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Biostabilization assessment of MSW co-disposed with MSWI fly ash in anaerobic bioreactors

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ABSTRACT

Municipal solid waste incinerator (MSWI) fly ash has been examined for possible use as landfill interim cover. For this aim, three anaerobic bioreactors, 1.2 m high and 0.2 m in diameter, were used to assess the co-digestion or co-disposal performance of MSW and MSWI fly ash. Two bioreactors contained ratios of 10 and 20 g fly ash per liter of MSW (or 0.2 and 0.4 g g^{-1} VS, that is, 0.2 and 0.4 g fly ash per gram volatile solids (VS) of MSW). The remaining bioreactor was used as control, without fly ash addition. The results showed that gas production rate was enhanced by the appropriate addition of MSWI fly ash, with a rate of ~6.5 l day^{-1} kg^{-1} VS at peak production in the ash-added bioreactors, compared to ~4 l day^{-1} kg^{-1} VS in control. Conductivity, alkali metals and VS in leachate were higher in the fly ash-added bioreactors compared to control. The results show that MSW decomposition was maintained throughout at near-neutral pH and might be improved by release of alkali and trace metals from fly ash. Heavy metals exerted no inhibitory effect on MSW digestion in all three bioreactors. These phenomena indicate that proper amounts of MSWI fly ash, co-disposed or co-digested with MSW, could facilitate bacterial activity, digestion efficiency and gas production rates.

1. Introduction

Municipal solid waste (MSW) is disposed of as landfilling in many countries, including Taiwan. It is also a possible renewable energy source due to its potential methane recovery [1,2]. However, owing to difficulties in finding appropriate landfill sites in Taiwan, municipal solid waste incinerators (MSWI) have been chosen as an effective alternative to treat MSW. It has been found that MSWI could reduce MSW volume by up to 90% and weight by up to 75% [3], while gaining the beneficial recovery of electricity and steam. However, residues generated from MSWI remain an environmental concern, needing further treatment to prevent secondary pollution.

MSWI bottom ash has been used as industrial aggregate, soil amendment, backfill, and landfill cover [4–6]. MSWI bottom ash has been treated by mono landfill or used as landfill cover accounting for mostly treatment and disposal and a suitable added ratio of MSWI bottom ash to MSW has been found to be beneficial to MSW anaerobic digestion, through improved acids neutral capacity and increased gas production [7]. In addition, alkalinity in the bottom ash has been shown to assist anaerobic digestion of the organic fraction of MSW [8].

Several investigations have also been presented in the co-composting or co-digestion of coal ashes with sludge or organic materials. Coal fly ash co-digested or co-composted with sewage sludge was investigated by Fang et al. [9,10]. In addition, co-composting of pulp and paper mill fly ash with wastewater sludge was reported by Hackett et al. [11]. Co-composting of organic materials such as chicken feces, urea, manure and food garbage with inorganic substances including coal ash and volcanic ash was also presented by Suzuki et al. [12]. Generally, the quality of compost was assessed by its C/N ratio, total P, P_2O_5 and microbial population [13]. Comprehensive report of non-coal ashes utilization was

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described by Ribbing [14]. These utilizations include forest spreading, construction, cement replacement, and as a liner cover for landfills and mine tailings. In addition, utilization of MSWI bottom ash with MSW in co-disposal or co-digestion process is reported. Co-landfilling of proper MSW bottom ash with MSW [15] and co-digestion of suitable MSW bottom ash with OFMSW [7] were reported to be beneficial to the MSW digestion.

MSWI fly ash has been used in some aspects of applications including soil amendment, aggregate and effective adsorbent [16–18]. However, there are few investigations regarding the co-disposal or co-digestion of MSWI fly ash with MSW, as MSWI fly ash has been considered an environmental hazard, needing further appropriate treatment and disposal. Thus, co-disposing or co-digesting MSWI fly ash with MSW is a testing challenge requiring theoretical, experimental and field investigations to obtain clear baseline data.

This study aims to investigate the effects of MSWI fly ash co-digested or co-disposed with MSW, on the decomposition of MSW via laboratory-scale anaerobic bioreactors, with particular attention to digestion performance and biostabilization.

2. Materials and methods

2.1. Composition of synthetic MSW

The synthetic MSW comprised of 35% office paper, 30% newspaper, 30% hay and 5% potato, on a dry weight basis, as described by Lo [7], and was typical of organic fraction of MSW (OFMSW). Each MSW fraction was oven-dried in advance to be water-free. They were shredded, cut into <5 mm pieces and further blended with distilled water to produce the final MSW substrate with total solids (TS) of ~6% and volatile solids (VS) of ~5%. This rather higher water content of MSW seemed to differ from a real MSW of ~50% VS (dry weight basis) with a moisture content of around 35%. However, the chemical percentage composition of the synthetic refuse for C, H, O, N and others was typical and was approximately 46, 6, 41, 1.4 and 5.6%, respectively. Although OFMSW has higher C and N content than that of real MSW. C/N ratio of 32.86 of OFMSW was similar to 39.68 of real MSW suitable for digestion and composting (C/N = 25). This set up of experimentation attempted to reduce the unwanted materials such as heavy metals and interferences from real MSW complexity. In addition, higher water content may help the microbial attack and quicker biodegradation in a shorter period.

Selected alkali and heavy metal content of MSW are listed in Table 1. The MSW substrates were stored in plastic containers in a freezer for experimental use.

2.2. MSWI fly ash

MSWI fly ash was obtained from a mass-burning incinerator in central Taiwan. The physical composition of receiving MSW contained paper and cardboard (30.63%), textile (6.52%), leaves, straw and wood (3.61%), domestic food (19.22%), plastics (24.05%), metals (2.86%), glasses (4.23%), stone and sand diameter >5 mm (3.35%), and others (5.53%), respectively. In addition, the chemical constituents of MSW covered water content (50.77%), ash (9.69%) and combustible (39.54%). Major element of C (20.91%), H (2.89%), O (15.10%), N (0.3%), S (0.20%) and Cl (0.14%) were also measured within the combustible.

It was collected from air pollution control devices, such as the semi-dry scrubber with $Ca(OH)_2$ as flushing reagent and bag filter for ash filtration. Final control of flue gas was sprayed with powder carbon for dioxin and hazardous gas removal. Then, flue gas was induced by fans to emit into the atmosphere by a stack (with three steel pipes inside) of ~120 m high. Fly ash settled from semi-dry scrubber and bag filter was conveyed to the ash pit. Fly ash was taken from the ash pit with plastic bag for experiment. The MSWI was operated at temperature range 850–1050 °C. Selected metal levels of MSWI fly ash are also listed in Table 1 [19–27].

2.3. Anaerobic bioreactor

Three bioreactors were employed to examine the effects of MSWI fly ash addition on MSW anaerobic digestion. Each anaerobic bioreactor was 1.2 m high and 0.2 m in diameter, with a working volume of ~34 l (Fig. 1). One bioreactor was used as control. It contained a mixture of 22 l synthetic MSW substrate (TS 6%; VS 5%) and 12 l anaerobic sludge seeding (TS 3%; VS 2.5%;) from the sludge anaerobic digester at Fu-Tian municipal wastewater treatment plant located at central Taiwan. This plant collects ~ 50,000–55,000 CMD waste water and adopts aerobic biological treatment process with activated sludge method (HRT, 6 h). Settled sludge from first (HRT, 1.5 h) and secondary sedimentation tank (HRT, 4 h) is sent to gravity thickener (HRT, >12 h) and then the anaerobic digester (SRT, 30 days) for anaerobic digestion. The digested sludge are then dewatered by pressure filtration. Dewatered sludge (75% water content) is landfilled or reused in agricultural purpose. After secondary sedimentation tank, the effluent is treated with 10% NaOCl in a disinfection tank for 20 min and discharged. Digested sludge in the anaerobic digester was collected in 20-l plastic bottles and was settled in laboratory to obtain a VS of ~2.5% (anaerobic sludge seeding) and immediately mixed with MSW to conduct the experiment. The combined VS of MSW and anaerobic sludge seeding was measured and calculated to be 4.12%. The leachate had a pH, alkalinity, COD and volatile acids of ~7.7, ~208 mg l^{-1}, ~4734 mg l^{-1} and ~83 mg l^{-1}, respectively. The two fly ash-added bioreactors also contained ~34 l of MSW substrate and anaerobic sludge seeding, the same as the control, but with a further addition of two weight ratios, corresponding to 10 and 20 g l^{-1}, respectively (10 and 20 g fly ash per liter MSW or 0.2 and 0.4 g g^{-1} VS).

The three bioreactors were arranged in four layers. In the control bioreactor, each layer contained 8.5 l of the mixture of MSW substrate and anaerobic sludge seeding. In the ash-added bioreactors, each layer contained 6.5 l of the mixture of MSW substrate and anaerobic sludge seeding, with a cover of a 2-l mixture of MSW and anaerobic sludge seeding blended with the designated MSWI fly ash weight ($22 \times 10/4 = 55$ and $22 \times 20/4 = 110$ g for each layer, respectively), simulating co-digestion of MSW and MSWI fly ash for the potential application to landfill-cover practice (Fig. 1). The three arrangements, including control and two fly ash addition ratios, corresponded to 0, 10 and 20 g l^{-1}, respectively. Leachate from the three bioreactors was recirculated by peristaltic pumps at a volume of 100 ml day^{-1}. Leachate recirculation was operated carefully to avoid the digesters disturbance. To measure operational parameters for assessment of MSW biostabilization, 100 ml leachate was sampled daily or weekly. The three anaerobic bioreactors were placed in a homeostatic oven, maintained at ~35 °C, suitable for anaerobic digestion.

2.4. Parameter analyses

The parameters chosen for bioreactor performance assessment (pH, conductivity, alkalinity, chemical oxygen demand (COD), volatile solids (VS), volatile acids (VAs), selected metals, etc.) were assessed from 100 ml leachate samples, taken daily or weekly. pH and conductivity were measured with pH and conductivity meter. Gas production was collected from the exit of anaerobic bioreactors with pipes connected to plastic bottle by using water replacement method every day. Alkali metals, heavy metals and other ions, such

Table 1
Selected metals content (mg kg^{-1}) in seeded sludge, MSW substrate and MSI fly ash (MSWI FA) compared to those of other articles [19–27]

Element	Seeded sludge	Substrate MSW	MSWI FA (this study)	MSWI FA (Aubert et al. [19])	MSWI FA (Lundtorp et al. [20])	MSWI FA (Le Forestier and Libourel [21])	MSWI FA (Eighmy et al. [22])	MSWI FA (Wikström et al. [23])	MSWI FA (Saikia et al. [24])	MSWI FA (Song et al. [25])	MSWI FA (Sun et al. [26])	MSWI FA (Wan et al. [27])
Ca	12860	10838.33	294033.3	ND	183000	203100	46300	40300	ND	80008.99	143500	ND
K	2259.67	5993.33	51300	ND	46000	15700	109000	62000	ND	ND	41000	ND
Mg	2388.67	856	10939	ND	ND	22400	<1100	3900	ND	8854.22	ND	ND
Na	685	776.33	39116.67	ND	38000	13800	84000	28600	ND	17442.86	37500	ND
Ag	275.73	0.02	119.13	ND	ND	ND	192	ND	ND	ND	ND	11.75
Al	2.357	7.22	0.31	ND	44000	56000	20800	25400	ND	14120.24	25000	ND
B	63.2	13.38	72.67	ND	ND	ND	ND	ND	110	ND	ND	ND
Ba	42.1	10.91	46.8	1059	810	816	<2400	ND	ND	46.58	ND	ND
Cd	1.447	0.03	93.53	609	210	240.33	1660	ND	110	73.35	ND	72.02
Co	10.85	0.17	14.88	44	20	15.67	13.3	ND	ND	4.04	ND	36.94
Cr	108.87	4.03	160.5	778	230	352.67	494	ND	260	155.82	ND	318.43
Cu	203.9	30.03	624.5	1837	1500	838.67	2220	1600	ND	359.72	ND	976.74
Fe	19680	736.83	4891.67	ND	12000	ND	<1600	9100	ND	2064.95	13000	ND
Mn	2569	150.47	360.35	ND	ND	ND	448	ND	ND	566.28	ND	2034.66
Mo	4.11	0.51	12.32	<40	34	27	47.1	ND	40	ND	ND	ND
Ni	63.07	ND	58.26	<500	66	73.33	69.8	ND	ND	ND	ND	185.67
P	5023.33	178.82	2180.33	ND	ND	ND	ND	5800	3490	ND	ND	ND
Pb	66.83	1.10	1865.33	8396	6370	4215.67	27000	14000	ND	845.16	8500	4769.96
S	8460	740.33	14845	ND	26000	ND	ND	ND	ND	ND	14000	ND
Sb	4.33	0.09	351.53	2149	ND	452.67	2073	ND	ND	93.25	ND	ND
Si	185.67	175.42	162.48	ND	1200	86500	38000	84800	ND	ND	62500	ND
Sn	16.03	0.85	262.93	3132	ND	1255.67	5900	ND	ND	526.95	ND	5879.51
Ta	24.81	0.62	2.65	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ti	103	5.08	1430.33	ND	ND	6200	6100	ND	ND	ND	8500	ND
Tl	0.10	2.62	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
W	ND	ND	25.37	192	ND	16.33	ND	ND	ND	ND	ND	ND
Zn	1347	31.11	3970	25250	17000	10141.33	104400	41400	ND	8788.48	29500	6089.93
Zr	0.87	0.20	1.85	132	ND	93.33	<600	ND	ND	ND	ND	ND
LOI	ND	ND	2.9%	8.7%	ND	ND	ND	ND	4.59%	ND	ND	ND
pH	ND	ND	10.8	10.3	ND	ND	ND	ND	10.5	ND	ND	ND

ND: No data.

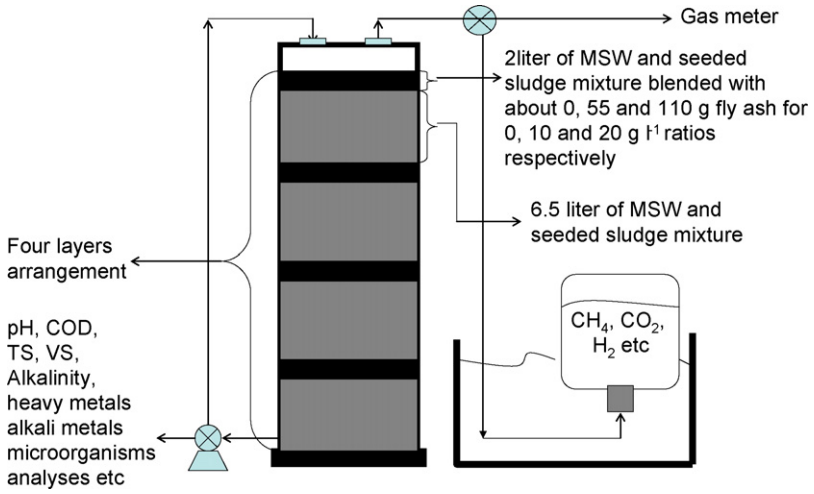

Fig. 1. Schematic diagram of anaerobic bioreactor.

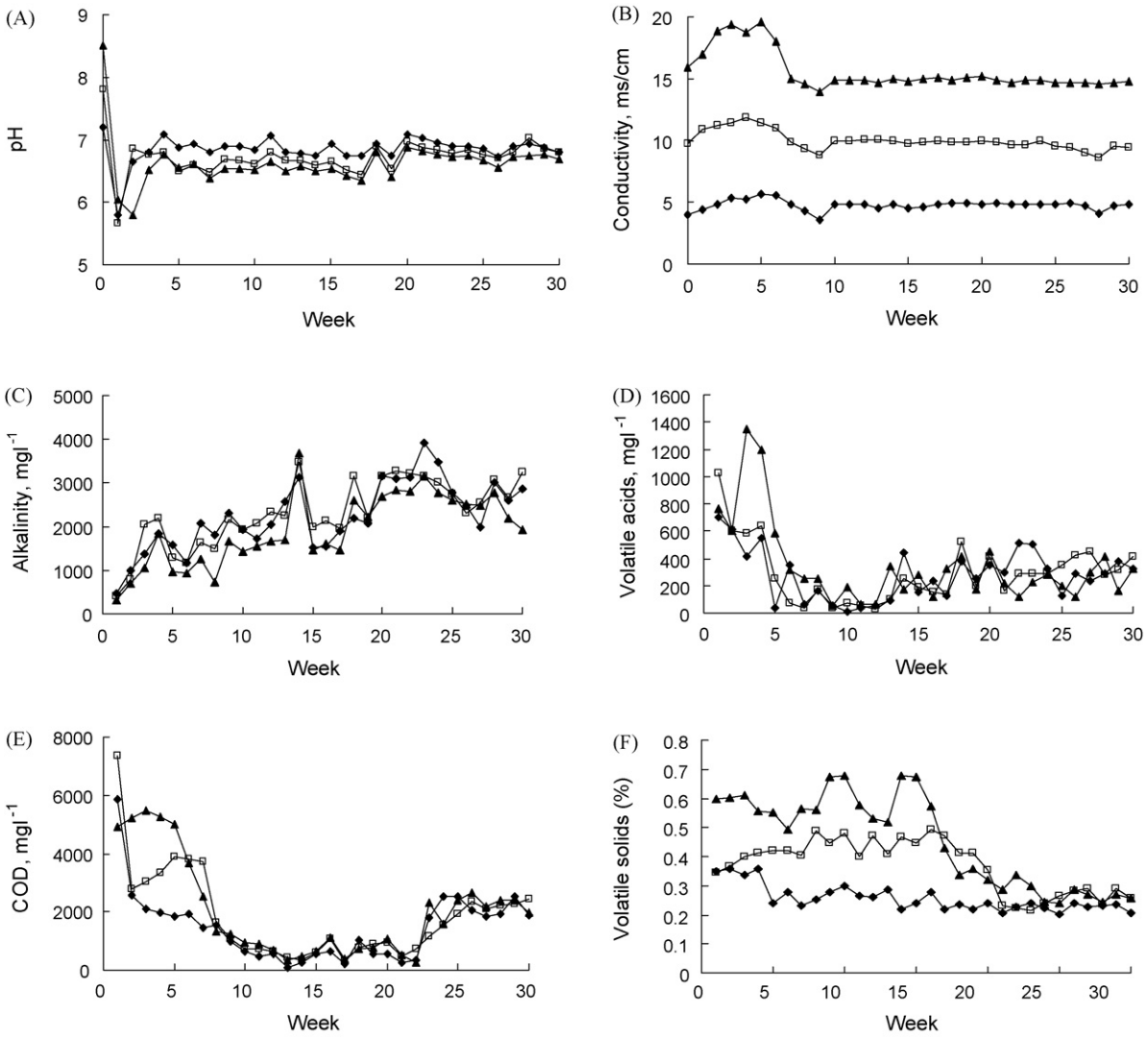

Fig. 2. pH (A), conductivity (B), alkalinity (C), volatile acids (D), COD (E), and volatile solids (F) in leachate of MSW anaerobic digestion from the (□) 10 g l^{-1} ash-added bioreactor; (▲) 20 g l^{-1} ash-added bioreactor; and (♦) control bioreactor without fly ash addition.

as Cl^{-1} and $SO_4{}^{-2}$, were analyzed by ICP-OES (Thermo Electron Corp.) and IC (Dionex Ltd.). Most measurement procedures such as pH, COD, alkalinity, TS, VS and VAs were in accordance with AWWA's [28] standard methods for the examination of water and wastewater. Metals, Cl^{-1} and $SO_4{}^{-2}$ analyses referred to the manual of ICP-OES (Thermo Electron Corp.) and IC (Dionex Ltd.).

In addition, the relative percentage of the archaea and bacteria domains, sulfate-reducing bacteria (SRB) and selected methanogens were analyzed by fluorescence in situ hybridization (*FISH*) molecular technology for bacterial characterization. The oligonucleotide acid probes used for archaea, bacteria and SRB analyses were ARCH915 [29], EUB338 [30] and SRB385 [31]. The selected methanogens groups were *Methanobacteriales*, *Methanococcales*, *Methanosarcinales* and *Methanomicrobiales*, with target probes MB310, MC1109, MSMX860 and MG1200 [32], respectively. Methanogens could indicate the degree of methanogenesis for MSW anaerobic digestion in fly ash-added bioreactors as compared to the control one.

2.5. Statistical analysis of measured parameters

Parameters of gas production, pH and conductivity were measured daily and alkalinity, COD, VS, VAs, Cl^{-1} and $SO_4{}^{-2}$ were measured weekly. Similarly, heavy metals of Cd, Cr, Cu, Ni, Pb and alkali metals of Ca, K, Mg and Na were analyzed once per week. In addition, the relative percentage of the bacterial community as mentioned in Section 2.4 was measured with duplicates ($n = 2$) and the results were presented with average ($\bar{x}$), standard deviation(s) and coefficient of variation (CV). Heavy metals of Cd, Cr, Cu, Pb, Ni and Zn were tested with method detection limit (MDL) for potential low concentration and data precise. The detection limits of Cd, Cr, Cu, Ni, Pb and Zn were used to evaluate the dissolved heavy metals in the leachate.

Correlation of pair parameters were examined including gas accumulation, pH, alkalinity, VAs, VS, COD, Ca, Mg, K, Na, Cd, Cr, Cu, Ni, Pb, Zn, Eub338, Arch195, SRB385, MB310, MC1109, MSMX860 and MG1200. In addition to correlation analysis, multiple regression of gas accumulation with respect to pH, alkalinity, VAs, VS, COD, Ca, Mg, K, Na, Cd, Cr, Cu, Ni, Pb, Zn, Eub338, Arch195, SRB385, MB310, MC1109, MSMX860 and MG1200 were examined.

Analysis of variance (ANOVA) of different ash addition on gas accumulation and measured parameters was analyzed. The result can be used to evaluate the significance of different ash-added amount of 0, 10 and 20 g l^{-1} on the measured parameters and gas accumulation, that is, ash-added amount on MSW digestion performance and potential stimulation or inhibition.

3. Results and discussion

3.1. pH, conductivity, alkalinity, VA, COD and VS

The pH trends in bioreactors' leachate are shown in Fig. 2A. pH values showed a large initial drop in the three bioreactors. Thereafter, they recovered to steady values of 6.2–7.2. The higher initial pH values during the first week in the 20 g l^{-1} ash-added bioreactor were attributed to the sudden release of large amounts of alkali metals. Furthermore, the pH values below 6, initially found in the three bioreactors, with the exception of the first week, are believed to be due to the large amounts of VAs produced in the initial stage of MSW hydrolysis, leading to high levels of volatile acids and lower pH values. However, pH values soon returned to 6.2–7.2, possibly due to alkali metal release associated with OH^{-1} and $CO_3{}^{-2}$, which could potentially provide buffer alkalinity and neutralize VAs produced. This range of near-neutral pH values is suitable for anaerobic digestion [33]. In addition, levels of metal release [34] in this pH range in the ash-added bioreactors might stimulate gas generation rates compared to the control.

Conductivity was higher in the ash-added bioreactors than control (Fig. 2B). In the 20 and 10 g l^{-1} ash-added bioreactors, conductivity was ~3- and ~2-fold higher than the control bioreactor, respectively. This is because the higher ash addition released more ions, such as metals, chloride ions, etc., resulting to a higher conductivity. Alkalinity in the three bioreactors (Fig. 2C) had similar trends of between 500 and 3500 mg l^{-1}, and was in the range suitable for anaerobic digestion, as described previously by Parkin and Owen [33].

VAs in the three bioreactors decreased, except for an increase in the 20 g l^{-1} ash-added bioreactor between weeks 2 and 5 (Fig. 2D), and remained at the lowest levels between weeks 6 and 12. From week 13, the VAs started to increase slightly. The comparatively high levels of VAs found in the first month are due to hydrolysis of MSW during the initial digestion stage. As mentioned above, VAs in the 20 g l^{-1} ash-added bioreactor was initially slightly higher

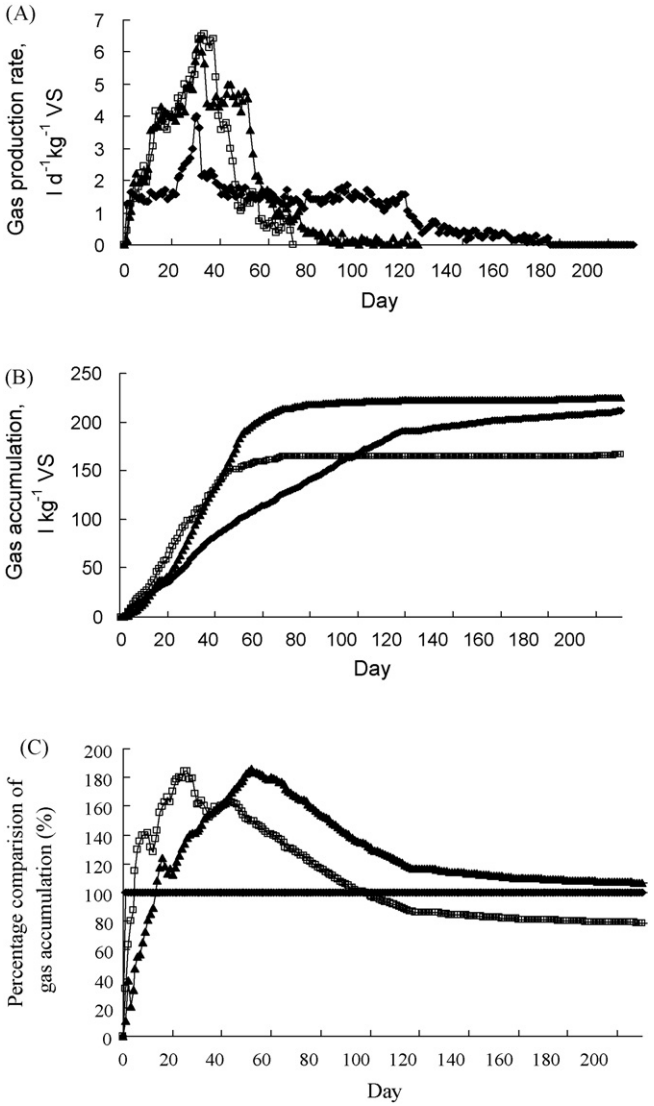

Fig. 3. Gas production rate (A) and gas accumulation (B) of MSW anaerobic digestion from the (□) 10 g l^{-1} ash-added bioreactor; (▲) 20 g l^{-1} ash-added bioreactor and (♦) control bioreactor without fly ash addition. (C) shows the percentage of gas accumulation by comparing the (□) 10 g l^{-1} ash-added bioreactor and (▲) 20 g l^{-1} ash-added bioreactor with (♦) control bioreactor without fly ash addition.

than in the other two bioreactors. From the fourth month onwards, VAs in the three bioreactors increased slightly, indicating that methanogenic activity began to decrease, with less MSW substrate left to be utilized.

COD levels in the three bioreactors showed a similar trend, decreasing from ~8000 to ~500 mg l^{-1} (Fig. 2E). COD was degraded by microorganisms, resulting in a gradual decrease in digestion period. In addition, COD showed a similar trend to VAs, which contributes in part to COD.

VS levels in leachate were between 0.2 and 0.7% (Fig. 2F). VS was clearly higher in the ash-added bioreactors than in control, particularly during the period of high methanogenic activity with higher gas production rates. Higher VS indicates that the bacterial community, during the highly methanogenic activity period, in the ash-added bioreactors was potentially higher than in control. This result implied that potentially higher gas generation rates could be achieved in the ash-added bioreactors than in the control.

3.2. Gas production

Fig. 3A shows that gas production rate of the ash-added bioreactors, during the first 8 weeks, was higher compared to the control. Furthermore, gas production rate showed nearly the same increasing trend for both ash-added bioreactors between weeks 1 and 4. However, the rate was slightly higher in the 10 g l^{-1} ash-added bioreactor in week 5, while it was higher in weeks 6 and 8 in the 20 g l^{-1} ash-added reactor.

Nevertheless, gas accumulation in the 10 g l^{-1} ash-added bioreactor was lower compared to the 20 g l^{-1} ash-added and the control bioreactors (Fig. 3B), in the order 20 g l^{-1} ash-added bioreactor (~225 l kg^{-1} VS) > control bioreactor (~211 l kg^{-1} VS) > 10 g l^{-1} ash-added bioreactor (~167 l kg^{-1} VS). Further analysis by percentage comparison of gas accumulation can be found in Fig. 3C. This is believed to be due to the greater release of soluble alkali metals of Ca, K, Mg and Na, and soluble trace metals, such as Co, Mo, Ni and W, in the 20 g l^{-1} ash-added bioreactor, exerting an optimal and greater stimulatory effect on MSW anaerobic digestion than in the 10 g l^{-1} ash-added and control bioreactors. As a result, there was greater stimulation of MSW anaerobic digestion, gas production rate lasted longer (~4 weeks) between weeks 5 and 8 with ~4.5 l day^{-1} kg^{-1} VS (Fig. 3A). Therefore, gas accumulation was higher in the 20 g l^{-1} ash-added bioreactor than in the 10 g l^{-1} ash-added or control reactor.

3.3. Performance assessment

Fig. 4 showed the release trend of Ca, K, Mg and Na. Released levels of Ca and K appeared to be higher than that of Na and Mg. Mg

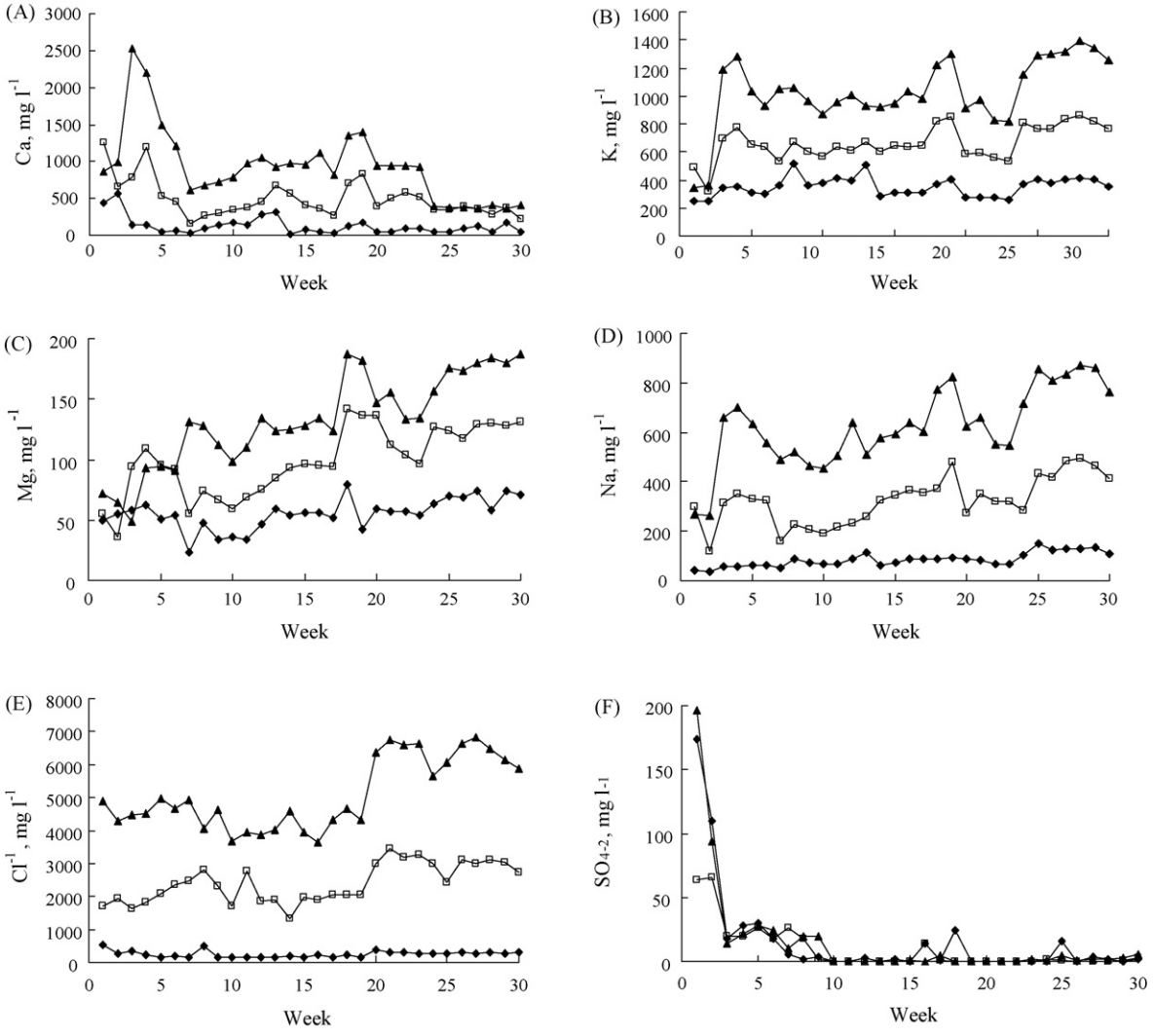

Fig. 4. Ca (A), K (B), Mg (C), Na (D), Cl^{-1} (E) and SO_4^{-2} (F) levels in leachate of MSW anaerobic digestion from the (□) 10 g l^{-1} ash-added bioreactor; (▲) 20 g l^{-1} ash-added bioreactor and (♦) control bioreactor without fly ash addition.

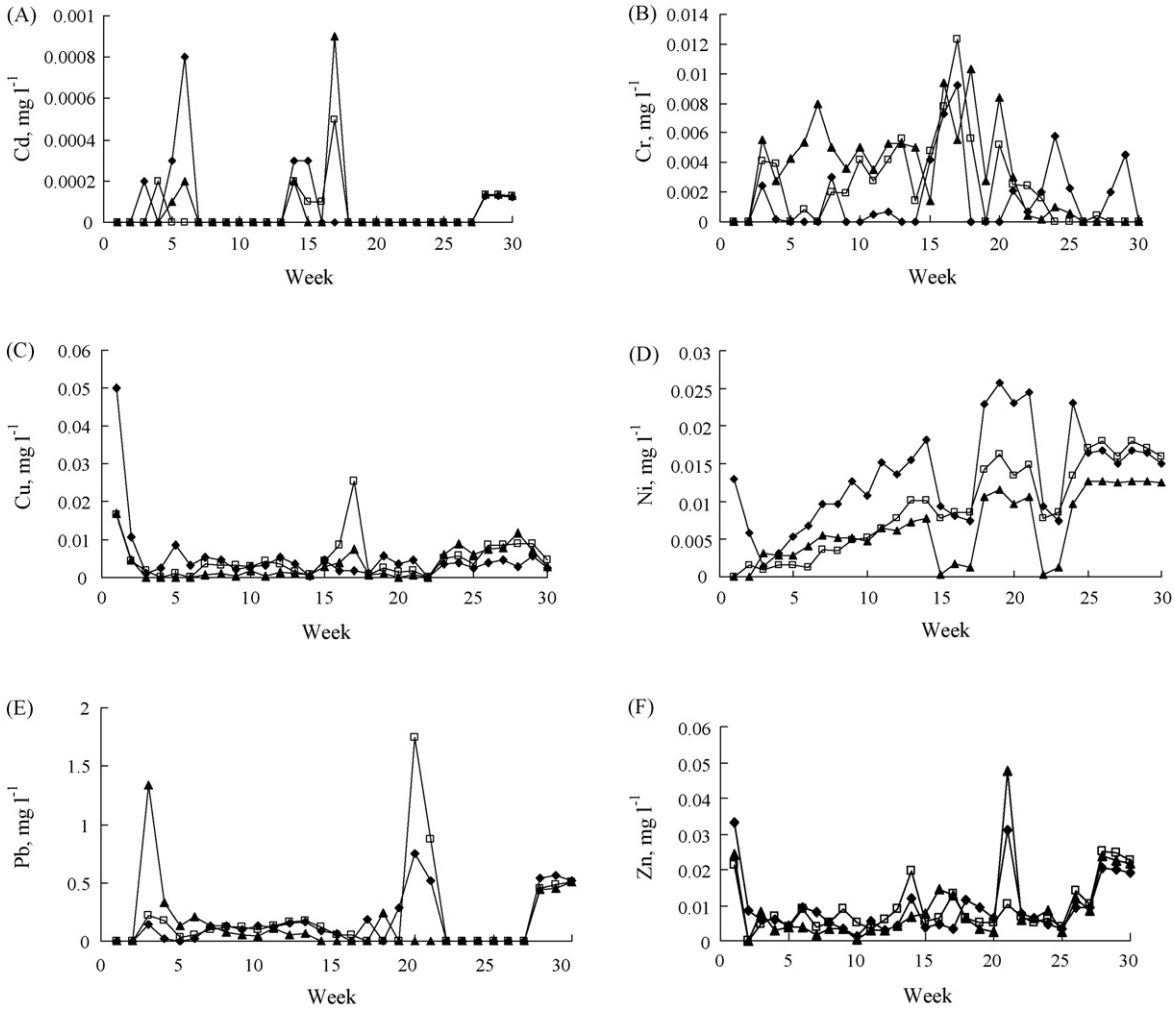

Fig. 5. Cd (A), Cr (B), Cu (C), Ni (D), Pb (E), and Zn (F) levels in leachate of MSW anaerobic digestion from the (□) 10 g l^{-1} ash-added bioreactor; (▲) 20 g l^{-1} ash-added bioreactor and (♦) control bioreactor without fly ash addition. The detection limits of Cd, Cr, Cu, Ni, Pb and Zn are 0.001, 0.001, 0.002, 0.005, 0.022 and 0.003 mg l^{-1}, respectively.

concentration in leachate was found to be the least. These released concentrations were found to below the potential inhibitory levels [33]. Alkali metals were reported to be between 2500–4500, 1000–1500, 2500–4500 and 3500–5500 mg l^{-1} for moderate inhibition and 8000, 3000, 12,000 and 8000 mg l^{-1} for severe inhibition for Ca, Na, K and Mg, respectively [33].

As regard to heavy metals (Fig. 5), Cd, Cr, Cu, Ni, Pb and Zn were measured to be <~0.0009, <~0.0123, <~0.05, <~0.0258, <~1.7455 and <~0.0477 mg l^{-1}, respectively. These heavy metal concentrations were also reported to be not inhibitory to the anaerobic process [33]. Soluble heavy metal concentrations such as Cu, Cr(VI), Ni and Zn of 0.5–0.7, 3.0, 1.6–2.0 and 0.1–1.0 mg l^{-1} were reported to be strong inhibitory to anaerobic digestion [33]. In addition, inhibition of $C_{I,50}$ values (Cu, 30 mg l^{-1}; Ni and Zn 1600 mg l^{-1}; Cr, 3000 mg l^{-1}; Cd, 3500 mg l^{-1}; Pb > 5000 mg l^{-1}) were also reported by Li and Fang [35]. These soluble metals showed higher metal levels than this study.

Mineral requirements for methane fermentation indicated that optimal or stimulatory concentrations addition of Ca, Mg and Ni, depending on microorganisms or substrate were found to be >0.54–40, 360–4800 and 0.0059–5 mg l^{-1}, respectively [34]. Other study of Cu, Cd and Cr concentrations of 2.4, 1.6 and 4.0 mg l^{-1} were found to achieve the maximum methane production [36]. However, concentrations higher than these levels were found to inhibit the cattail anaerobic degradation resulting gradual lower methane production. These beneficial levels appeared to be higher than this study of potential stimulatory levels of Cd and Cr around <0.0009 and <0.013 mg l^{-1}, respectively. As expected, Ca, K, Mg and Na released higher levels than six heavy metals due to their higher content in the ash matrix. All these metals' levels have potential to be beneficial to the anaerobic process [34,37].

It is known that alkali metals provide inorganic nutrients [34], and their acid-neutralizing capacity [38,39] and alkalinity buffering might maintain the anaerobic bioreactors in a neutral and stimulatory anaerobic environment. The pH range of 6.7–7.2 in all bioreactors was found to be suitable for anaerobic digestion [33]. Released alkali metals, such as Ca, Mg, K and Na, as a function of pH, for the three anaerobic bioreactors were in the range 50–2,500 mg l^{-1}, which displayed optimal rather than detrimental effects [33]. Ca, Mg, K and Na levels in the 20 g l^{-1} ash-added bioreactor were higher than that in the 10 g l^{-1} ash-added and control reactors (Fig. 4A–D). Higher and optimal alkali and trace metals in the ash-added bioreactors seemed to stimulate anaerobic digestion, thereby, enhancing gas production rate. Other released ions, such as Cl^{-1} and $SO_4{}^{-2}$, were thought to exert an insignificant impact on anaerobic digestion. The fly ash-added bioreactors, with a higher Cl^{-1} release of ~1300–6850 mg l^{-1}, show similar gas production trends as the control, with a Cl^{-1} release of ~150–550 mg l^{-1}. Furthermore, $SO_4{}^{-2}$ was rapidly consumed by SRB, as they were found

to decrease from ~200–20 mg l^{-1} in the three bioreactors at the beginning of the digestion period (Fig. 4E–F).

Methanogens, such as *Methanobacteriales*, *Methanococcales*, *Methanosarcinales* and *Methanomicrobiales*, were higher occasionally in the 20 and 10 g l^{-1} ash-added bioreactors, particularly during the period of higher gas production rate, compared to control. Three of the above-mentioned families were hydrogenotrophic methanogens (MB310, MC1109 and MG1200) and the other, *Methanosarcinales* (MSMX860), was an aceticlastic methanogen. This implied that the released metals and ions in the ash-added bioreactors contained suitable concentrations with the potential to enhance hydrogen and acetate metabolic utilization. It was further noted that fly ash provided rather high specific surface with the potential to enhance the microbial habitat and attack. As a result, gas production rate in the ash-added bioreactors was enhanced. Furthermore, the percentage of methanogens was higher, compared to SRB, in the ash-added bioreactors. This indicates that methanogenesis evolved and increased through ash addition, although fly ash could release SO_4^{-2} at concentrations of ~200 mg l^{-1}, suitable for SRB utilization. Under these circumstances, the methanogens competed better than the SRB, and the gas production rates were facilitated.

3.4. Statistical meaning of analyzed parameters

CV of bacterial data was calculated and plotted as can be seen in Fig. 6A–C. MDL of heavy metals of Cd, Cr, Cu, Ni, Pb and Zn were measured and found to be 0.001, 0.001, 0.002, 0.005, 0.022 and 0.003 mg l^{-1}, respectively. These levels were used to evaluate the dissolved heavy metals in the leachate.

Pearson correlation with one-tailed significance of each pair parameters can be found by SPSS 15.0 version in the three bioreactors. The correlations were focused on the gas accumulation and measured parameters. Parameters with significant correlations with gas accumulation in the control bioreactor were found to be alkalinity, VS, Mg, Na, Cd, Pb, Ni and Zn, respectively. Similarly, parameters with significant correlations with gas accumulation were found to be pH, alkalinity, EC, VS, Cl, SO_4, Mg, K, Na, Ni and Zn for the 10 g l^{-1} bioreactor and pH, alkalinity, EC, COD, VAs, VS, Cl, Ca, Mg, K, Na, Cr, Cu, Ni and Zn for the 20 g l^{-1} bioreactor, respectively. By stepwise regression, the multiple regression equations of gas accumulation the three bioreactors were found as following:

$$\text{Gas accumulation (control bioreactor)} = 3.207 - 0.013\,\text{Na} + 0.000\,\text{alkalinity} \quad (1)$$

$$\text{Gas accumulation (10 g } l^{-1}\text{ bioreactor)} = 0.488 - 84.075\,\text{Ni} + 3.398\,\text{VS} \quad (2)$$

$$\text{Gas accumulation (20 g } l^{-1}\text{ bioreactor)} = -12.311 + 3.841\,\text{VS} + 0.259\,\text{EC} + 1.243\,\text{pH} - 0.01\,\text{VAs} + 0.000\,\text{alkalinity} \quad (3)$$

Among them, pH, alkalinity, VAs, VS, Na, Ni and EC containing alkali and heavy metals were found to contribute significantly to the MSW digestion and gas accumulation. Further ANOVA of one-way analysis showed that different ratios of ash addition had the significant effects on conductivity, VS, Ca, K, Mg, Na, Cl, Cr and Ni (Table 2). Particularly, the gas accumulation was found to be affected by the different ash addition. The percentage comparison of gas accumulation pertaining to MSW digestion efficiency in the three bioreactors can be found in Fig. 3C. This result also corresponds to the fact that higher gas accumulation was found by suitable ash addition in the 10 and 20 g l^{-1} bioreactors.

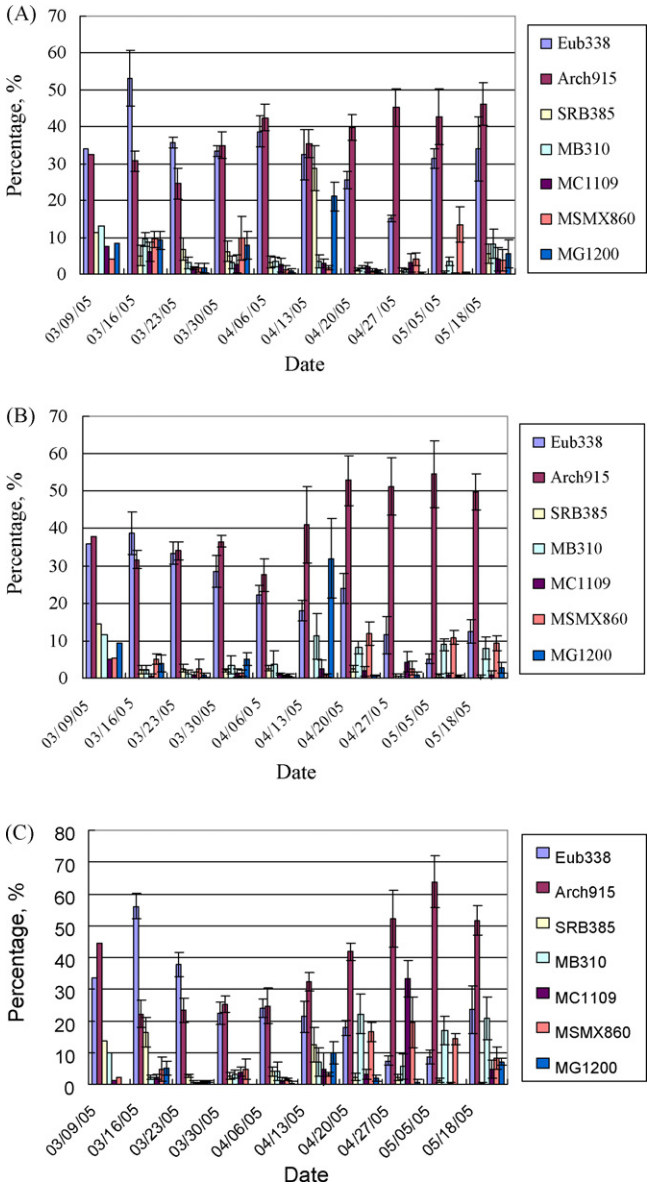

Fig. 6. The percentage of the seven selected bacterial community in the control (A), 10 g l^{-1} (B) and 20 g l^{-1} (C) anaerobic bioreactors.

3.5. Potential implications

The results in this study implied that adequate ratios of MSWI fly ash addition showed a positive potential for landfill cover alternative. It might enhance the gas generate rates and also brought a faster biostabilization of a landfill. In addition, it had the benefit to reduce the cost of solidification that needing transportation and adding reagent. Except Ca, Mg, K, Na, and Cl, leachate levels in the ash-added bioreactors showed rather the same compared to the control one. This phenomenon indicated that ash addition might not increase the leachate strength and treatment cost. Rather, suitable levels of alkali metals and trace metals might exert the beneficial effect on MSW digestion. Perhaps, these levels of alkali metals might help when leachate treated in the coagulation and flocculation process suitable for suspended solid removal. However, potential generation of H_2S and other pollutants such as volatile organic compounds, polyaromatic hydrocarbons and dioxins needs further investigation. Particularly, these pollutants that may cause risks to human

Table 2
ANOVA of the effects of three different MSWI fly ash addition ratios (0, 10 and 20 g l^{-1}) on measured parameters and gas accumulation

Parameters	*P*-values (significance)	α-values	Note
pH	0.159	0.05	Has not significant effect on pH
Conductivity	0.000	0.05	Has significant effect on conductivity
Alkalinity	0.150	0.05	Has not significant effect on alkalinity
Volatile acids	0.558	0.05	Has not significant effect on volatile acids
COD	0.286	0.05	Has not significant effect on COD
Volatile solids	0.000	0.05	Has significant effect on volatile solids
Gas accumulation	0.020	0.05	Has significant effect on gas accumulation
Ca	0.000	0.05	Has significant effect on Ca
K	0.000	0.05	Has significant effect on K
Mg	0.000	0.05	Has significant effect on Mg
Na	0.000	0.05	Has significant effect on Na
Cl	0.000	0.05	Has significant effect on Cl
SO_4	0.723	0.05	Has not significant effect on SO_4
Cd	0.945	0.05	Has not significant effect on Cd
Cr	0.048	0.05	Has significant effect on Cr
Cu	0.540	0.05	Has not significant effect on Cu
Ni	0.000	0.05	Has significant effect on Ni
Pb	0.781	0.05	Has not significant effect on Pb
Zn	0.998	0.05	Has not significant effect on Zn

health and ecological environment need to be thoroughly evaluated.

4. Conclusions

MSWI fly ash has been examined for possible use as landfill interim cover. The results showed that gas production rate was enhanced by the appropriate addition of MSWI fly ash, with a rate of ~6.5 l day^{-1} kg^{-1} VS at peak production in the ash-added bioreactors, compared to ~4 l day^{-1} kg^{-1} VS in control. Conductivity, alkali metals and volatile solids were higher in the fly ash-added bioreactors compared to control. In addition, they were found to have higher correlations and significance with gas accumulation by statistical analysis. Heavy metals, such as Cd, Cr, Cu, Pb, Ni and Zn, potentially toxic to anaerobic digestion, were analyzed at <1 mg l^{-1}, except for Pb <1.745 mg l^{-1}. Other released ions, such as Cl^{-1} and $SO_4{}^{-2}$, were thought to exert an insignificant impact on anaerobic digestion.

From the above results, it was concluded that enhanced gas production rate by methanogenic activity in the fly ash-added bioreactors was potentially stimulated by optimal alkali and trace metals concentrations with near-neutral pH. These phenomena indicated that proper amounts of MSWI fly ash, co-disposed or co-digested with MSW, could facilitate bacterial activity, digestion efficiency and gas production rates.

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