-1} dosed bioreactor).

and Fang, 2007; Lin and Shei, 2008; Yue et al., 2007; Ma et al., 2009; Worm et al., 2009) as listed in Table S5. Those levels in the control and ashes dosed bioreactors were found to have potential stimulation rather than inhibition particularly occurred in the ashes dosed bioreactors (Table S5). It is therefore thought that proper BA and FA dose might release suitable levels of alkali metals, heavy metals and trace metals that could enhance the MSW digestion performance.

3.3. Modeling

Fig. 2 showed the liner plots of biogas production rates in control and three various ashes dosed bioreactors. R^2 of all bioreactors in the rising and falling limb ranged from 0.712 to 0.9579. Similarly, Fig. 3 depicted the exponential plot of biogas production rates in control and three various ashes dosed bioreactors. R^2 of exponential plot ranged from 0.7227 to 0.9579 showing slightly rather better simulation than those of linear regression particularly found in the rising and falling limb of FA/MSW 10 g L^{-1} dosed bioreactors. For Gaussian plots (Fig. 4), R^2 was found in the order of FA/MSW (20 g L^{-1}, 0.9486) > FA/MSW (10 g L^{-1}, 0.9097) > control bioreactor (0.8407) > BA/MSW (100 g L^{-1}, 0.7308). This result implied that the Gaussian plots of biogas production rates favored the FA dosed bioreactors. All results stated above were also tabulated in Table S2 (Supplementary).

As respect to biogas accumulation simulation, modified Gompertz plots showed better R^2 (0.9938–0.9977) than exponential rise to maximum plots (0.9316–0.9907) (Figs. 5 and 6). These results also could be found in supplementary (Supplementary Table S3). In exponential rise to maximum equations (Fig. 5, Supplementary Table S3), first order kinetic constants (k values) were found in the order of BA/MSW (100 g L^{-1}, 0.0501) > FA/MSW (10 g L^{-1}, 0.0340) > FA/MSW (20 g L^{-1}, 0.0235) > control (0.0112). However, the total biogas production showed the different order as follow: control (~241.9 L kg^{-1}) ≈ FA/MSW (20 g L^{-1}, ~234.6 L kg^{-1}) > FA/MSW (10 g L^{-1}, ~168.9 L kg^{-1}) > BA/MSW (100 g L^{-1}, ~124.4 L kg^{-1}). In modified Gompertz equation, FA and BA dosed bioreactors demonstrated comparatively higher maximal biogas production rate (μ_m) and lag phase (λ) as depicted in Fig. 6 and Table S3. μ_m and λ were found 5.40 L kg^{-1} d^{-1} and 12.74 d for FA/MSW 20 g L^{-1}, 5.533 L kg^{-1} d^{-1} and 6.218 d for BA/MSW 100 g L^{-1}, 4.507 L kg^{-1} d^{-1} and 5.67 d for FA/MSW 10 g L^{-1}, 1.985 L kg^{-1} d^{-1} and 1.55 d for control bioreactor, respectively. μ_m values of modified Gompertz equation seemed to be lower than those of experimental peak biogas production rates in the four bioreactors. Higher μ_m values and higher experimental peak biogas production rates were found in the ashes dose bioreactors.

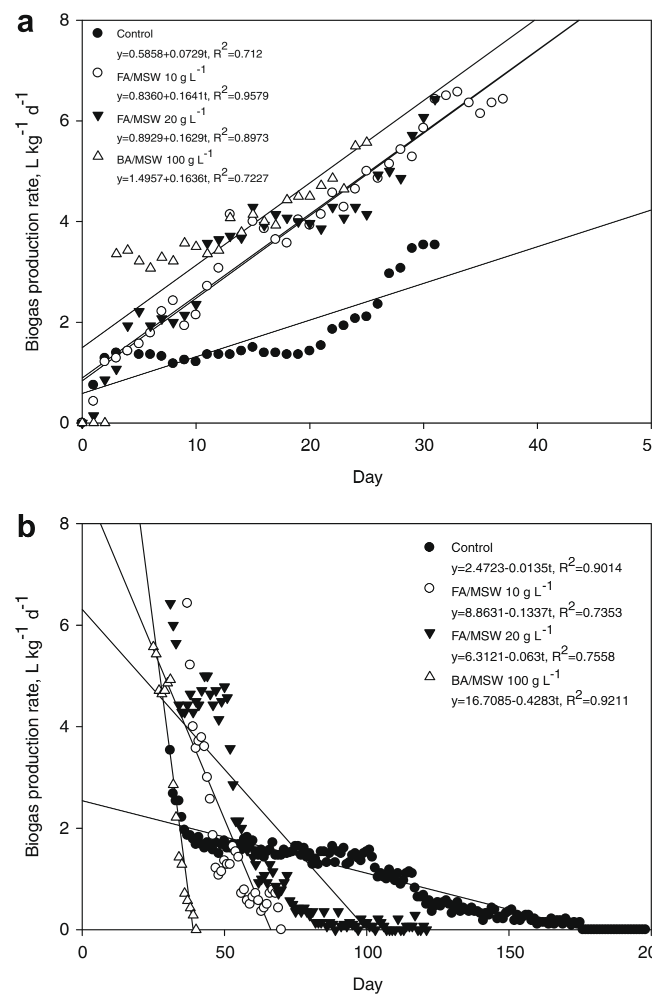

Fig. 2. Linear plots of biogas production rates of ascending (a) and descending limb (b) in control and three different ashes dosed bioreactors (●: control bioreactor without ash addition; ○: FA/MSW 10 g L^{-1} dosed bioreactor; ▼: FA/MSW 20 g L^{-1} dosed bioreactor; △: BA/MSW 100 g L^{-1} dosed bioreactor).

3.4. Statistical analysis

Biogas accumulation and biogas production rates of experimental data were analyzed with ANOVA test for the significance of BA and FA addition. Results of ANOVA test were shown to have significant results ($p < 0.05$) by various ashes dosing. This phenomenon

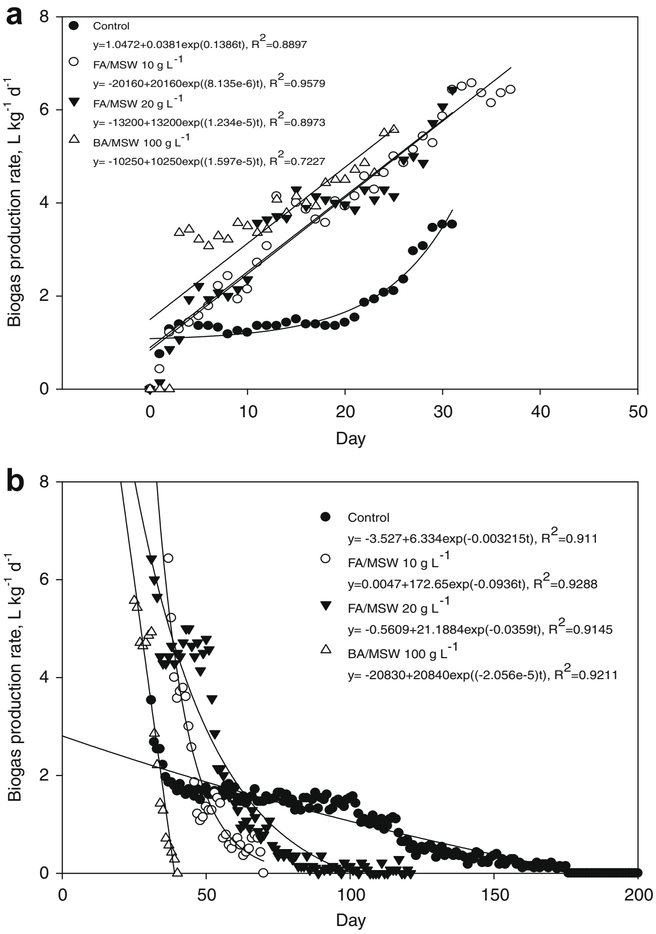

Fig. 3. Exponential plots of biogas production rates of ascending (a) and descending limb (b) in control and three different ashes dosed bioreactors (●: control bioreactor without ash addition; ○: FA/MSW 10 g L^{-1} dosed bioreactor; ▼: FA/MSW 20 g L^{-1} dosed bioreactor; △: BA/MSW 100 g L^{-1} dosed bioreactor).

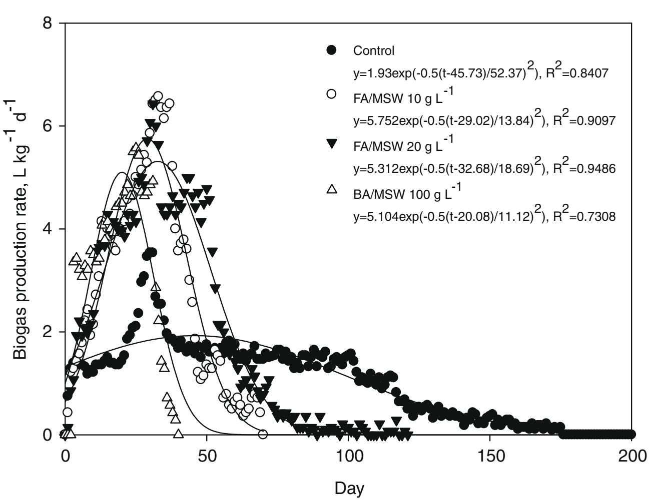

Fig. 4. Gaussian plots of biogas production rates in control and three different ashes dosed bioreactors (●: control bioreactor without ash addition; ○: FA/MSW 10 g L^{-1} dosed bioreactor; ▼: FA/MSW 20 g L^{-1} dosed bioreactor; △: BA/MSW 100 g L^{-1} dosed bioreactor).

also reflected the facts that peak (maximal) biogas production rates (μ_m) in modified Gompertz plot and first order kinetic constants (k) in the exponential rise to maximum plot in the ashes dosed bioreactors were enhanced and were significantly different from those in the control one ($p < 0.05$). Although ashes dosing could enhance the biogas production rates, on the other hand, BA/MSW 100 g L^{-1} and FA/MSW 10 g L^{-1} dosed bioreactors seemed to have the less total biogas production compared to control and FA/MSW 20 g L^{-1} dosed bioreactors. This result was interpreted that proper ashes dose might have the potential to enhance the MSW biodegradation leading to a faster VFA production that would be further metabolized to biogas production. However, VFA might be neutralized by the released alkalinity and anions such as OH^{-1} leading to a comparatively lower total biogas production particularly found in the BA/MSW 100 g L^{-1} dosed bioreactor.

Distribution of biogas production rates in the control and ashes dosed bioreactors could be distinguished by skewness and kurtosis (Table S4). Coefficients of skewness (β) was found negative (−0.7279, left skewness) in the BA/MSW 100 g L^{-1} dosed bioreactor while those were found positive in the control (0.4825, right skewness), FA/MSW 10 g L^{-1} (0.3983, right skewness) and 20 g L^{-1} (0.5465, right skewness) dosed bioreactors, respectively. These results demonstrate the facts that left skewness might shorten the digestion period and lead to the least total biogas production potentially found in the BA/MSW 100 g L^{-1} dosed bioreactor. As respect to the kurtosis, coefficient of kurtosis (γ) in the control bioreactor was found to be positive (0.5669, leptokurtotic) while those in the FA/MSW 10, 20 g L^{-1} and BA/MSW 100 g L^{-1} dosed bioreactors were found to be negative corresponding to −1.1109 (platykurtotic), −1.2655 (platykurtotic) and −0.7309 (platykurtotic), respectively. This result was attributed to the phenomenon that biogas production rates in the control bioreactor were not enhanced (but also not inhibited) possibly due to the lack of ash addition that might provide the necessary growth nutrients for anaerobic bacteria. Therefore, biogas production rates in the control bioreactor over the digestion period were comparatively lower. However, biogas production rates in the control bioreactor lasted a comparatively longer period and show to have rather peak generation rates in a shorter period over the whole digestion period leading to a comparatively higher total biogas production (only slightly less than that of FA/MSW 20 g L^{-1} dosed bioreactor) and leptokurtotic distribution.

3.5. Implication and application

The three bioreactors with varying doses (10 and 20 g L^{-1} of FA/MSW and 100 g L^{-1} of BA/MSW) were found to be able to improve the MSW biodegradation and enhance the biogas production rates compared to the control. Depending on their concentrations, the ashes could release soluble metal as nutrients required for the growth of anaerobic microbes, thus stimulating the MSW anaerobic digestion (Figs. S2–S4). In this regard, the metal levels of stimulation on the anaerobic process have been reported previously (Kuo and Genthner, 1996; Kida et al., 2001; Gikas, 2007; Li and Fang, 2007; Yue et al., 2007; Chen et al., 2008; Altaş, 2009; Fermoso et al., 2009; Yuan et al., 2009; Tan et al., 2009; Lin and Shei, 2008; Ma et al., 2009; Worm et al., 2009) and their data are presented in Table S5. The metal concentrations in the bioreactors after MSW biosorption at varying doses in this study were comparable to the data collected from literatures and showed a stimulatory effects rather than inhibitory consequences on the MSW anaerobic digestion.

These studies showed that an optimum dose of ashes could release suitable metal nutrients which could enhance microbial activities, thus improving the MSW biodegradation (Lo, 2005; Lo et al., 2009). On the other hand, as reflected by Table S1, both PAHs and PCDD/Fs were likely to be released, resulting from the addition of ashes (Nam et al., 2005; Yasuhara and Katami, 2007; Lin et al., 2008; Ham et al., 2008; Liu et al., 2008; Wyrzykowska et al.,

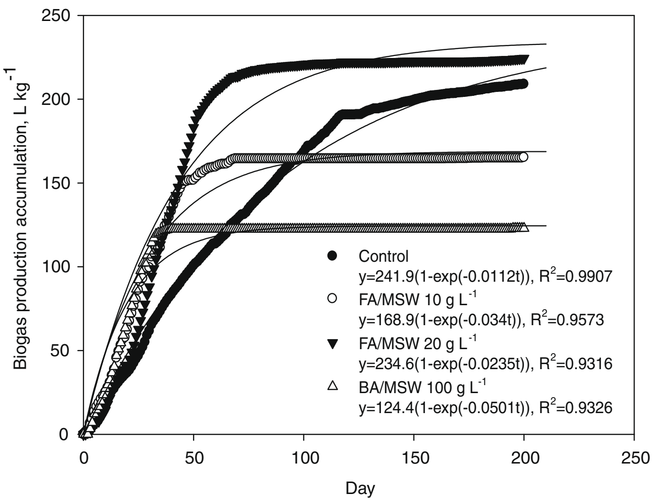

Fig. 5. Exponential rise to maximum plots of biogas accumulation in control and three different ashes dosed bioreactors (●: control bioreactor without ash addition; ○: FA/MSW 10 g L^{-1} dosed bioreactor; ▼: FA/MSW 20 g L^{-1} dosed bioreactor; △: BA/MSW 100 g L^{-1} dosed bioreactor).

2009; Wang et al., 2010). However, the toxic compounds might be partly adsorbed by the MSW and partly biodegraded by the anaerobic bacteria (Stringfellow and Alvarez-Cohen, 1999; Nam et al., 2005; Shitamura et al., 2005; Antizar-Ladislao et al., 2006; Li et al., 2008; Haritash and Kaushik, 2009; Oleszczuk, 2009). This suggests that PAHs and PCDD/Fs levels might pose no adverse effects on the MSW anaerobic digestion.

The ashes-added bioreactors showed higher k values in the exponential rise to maximum and higher μ_m and λ values in the modified Gompertz plots compared to the control. This implies that the suitable addition of MSWI ashes might have enhanced the biodegradation of MSW and biogas production rates as indicated in Figs. 5 and 6 and Table S3 although ashes dosed bioreactors showed a higher lag in the start. The mathematical modeling was employed to simulate biogas production rates and its accumulation with or without the addition of ashes. Anaerobic parameters might be affected by the operating conditions such as the various doses of ash (Tables S2 and S3), pH and temperature. In theory, temperature of 35 and 55 °C and pH of 6.5–7.5 were the suitable ranges for anaerobic digestion. In this study, the amount of ash was varied, while keeping temperature constants (35 °C). Original pH of MSW was ~pH 7. After various ashes addition, the most pHs varied between ~6.3 and ~7.1 (Fig. S1a) which was suitable for anaerobic digestion. Extreme pHs higher than pH 8.5 or lower than pH 5.5 were not applicable for anaerobic digestion. Under the experimental conditions, the findings indicated the applicability of the model in this study.

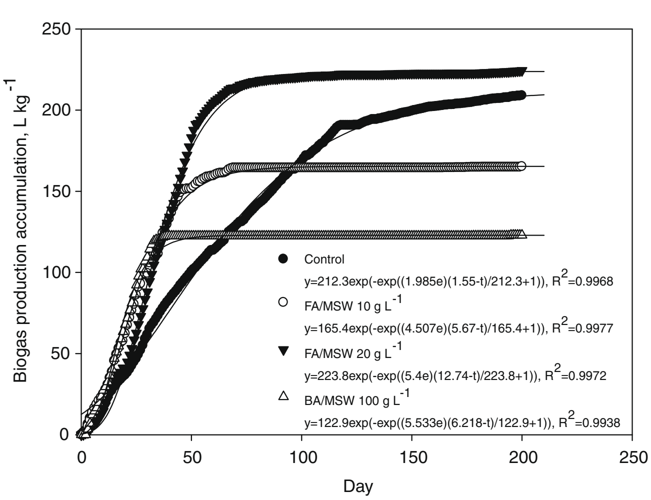

Fig. 6. Modified Gompertz plots of biogas accumulation in control and three different ashes dosed bioreactors (●: control bioreactor without ash addition; ○: FA/MSW 10 g L^{-1} dosed bioreactor; ▼: FA/MSW 20 g L^{-1} dosed bioreactor; △: BA/MSW 100 g L^{-1} dosed bioreactor).

MSW anaerobic digestion is an important option for the MSW treatment due to the potential energy recovery of biogas (CH_4 and H_2) and further electricity utilization. In this study, suitable MSWI ashes addition had the potential to enhance the MSW anaerobic digestion. Organic fraction of MSW could be prepared to be ~6–10% (TS), then it could be mixed with suitable MSWI ashes from the result of study for a typical full scale anaerobic digester operation. As the environmental conditions such as suitable pH, temperature and other factors were performed, the efficiency of anaerobic co-digestion of MSW and ashes could be improved. Except the biogas utilization, the anaerobic digestate might be further tested to comply with regulatory standard for further fertilizer or soil amendment use.

4. Conclusions

Biogas production rates of MSW were enhanced by applying suitable ashes dose of FA/MSW (20 and 10 g L^{-1}) and BA/MSW (100 g L^{-1}) compared to control. FA/MSW 20 g L^{-1} bioreactor showed higher biogas production and rate indicating its potential option of MSW anaerobic co-digestion. Exponential plot simulated better for FA/MSW 10 g L^{-1} and control while Gaussian plot was applicable for FA/MSW 20 g L^{-1}. Linear and exponential plot of descending limb both simulated better for BA/MSW 100 g L^{-1}. Modified Gompertz plot had higher correlation than exponential rise to maximum plot for simulating biogas accumulation.

Acknowledgements

The first author is grateful to the National Science of Council of Taiwan (ROC) for providing research grant No. NSC 94-2211-E-324-003. The authors also thank The European Commission (EC) for the Marie Curie research fellowship for transfer of knowledge (No. MTKD-CT-2006-042637).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2010.03.048.

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