Anaerobic digestion of landfill leachate

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Abstract

A landfill leachate from Kaushung City municipal refuse disposal site was treated by mesophilic conventional and two-phase anaerobic digestion with modes of batch and semi-continuous operation. Conventional anaerobic digestion resulted in 92 to 95% of COD removal for an influent of 22 750 mgCOD/ℓ at digestion times of 8 to 20 d. No efficient acidogenesis was observed for the two-phase digestion for an influent of 39 100 mgCOD/ℓ; the volatile fatty acids only increased 6,4% after 90 h of acidogenesis. However, at a digestion time of 11,1 d and an influent of 37 920 mgCOD/ℓ, the COD and BOD removal for the methanogenic reactors was more than 90%. Methanogenic kinetics were also studied.

Introduction

In Taiwan refuse production has increased dramatically from 0,6 kg/d to 0,92 kg/d per capita in the past ten years. The collected municipal refuse was 17 147 t/d in 1989 and more than half of that (59,6%) was disposed by landfill. There are 104 landfill sites in operation now and about 30 sites are being planned. Leachate from landfills is high in biochemical oxygen demand (BOD), chemical oxygen demand (COD), and inorganic constitution. On account of the 1987 amendment to the administrative regulations, it is no longer permitted to discharge leachate without any treatment.

Though the leachate quality varies from landfill to landfill and is age-dependent, high kitchen residual content in the refuse from the characteristic Oriental eating habits makes the refuse high in moisture and oil content. In order to treat the leachate in Taiwan, chemical and biological treatment processes were evaluated (Yu, 1983; 1984). Chemical processes were reported to be inefficient in organic removal and produced large amounts of chemical sludge. The aerobic biological process was reported to be unpractical because of high dilution requirements. The anaerobic process is suitable for high strength organic waste water and has been popular in the waste treatment field because of its many advantages, such as high treatment efficiency and methane producing ability (i.e. energy product recoverable potential). The disadvantages of the process include heat input and longer digestion time (Grady and Lim, 1980). A two-phase digestion process has been suggested (Ghosh and Klass, 1978) to improve the treatment efficiency with a shorter digestion time.

In this study conventional and two-phase anaerobic digestion were used to treat the landfill leachate. The purpose of this research was to find an efficient and practical treatment method for the increasing volume of leachate from increasing landfill operations in Taiwan.

List of symbols

BOD — biochemical oxygen demand
BOD_5 — 5-day BOD
COD — chemical oxygen demand
HAc — acetic acid
HBu — butyric acid
HPr — propionic acid
HVa — valeric acid
MLVSS — mixed liquor volatile suspended solids
ORP — oxidation-reduction potential
STP — standard temperature and pressure
VFA — volatile fatty acid

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Materials and methods

Leachate substrate

The landfill leachate from Kaushung City municipal refuse disposal site was used. The landfill age was 2 years and served a population of about one million. High organic concentration was found with total COD of 37 000 to 66 660 mg/ℓ. The BOD/COD ratios were from 0,4 to 0,6. After collection, the leachate was sealed in plastic containers and was stored at 5°C until used, but was replaced every 20 d. During 20 d storage at 5°C, only a 3,9% increase in volatile fatty acid (VFA) (as COD), was found which could be neglected and consequently the variation was disregarded throughout the experiment. Stored leachate diluted with distilled water was used as leachate substrate in the experiments.

Experimental methods

Table 1 summarises the experimental conditions. Laboratory-scale semi-continuously fed completely-mixed type experimental systems were operated in a temperature-controlled chamber at 35 ± 1°C. In batch test four 500 mℓ (effective volume) reactors were used. For conventional digestion the effective reactor volume was 2 ℓ. For two-phase digestion, the effective reactor volumes were 3 ℓ and 1 ℓ for acetogenesis and methanogenesis respectively. The substrate and reactor contents were fed and drawn once daily. Each digester was connected to a gas collection cylinder placed in a saturated salt solution.

Seed sludge

The seed sludge was obtained from a mesophilic digester which had been acclimated with a mixture of acetic acid (HAc), propionic acid (HPr), and n-butyric acid (n-HBu) for over one year. After collection into 2 digesters, the sludge was then acclimated with the landfill leachate at digestion times of 12 and 15 d for 45 d and the digestion time was then adjusted to 8 and 20 d, respectively. After reaching a steady-state condition, the acclimated seed sludges were used for the experiments on conventional digestion.

For the two-phase digestion, after seeding with 3 ℓ of mixed acids acclimated sludge, the acetogenic digester was then fed with the leachate and the digestion time was controlled at 3,75 d. Four 1 ℓ methanogenic digesters were seeded with the mixed acids ac-

TABLE 1
SUMMARY OF EXPERIMENTAL CONDITIONS

Working volume (ℓ)	Detention time* (d)	Substrate concentration (mg COD/ℓ)
Batch test		
0,5	20	5 029;2 287
Semi-continuous conventional digestion		
2	8;12;15;20	22 750
Semi-continuous two-phase digestion		
Acidogenesis		
3	3,75	39 100
Methanogenesis		
1	11,1	37 920;22 750;11 380;5 688
	8;14;3;20	37 920

*The acclimation detention time of the seed sludge

TABLE 2
EXPERIMENTAL RESULTS OF BATCH TEST

Initial COD (mg/ℓ)	pH		Total gas production (mℓ)	Removal efficiency (%)*	
	Initial	Final		VFA	COD
5 029	7,40	7,61	1 750	98	67
2 287	7,55	7,63	610	98	49

*Digestion after 24 h

climated sludge and then fed individually with 37 920, 22 750, 11 380, and 5 688 mgCOD/ℓ leachate at a digestion time of 11,1 d. To determine the kinetic constants, another 3 methanogenic digesters were fed with 37 920 mgCOD/ℓ leachate and the digestion times were controlled at 8, 14,3 and 20 d. When the digesters reached their steady-state condition, the experiments started.

Analytical methods

The mixed liquor volatile suspended solids (MLVSS) used to express biomass concentrations and other water quality parameters were determined according to the procedure in Standard Methods (1980). Gas analyses were carried out with a gas chromatograph equipped with a thermal conductivity detector. Volatile fatty acids (VFAs) were analysed with a gas chromatograph fitted with a flame ionisation detector. The gas volumes were corrected for water-vapour content, assuming vapour-saturated gas, and to standard temperature (0°C) and pressure (760 mm Hg) (STP).

Results and discussion

VFA removal in batch test

Experimental results of the batch test are listed in Table 2. Figure 1 shows the time course of VFA and COD. VFA degraded almost completely (98%) during 24 h at initial COD concentrations of 5 029 and 2 287 mg/ℓ. However, COD did not decrease after 24 h (removal efficiencies were 67 and 49% at the two loading rates, respectively). This indicates that the component of the biodegradable COD in the leachate was volatile organic acids.

The distribution of VFA in landfill leachates varies with the chemical nature of the waste accepted at the landfill and the age of the landfill. It is recognised that different VFAs have different degradation rates. For the major intermediate products of anaerobic digestion, such as HAc, HPr, and HBu, the order of maximum specific substrate utilisation rate is HAc > HPr > HBu (Lawrence and McCarty, 1969; Chang et al., 1982). As an example, Fig. 2 indicates that HAc and valeric acid (HVa) were the major VFAs, but HPr had the slowest degradation rate. HPr degradation has been reported to be sensitive to acetate concentration, hydrogen pressure and environmental factors (Heys and Hall, 1983; Lin et al., 1986).

Semi-continuous conventional anaerobic digestion

The influent COD concentration was controlled at 22 750 mg/ℓ during the conventional digestion. The ratio of VFA to COD was 0,6 and no buffer was added because the pH was higher than 6,3. Table 3 summarises the experimental results. COD, BOD_5 and VFA removal efficiencies were higher than 93%. Residual VFA was only about 60 mgCOD/ℓ. Effluent BOD_5 to COD ratio reduced to 0,3 despite the high influent ratio value. The effluent pH was around 7,6 though the influent pH was near 6,4.

Effect of digestion time on organic removal. Figure 3 relates effluent BOD_5 and COD to digestion time and indicates that effluent BOD_5 and COD concentration reduced with increasing digestion time. At these digestion times, COD and BOD_5 removal

TABLE 3
EXPERIMENTAL RESULTS OF CONVENTIONAL ANAEROBIC DIGESTION

	Influent				Effluent			
Digester	**A**	**B**	**C**	**D**	**A**	**B**	**C**	**D**
Digestion time (d)	8	12	15	20				
Volumetric loading (kg COD/m³·d)	2,84	1,89	1,51	1,14				
Flow rate (mℓ/d)	250	165	133	100				
COD (mg/ℓ)	22 750				1 720	1 610	1 510	1 140
BOD_5 (mg/ℓ)	15 710				566	537	497	302
VFA (mg COD/ℓ)	13 740				63	35	37	27
pH	6,3 ~ 6,4				7,5	7,5	7,6	7,7
Alkalinity (mg/ℓ as $CaCO_3$)	2 330				3 820	5 040	5 200	6 400
MLVSS (mg/ℓ)	606				714	780	785	888
NH_3-N (mg/ℓ)	171				739	700	770	754
K (mg/ℓ)	1 297				1 210	1 040	950	954
Na (mg/ℓ)	688				840	776	704	515
Ca (mg/ℓ)	407				95	123	79	44
Mg (mg/ℓ)	618				404	381	397	360
Fe (mg/ℓ)	46				4,8	7,8	3,7	1,0
Gas production (mℓ/d)	--				1 900	1 520	1 200	800

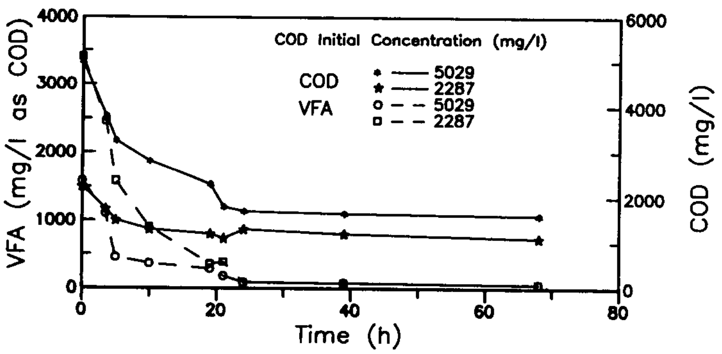

Figure 1
Time course of VFA degradation at various initial COD concentrations

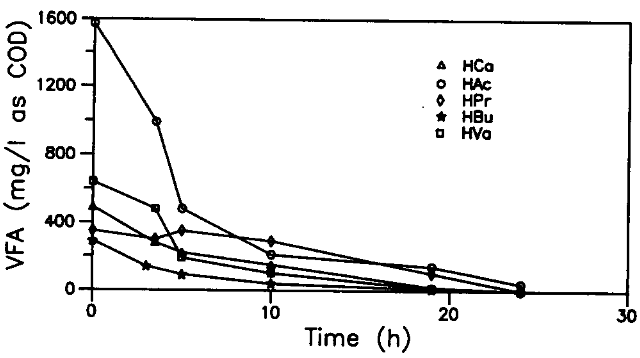

Figure 2
The volatile fatty acids in the leachate and their degradation

efficiencies were calculated to be more than 92,3% and 96,3% respectively. The volumetric loading rates ranged from 1,14 to 2,84 kgCOD/m³·d.

Sludge concentration. Sludge concentration (expressed as MLVSS) in the digester is one of the major factors affecting treatment efficiency. The sludge concentration decreased with decreasing digestion time and was equivalent to concentrations of 714 mg/ℓ and 888 mg/ℓ when the digestion times were 8 d and 20 d respectively. These values are in line with those of anaerobic digestion of pesticide-plant waste water (Lin, 1990).

Ammonia nitrogen. During digestion the organic nitrogen was converted into ammonia and this concentration reached 700 mg/ℓ (influent value was 171 mg/ℓ). Kroeker et al. (1979) reported that ammonia at concentrations higher than 5 020 mg/ℓ was inhibitive

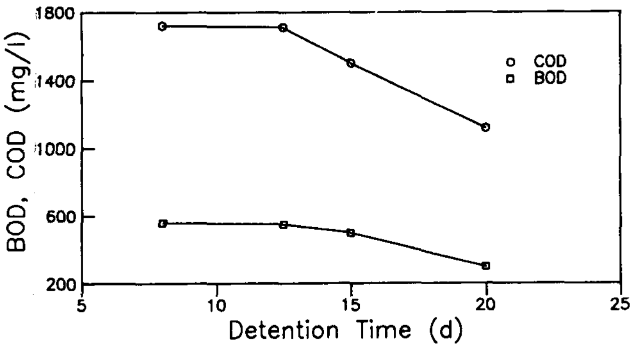

Figure 3
Relationships among BOD, COD and digestion time showing effluent organic concentrations decreasing with increasing digestion time

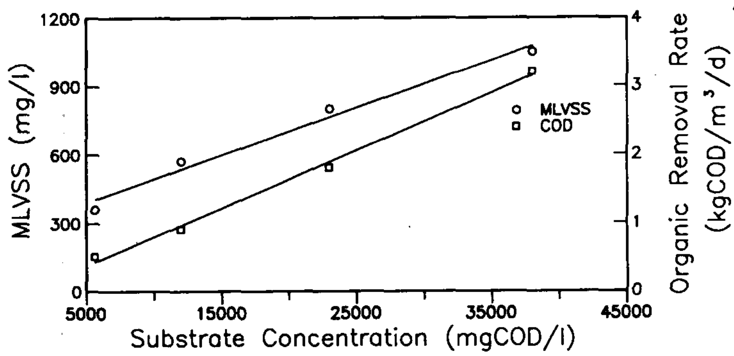

Figure 4
Relationships among biomass concentration, organic removal rate and substrate concentration

TABLE 4
EFFLUENT FROM ACIDOGENIC DIGESTER

Item	Influent	Effluent
COD (mg/ℓ)	39 100	37 920
Acetic acid (mg COD/ℓ)	9 006	10 711
Propionic acid (mg COD/ℓ)	1 589	2 369
Butyric acid (mg COD/ℓ)	5 299	4 671
Valeric acid (mg COD/ℓ)	10 596	10 429
Total VFA (mg COD/ℓ)	26 490	28 180
pH	6,42	6,32
ORP (-mV)	132	210
MLVSS (mg/ℓ)	1 102	559
Alkalinity (mg/ℓ as $CaCO_3$)	2 340	2 410
NH_3-N (mg/ℓ)	240	510

to methanogenesis. It can therefore be considered that the ammonia in each digester did not affect the digestion process adversely.

Semi-continuous two-phase anaerobic digestion

Acidogenic digesters. The influent COD was 39 100 mg/ℓ, and the ratio of VFA to COD was 0,68. At a digestion time of 3,75 d, under steady-state conditions the COD decreased to 37 900 mg/ℓ and the VFA concentration increased from 26 490 to 28 180 mgCOD/ℓ (Table 4). On the basis of VFA, HAc increased 19%, HPr increased 5%, and HBu decreased 12%. Since the total VFA increased only 6,4%, efficient acidogenesis was not obtained because the leachate originated from the anaerobic decomposition of the accepted wastes.

The digester liquid pH was maintained at 6,3 ± 0,1 which was at the same level as the influent value. Under steady-state conditions the values of ORP (oxidation-reduction potential) and ammonia were -210 mV and 510 mg/ℓ respectively, which were at the same levels as the reported values for acetogenic digesters (Ghosh et al., 1975).

Methanogenic digesters. The methanogenesis of the effluents from the acidogenic digester was studied by varying influent COD concentration and maintaining a constant digestion time. When digestion time was changed, the operating parameters were determined at an influent concentration. At various influent concentrations at a digestion time of 11,1 d, under steady-state conditions the ORP ranged from -354 mV to -404 mV and decreased with increasing influent COD concentration (Table 5). These ORP values were at the same level as the reported values (Ghosh et al., 1975; Shia, 1987). The pH values of digester contents ranged from 7,07 to 7,82 and were in good agreement with normal operating pH values for anaerobic treatment.

The alkalinity relates to the buffering capacity of a digester content. The alkalinity values ranged from 4 000 to 7 900 mg/ℓ (as $CaCO_3$) and increased with increasing substrate concentration at which more bicarbonate alkalinity was formed. It has been reported that 5 000 to 6 000 mg/ℓ of alkalinity did not affect a digester adversely (McCarty, 1964).

COD and BOD removal was more than 90%. The effluent COD and BOD in the digester fed with 37 920 mgCOD/ℓ of leachate were 2 841 and 994 mg/ℓ respectively. The effluent BOD to COD ratio was 0,35 and the difference between effluent COD and BOD could be considered as non-biodegradable COD and was calculated to be 4,8% on the basis of influent COD. For the other digesters non-biodegradable COD ranged from 4 to 6,2%. Figure 4 shows the relationships among biomass concentration, organic removal rate, and substrate concentration. Against the sludge concentration, the organic removal rate ranged from 1,28 to 3,03 gCOD/gVSS·d which indicates that the biomass activity increased with increasing substrate concentration. Volumetric organic utilisation rate increased with increasing influent substrate concentration and was 3,16 kg/m³·d.

The digester gas contained 74 to 78% of methane and the values are higher than a conventional anaerobic digester (61 to 66%) for a leachate (Shia, 1987). The methane conversion ranged from 0,32 to 0,34 ℓ/gCOD at STP and was comparable to the theoretical value, 0,35 ℓ/gCOD. Figure 5 relates to volumetric loading, gas production rate, and methane production rate and indicates that methane and gas production rates increased linearly with increasing volumetric loading.

TABLE 5
EFFLUENTS FROM METHANOGENIC DIGESTERS

Reactor	A	B	C	D
Influent COD (mg/ℓ)	37 920	22 750	11 380	5 688
Volumetric loading (kg COD/m³·d)	3,41	2,04	1,02	0,51
COD (mg/ℓ)	2 841	1 288	851	594
BOD_5 (mg/ℓ)	994	390	340	240
pH	7,82	7,59	7,41	7,07
ORP (mV)	-404	-383	-369	-345
Alkalinity (mg/ℓ as $CaCO_3$)	7 900	5 340	4 500	4 050
MLVSS (mg/ℓ)	1 042	798	568	358
NH_3-N (mg/ℓ)	1 160	784	369	251
Gas production (mℓ/d)	1 560	970	520	230

Kinetic constants

The Michaelis-Menten type equation, which has been used successfully in analysing methanogenic digestion kinetics (Lawrence and McCarty, 1969; Lin et al., 1986; Lin, 1990), and a commonly used bacterial growth expression were used to determine the biokinetic constants.

$$V = \frac{V_{max} S}{K_s + S} \quad (1)$$

$$D = V Y_g - K_d \quad (2)$$

where:

- V = specific substrate utilisation rate (mgCOD/mg·d)
- S = effluent substrate concentration (mgCOD/ℓ)
- K_s = substrate saturation concentration (mgCOD/ℓ)
- V_{max} = maximum specific substrate utilisation rate (mgCOD/mg·d)
- Y_g = growth yield of microorganism (mg/mg)
- K_d = endogenous decay coefficient of microorganism (ℓ/d)
- D = dilution rate (ℓ/d), inverse to hydraulic retention time

The kinetic values for V_{max}, K_s, Y_g, and K_d were determined by using the least squares method to plot S/V vs. S and V vs. D and the values were 3,38 ℓ/d for V_{max}; 0,04 mg/ℓ for K_s; 0,08 for Y_g; and 0,15 ℓ/d for K_d.

Comparison of conventional and two-phase digestion

Conventional digestion resulted in organic removal of 92,4% and is therefore comparable to two-phase digestion with 92,6% organic removal for the same magnitude of digestion times (8 to 20 d vs. 14,85 d). Figure 6 also indicates that the COD utilisation rates for the two processes were at the same incremental level with increased volumetric loading. These facts imply that the two-phase digestion process was not more efficient for leachate treatment than the conventional digestion process, because the acidogenic digesters did not function well. Some of the reasons why acidogenesis was not progressive were considered to be high VFA fraction in the leachate (VFA/COD = 0,55 to 0,69) and higher pH (6,4) for the

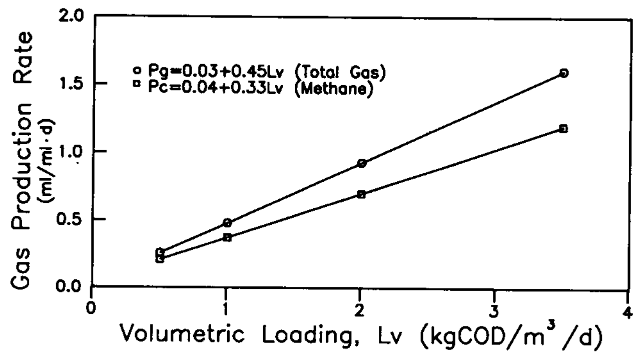

Figure 5
Gas and methane production rates increased linearly with increasing volumetric loading

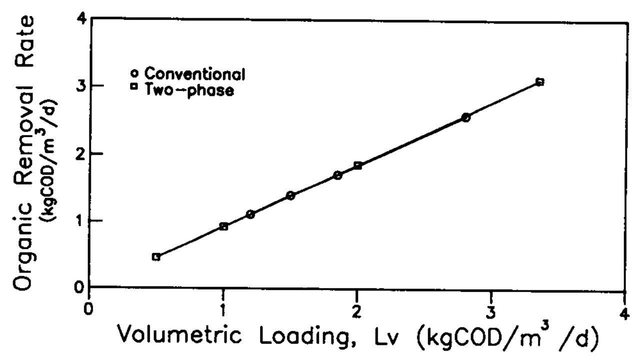

Figure 6
COD utilisation rates for conventional and two-phase digestion were at the same incremental level with increasing loading

acidogenic microorganisms, whose narrow optimum growth pH is near 5,7 (Ghosh et al., 1975).

Conclusions

The following conclusions can be drawn from the experimental results of the anaerobic treatment at 35°C using a landfill leachate:

- the conventional anaerobic digestion resulted in high efficiency of COD removal, but the acidogenic digesters of the two-phase digestion process were inefficient; and
- methanogenic reactors were efficient in COD and BOD removal.

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