

Full Length Research Paper

Semi-continuous anaerobic treatment of fresh leachate from municipal solid waste transfer station

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A semi-continuous leachate treatment process was developed in the present study. The fresh leachate was obtained from a municipal solid waste transfer station and palm oil mill effluent (POME) sludge was used as sources of anaerobic microbial complex. The semi-continuous treatment of leachate was operated in two phases; in Phase 1, the pH of the bioreactor was not adjusted, and in Phase 2, the pH of the bioreactor was adjusted by the addition of sodium hydroxide (NaOH). The initial values for both chemical oxygen demand (COD) and biochemical oxygen demand (BOD₅) of fresh leachate were extremely high compared with the stabilized landfill leachate. COD reduction rate for the semi-continuous process for Phase 1 and 2 were 37 and 52.7%, respectively. These results clearly showed that pH adjustment is important to enhance the COD removal in leachate treatment. In addition, we have analysed the evolution of volatile fatty acid (VFA) in the entire treatment process. The results indicated that the VFA concentration was a rapid indicator of the reactor's stability.

Key words: Anaerobic treatment, semi-continuous leachate treatment, fresh leachate, pH, COD, VFA.

INTRODUCTION

It has been observed that the solid waste generation in Malaysia has increased concurrently with the development of the country. For the past 20 years, Malaysia has undergone an economic growth with the rate of 5.2% (Agamuthu, 2001). The solid waste generated per capital has increased from 0.5 kg/capital/day in the 1980's to current volume of 1 kg/capital/day. This represents a 100% increased in the last 20 years (Agamuthu, 2001).

Municipal solid waste (MSW) is one of the major environmental problems faced by the Malaysian and world-

wide municipalities. Each year, there are about 8 million tonnes of solid waste being generated which accounts to each person generates about 1 kg of solid waste per day (LUMES, 2000 - 2001). Majority of the landfills in Malaysia and other developing countries are crude dumping ground and thus cause various environmental problems such as health hazards, surface water and ground water contamination, odour, etc. Sanitary landfills offer a viable option for the municipalities to deal with the environmental hazards caused by open dumps practice within its financial constraints.

Because of low cost and short term solution to solid waste problems, landfills are usually used in solid waste disposal. However, in modern cities such as Kuala Lumpur, there is a growing interest to use transfer station as an economic mode of transportation of MSW before it goes to the landfill. Leachate from wet constituents of solid wastes and water production from biological degradation of solid wastes becomes a source of water resource pollution. As leachate migrates away from land-fill or transfer station it may cause a serious pollution to ground water aquifer as well as adjacent surface waters.

There is a growing concern about surface and ground

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Nomenclatures: BOD, Biochemical oxygen demand; BOD₅, biochemical oxygen demand using a 5-day test; COD, chemical oxygen demand; BOD/COD, biodegradability; HAc, acetic acid; HBr, butyric acid; HPr, propionic acid; MSW, municipal solid waste; NH₃-N, ammonia nitrogen; PO₄⁻³, phosphate; SMP, soluble microbial product; TBTS, Taman Beringin Transfer Station; TVFA, total volatile fatty acid; VFA, volatile fatty acid; and VSS, volatile suspended solids.

water pollution from leachate. Different methods have been introduced for leachate treatment. Treatment of leachate is very complicated, expensive and requires various process applications due to high concentration of chemical oxygen demand (COD), biochemical oxygen demand (BOD), nitrogen, heavy metals as well as colour. Biological, chemical and physical processes have been used to treat leachate. High COD, BOD, ammonia, sulfate and presence of heavy metals in leachate cause different removal efficiency in each method. BOD/COD ratio is one of the factors in selecting treatment methods to remove organic matters. Biological treatment is usually used when BOD/COD ratio is equal or greater than 0.4 (Badkoubi et al., 2002).

Anaerobic treatment is a biological process ideally suited for the pretreatment of high strength wastewaters that are typical of many industrial facilities. The anaerobic process utilizes naturally-occurring bacteria to break down biodegradable material in an industrial waste stream. Due to its reliability, simplicity and high cost-effectiveness, biological treatment (suspended/attached growth) is commonly used for the removal of the bulk of leachate containing high concentrations of COD and BOD. Biodegradation is carried out by the microorganisms, which can degrade organics compounds to carbon dioxide and sludge under aerobic conditions and to biogas (a mixture comprising chiefly CO_2 and CH_4) under anaerobic conditions (Lema et al., 1988). The leachate composition from transfer station can be very much depending on several factors, including the degree of compaction, waste composition, climate and moisture content in waste. As a general rule, fresh leachate is characterized by high values of COD, ammonia nitrogen and heavy metals, low level of pH and as well as strong colour and bad odour (Ghasimi, 2008). At the same time, the characteristics of the leachate also vary with regards to its composition and volume, and biodegradable matter present in the leachate against time (Andreottola and Cannas, 1992; Chu et al., 1994). All these factors make leachate treatment difficult and complicated. Anaerobic treatment systems to treat the leachate have suffered many difficulties and it leads to instability of bioreactor systems as reported in many studies. Such instability is usually witnessed as a drop in the methane production rate, a drop in the pH, a rise in the volatile fatty acid (VFA) concentration, causing reactor failure. Hence, the primary objective of this research was to investigate the performance of anaerobic treatment of fresh leachate in terms of COD removal using semi-continuous process (Phase 1; using inoculum and no pH adjustment and Phase 2; using inoculum and pH adjustment) at the Taman Beringin Transfer Station, Kuala Lumpur, Malaysia.

MATERIALS AND METHODS

The start-up operation for the 10 L anaerobic reactor for the treat-

ment of leachate was achieved within a period of two months for semi-continuous processes, in which the maximum capacity of the system was tested at 6 kg COD/m³.day. Fresh leachate was taken directly from Taman Beringin Transfer Station (TBTS), Kuala Lumpur, Malaysia. The leachate were collected in 20 L plastic bottles, transported to the laboratory and sieved using a 1.5 mm mesh to remove solid particles such as shell, fiber, and small stone and then stored at 4°C before it was used for anaerobic treatment process. The leachate collected was checked for COD, BOD₅, total solids (TS), volatile solids (VS), total suspended solids (TSS), volatile suspended solids (VSS), alkalinity, VFA and pH according to the standard method for the examination of water and wastewater (APHA et al., 2000). Ammonia nitrogen concentration ($\text{NH}_3\text{-N}$) was detected by the Nessler method (380 HACH DR/2500 spectro-photometer) and phosphorous by the React PV method (490 HACH DR/2500 spectrophotometer). POME sludge was used as an inoculum to treat the fresh leachate since it contains low value of VFA and COD but enrich in TSS and VSS (source of anaerobic microorganisms). Before the inoculation, POME sludge was checked for COD, TS and pH as well as VFA value. Anaerobic treatment of fresh leachate was done for 2 series of experiments within a period of 27 and 30 days. These experiments were classified based on the condition where pH is uncontrolled (Phase 1) and controlled (Phase 2). The stirrer tank reactor (STR) used for this study was "BIOSTAT@B-10 L-MO (10 L working volume) and it was filled with 10 L POME sludge as seed bacteria at the marginal temperature range of mesophilic $28 \pm 2^\circ\text{C}$.

The fresh leachate with a flow rate of 1 L/day in semi-continuous mode was being added into bioreactor and mixed with POME sludge as the sources of microbial complex. During the start up, attempt was made to increase the organic loading rate (OLR) gradually and then fixed it for around 2 weeks. It was started from low value of OLR which were 1.5, 3, and 4.5 and finally maintained at 6 kg COD /m³.day with HRT 10 days. Discharging of treated leachate from the bioreactor was done prior to any loading of fresh leachate. Mixing was continuous during discharging and loading of fresh leachate. The treated leachate was kept for further analysis to determine the parameters value such as COD, BOD₅, VFA, TS, VS, TSS, VSS, $\text{NH}_3\text{-N}$, PO_4^{3-} and pH. The flow diagram for the semi-continuous anaerobic leachate treatment is depicted in Figure 1.

RESULTS AND DISCUSSION

Characteristic of fresh leachate

The mean characteristics of the fresh leachate sample from the transfer station are presented in Table 1. It was found that the leachate has BOD₅/COD ratio of 0.5. This showed that most of the organic materials were in acidic phase, thus having high ratio of biodegradability (BOD/COD) indicated the suitability of biological treatment process for treating the fresh leachate.

Characteristic of POME sludge

POME sludge was collected from the anaerobic treatment pond at the Seri Ulu Langat Palm Oil Mill Sdn.Bhd. located at Dengkil, Malaysia. It was used as a seeding in the bioreactor having characteristic shown in Table 2.

Figure 2 depicts the evolution of initial, effluent and removal percentage of COD in semi-continuous treatment process of leachate. The leachate treatment was

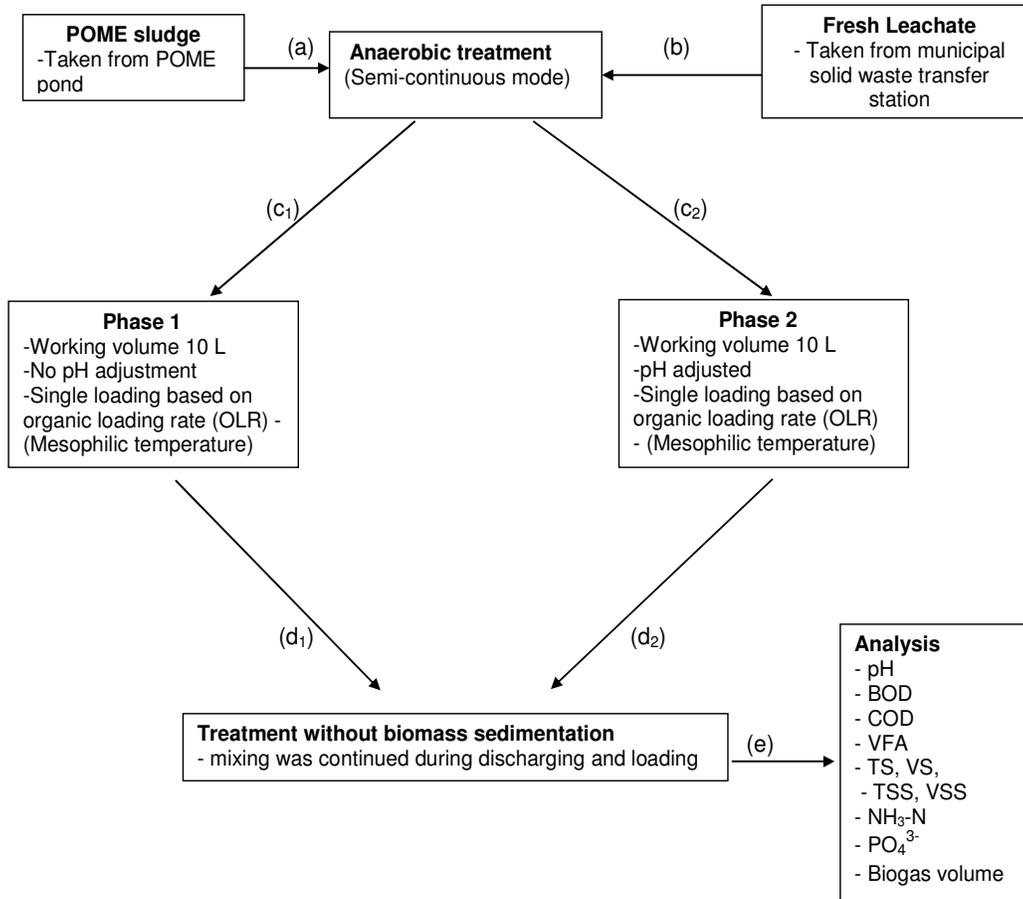


Figure 1. The flow diagram for the semi-continuous anaerobic leachate treatment operation.

Table 1. Mean characteristic of fresh leachate.

Parameters	Concentration
Acetic acid	1900
Propionic acid	680
I -Butyric acid	510
N - Butyric acid	3263
I -Valeric acid	370
N - Valeric acid	1190
pH	4.8
BOD ₅	30000
COD	60000
BOD ₅ /COD	0.5
TS	26790
VS	21060
TSS	4200
VSS	3350
FSS	850
NH ₃ -N	268
PO ₄ ³⁻	312

Note: All parameters unit is in mg/L except for pH.

Table 2. POME sludge initial conditions.

COD	VFA	TS	pH
2150	231	36000	7

Note: All parameters unit is in mg/L except for pH.

first operated by feeding the fresh leachate with a COD concentration of 60000 mg/L at a flow rate of 1 L/day. The pH was unadjusted, hence, after the feeding; the pH was decreased from 6.5 to 4.8 at the end of the Phase 1 operation. As the feeding started, the effluent COD was increased from 9600 mg/L at day 3 to 37760 mg/L at day 15. Thus, the COD removal percentage had decreased from 84 to 34.3% at day 15. The COD concentration of the feeding leachate was reduced from 60000 to 55000 mg/L at the end of the Phase 1 operation to investigate the effect of reduction in initial COD concentration on the COD removal efficiency. The decreased of COD concentration in the feeding has resulted in decreased in COD concentration in the effluent too. As depicted in Figure 2, the COD concentration of the effluent decreased to 34560 mg/L till end of phase 1 at day 27,

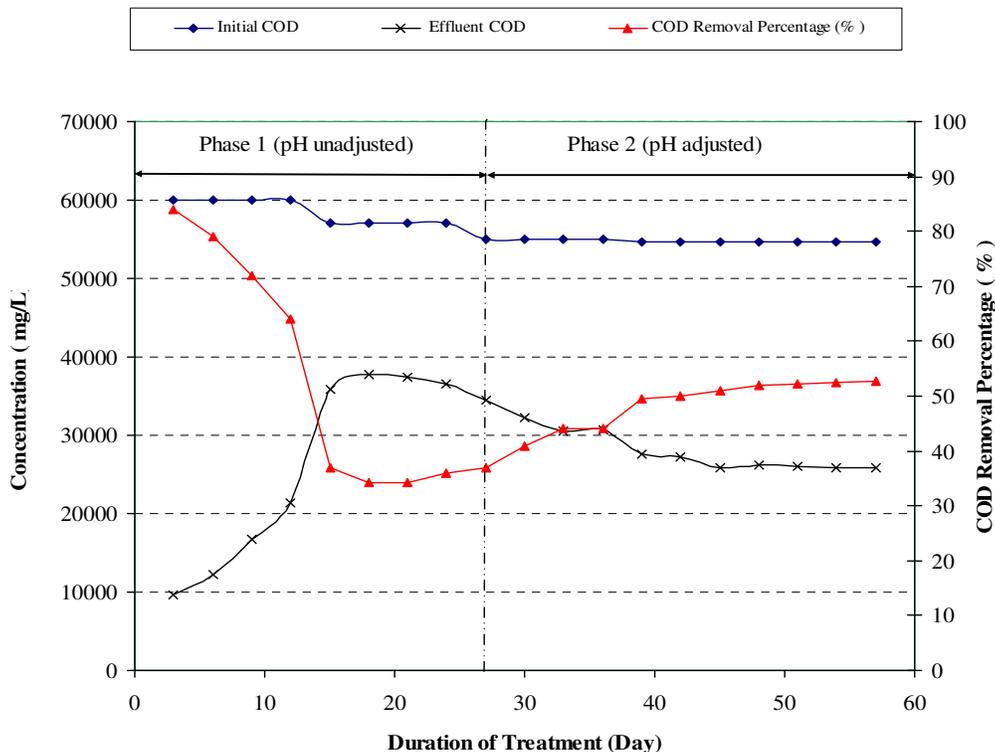


Figure 2. Variation of initial COD, COD effluent and COD removal percentage vs. duration of treatment (day).

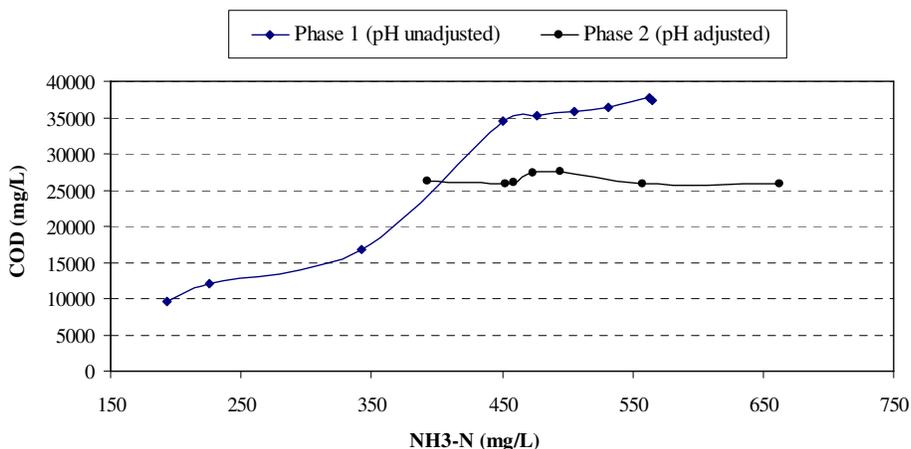


Figure 3. Variation of COD effluent vs. pH for phase 1.

corresponding to the increase in COD removal to 37% at day 27.

The Phase 1 of the semi-continuous leachate treatment operation showed that there was an increment of COD value exponentially. This perhaps was due to the soluble microbial products (SMP) production which in turn contributed to the COD value in the effluent. Various articles have proven that the formation of SMP in anaerobic systems indeed gave rise to a certain percentage of COD

in the effluent of wastewater treatment system (Barker and Stuckey, 1999; Aquino and Stuckey, 2003; Goorany and Ozturk, 2000; Lu et al., 2002).

Figure 3 presents the relationship between COD effluent and pH for Phase 1 of semi-continuous leachate treatments. The decrease of the COD concentration of the feeding in Phase 1 only led to a small increase in COD removal. Therefore, other operating factors may play an important role on the COD removal in this semi-

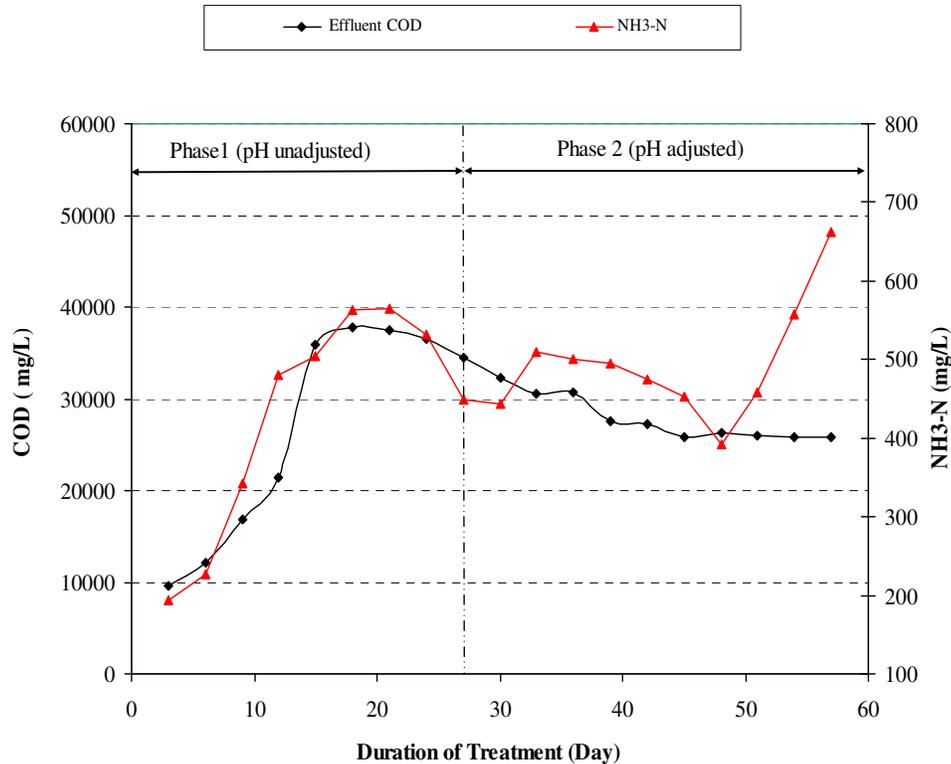


Figure 4. Variation of COD effluent and NH₃-N vs. duration of treatment (day).

continuous leachate treatment. At the beginning of the operation, pH of the POME was around 7 and by stabilizing the OLR at 6 kg COD /m³.day, it gradually declined to 6.5 at the first day of operation. The pH of the bioreactor was further declined to 4.5 at the end of the Phase 1 operation. As shown in the plot of effluent COD versus pH of bioreactor (Figure 3), the effluent COD was inversely proportional to the bioreactor pH. It is suggested that the decrease in COD removal may be due to the increase in pH in the bioreactor. Hence, in the Phase 2 of operation, the pH of the bioreactor was adjusted by the adding of caustic (NaOH 5 M).

Phase 2 started by feeding the bioreactor with fresh leachate with COD concentration of 54600 mg/L. The COD effluent was smoothly decreased from 32300 to 25780 mg/L from day 30 to day 57 and remained stable at this range. Therefore, by adding caustic (NaOH 5 M) to adjust the pH in phase 2, the COD removal increased from 37% at the end of Phase 1 to its final value of 52.7% at the end of Phase 2 operation. In Phase 2 operation, the pH was increased from 4.5 at the beginning to 7.6 at the end of the operation. Adding alkaline to the bioreactor has increased the alkalinity from zero to 5450 mg CaCO₃/L. Leachate variations as feedstock in terms of COD was roughly constant and only a 9% reduction of initial COD was observed through the whole experiment (low biodegradability of leachate). The increase in COD removal percentage from 37% in Phase 1 to 52.7% in

Phase 2 has indicated that adding caustic as a pH controller has helped to provide a better environment for the growth of methanogens bacteria and the degradation of the substrate. At day 39 and pH 6.7, COD removal tended to be constant while pH was going up smoothly. The BOD₅ removal was 78 and 90% for Phase 1 and 2, respectively. This indicated that the anaerobic treatment was more efficient in BOD₅ removal.

The evolution of COD and NH₃-N in the bioreactor was depicted in Figure 4. Ammonia content which is produced from hydrolyzation of complex protein was also increased and coincided with COD effluent reaching its maximum value at day 21. On the other hand, the decrease of COD concentration at the end of Phase 1 led to the decrease in ammonia nitrogen which was declined until the end of Phase 1. In Phase 2, ammonia nitrogen was first increased slightly and then decreased again until day 48. However, it rose up sharply at the day 48 while COD was slowly declining and stabilizing at the end of experiment. Although methane forming bacteria has been reported that can acclimate to free ammonia, however, unacclimated methane forming bacteria can be inhibited at free ammonia concentration > 50 mg/L (Gerardi, 2003). Therefore, the high ammonia nitrogen level observed in the present experiment may inhibit the growth of methanogenesis bacteria. On the other hand, adjusting pH above 7.3 caused the released and the increased of ammonia level while COD was generally constant in the

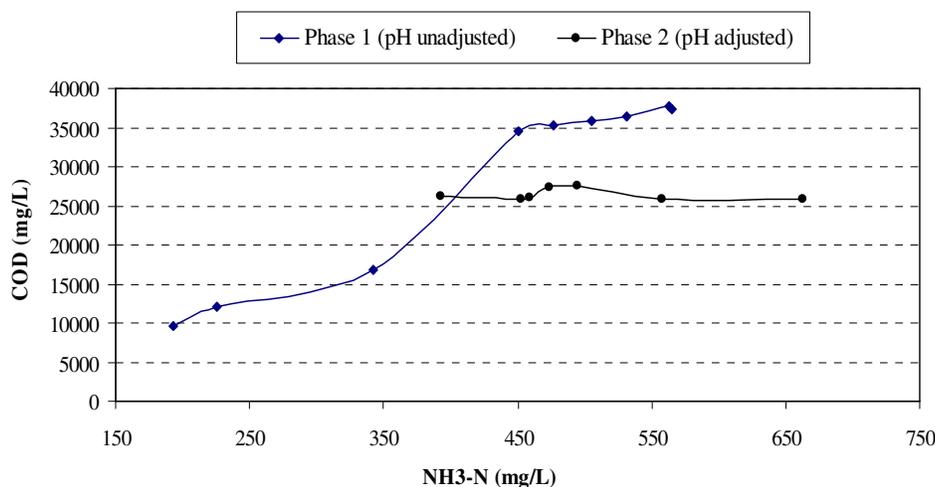


Figure 5. Variation of COD vs. NH₃-N for phase 1 and 2.

Table 3. Effect of free ammonia on anaerobic process.

Concentration (as N, mg/L)	Effect
50 to 200	Beneficial
200 to 1000	No adverse effect
1,500 to 3,000	Inhibitor for pH > 7.4 to 7.6
Above 3,000	Toxic

Source: McCarty (1964).

system.

As it is clearly shown in Figure 5, COD value increases with the increase of ammonia nitrogen for Phase 1 (pH unadjusted). The COD concentration increased from 9600 exponentially to 34560 mg/L while ammonia nitrogen was increased from 193 to 450 mg/L. This was followed by a gradual increase in COD and NH₃-N to 37440 and 565 mg/L, respectively at the end of Phase 1. A 65% increase in ammonia nitrogen was observed. In Phase 2 (pH adjusted), COD concentration was relatively constant at pH range of 7.25 - 7.6 and decreased from 26240 to 25780 mg/L while ammonia still was increasing from 393 to 663 mg/L and obtained 40% increment at the end of Phase 2.

A similar trend in the evolution of COD and NH₃-N concentration was observed in Phase 1 (Figure 4), in which a 74 and 65% increase in COD and ammonia nitrogen were recorded. In Phase 2, there were no significant fluctuations in COD variation while NH₃-N was continuously rising up. The reason for that was implicated by the pH adjustment in this phase, where considerable increase in alkalinity was obtained. It is noted that alkalinity is the result of the release of amino groups (-NH₂) and production of ammonia (NH₃) as the proteinaceous wastes are degraded (Gerardi, 2003). In the acid phase,

concentrations were generally higher due to enhanced formation of dissolved organic matter and release of ammonia but in the methanogenic phase, the content of dissolved organic matter significantly decreased and the composition of the organic matter changes was indicated by BOD: COD ratios 0.11. The ammonia concentration seemed not to follow the same decreasing trend and may constitute one of the major long-term pollutants in landfill leachate as occurred exactly in this study (Kjeldsen et al., 2002).

Table 3 shows the effect of free ammonia on anaerobic process. Ammonia was produced as a by-product of anaerobic digestion, principally from the mineralization of organic nitrogen during the deamination of proteins and amino acids. Decrease in pH from 6.3 to 4.8 resulted in increment of NH₃-N concentration, which showed a steady increase due to deamination of proteins and amino acids. Ammonia nitrogen at pH 7.3 until end of treatment was drastically increased and this indicated that protein and amino acids were broken down rapidly and caused the increase in alkalinity in the reactor.

The evolution of acetic acid, propionic acid and COD effluent of the semi-continuous leachate treatments is illustrated in Figure 6. At the beginning of the operation the concentration of acetic acid (HAc) was higher than propionic acid. However, while the concentration of acetic acid was increased gradually to 2180 mg/L, the propionic acid (HPr) was drastically increased coinciding with increment of COD effluent at day 9 of the treatment. The COD effluent reached its maximum level of 37760 mg/L at day 18, while acetic and propionic acids both were slightly constant at the same range of concentration at pH 5. Propionic acid was constant approximately until end of Phase 1, whereas acetic acid had an increase until day 27 (end of phase 1).

Increasing in COD value in the treated leachate was observed to be inline with the increment in the VFAs

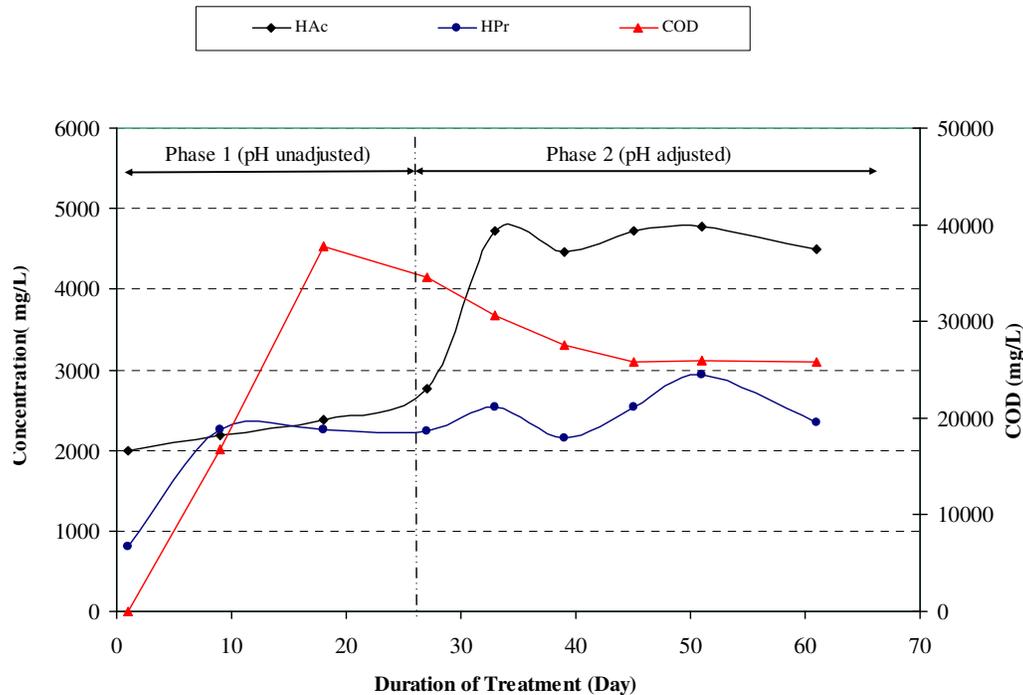


Figure 6. Variation of acetic acid, propionic acid and COD effluent vs. duration of treatment (day).

value, especially for propionic acid in Phase 1 which had 65% increase. This is because large amount of VFAs has also contributed to the COD measured in the treated leachate. In Phase 2, as a result of adjustment of pH by sodium hydroxide, COD effluent was continuously decreased until end of experiment. Since day 27 until day 33 increments in both acids were observed, but the rate of HAc production was higher than HPr at pH 5.8 that indicated the capability of the system in production of acetic acid. However, after that both acids declined till day 39 at pH 7.3, then increased again to their maximum values of 4778 and 2931 mg/L for day 51 at pH 7.6, respectively. COD effluent was generally constant from day 45 till end of Phase 2.

However, at the end of Phase 2, both acids, HAc and HPr, declined to 4500 and 2350 mg/L, respectively. The results showed the possible presence of methanogenesis bacteria to degrade the organic compounds inside the leachate. The production of acetate is accomplished through the activity of acetogenic or acetate-forming bacteria. In normal situations, acids are used as substrate by the methanogens bacteria at about the same rate as they are produced (Yacob et al., 2006). However, as VFA value increased drastically, it indicated the slow conversion of VFA by methanogens. It is important to be noted that from day 39, biomass (VSS) also declined till end of the treatment, while increase in both acids concentration was observed. Therefore, it was possible that washout and death of methanogens bacteria were the reasons of VFAs accumulation in the bioreactor which will be dis-

cussed further in Figure 8.

Figure 7 shows the evolution of phosphate in the semi-continuous leachate treatment. In Phase 1, concentration of PO_4^{3-} rapidly commenced to increase from low level of 151 mg/L at day 3 to the maximum value of 403 mg/L at 21. The increase in PO_4^{3-} was associated with a decrease in pH from 6.2 to 4.8 in Phase 1 of operation. In Phase 2 attempts were made to raise the pH from 4.5 to the methanogenesis growth range (6.8 - 7.5). The PO_4^{3-} concentration was decreased gradually as the pH was increased. The trend of the evolution of PO_4^{3-} was similar to that of $\text{NH}_3\text{-N}$ in Phase 1 operation as depicted in Figure 7.

The evolution of VSS of the semi-continuous leachate treatments is depicted in Figure 8. The VSS concentration was first decreased sharply from 5812 mg/L (pH 6.5) at day 3 to 3937 mg/L (pH 5.6) at day 12. After that, the VSS was increased and reached its maximum value of 4850 mg/L at day 24, and was decreased again to 3988 mg/L at the end of Phase 1 at day 27 (pH 4.5). Average VSS/TSS ratio for Phase 1 was determined 76.8%.

In Phase 2 of leachate treatment, the VSS was sharply increased to the maximum concentration of 5700 mg/L at day 36 (pH 6.4). Subsequently, the VSS was further decreased to the lowest value of 2262.5 mg/L at the end of Phase 2, although the pH of the bioreactor was further increased. Increase in alkalinity in the system caused increment in VSS from 3988 mg/L at day 27 to 5700 mg/L at day 36 in Phase 2, which may indicate that pH adjust-

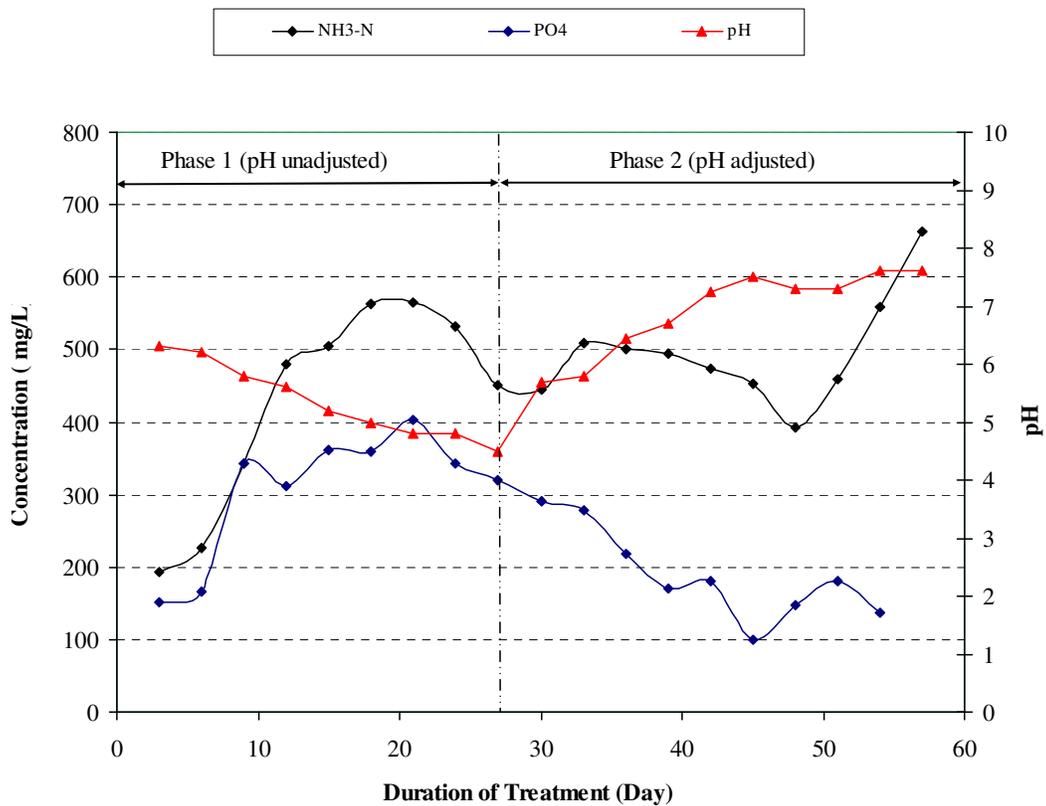


Figure 7. Variation of ammonia nitrogen, phosphate and pH vs. duration of treatment (day).

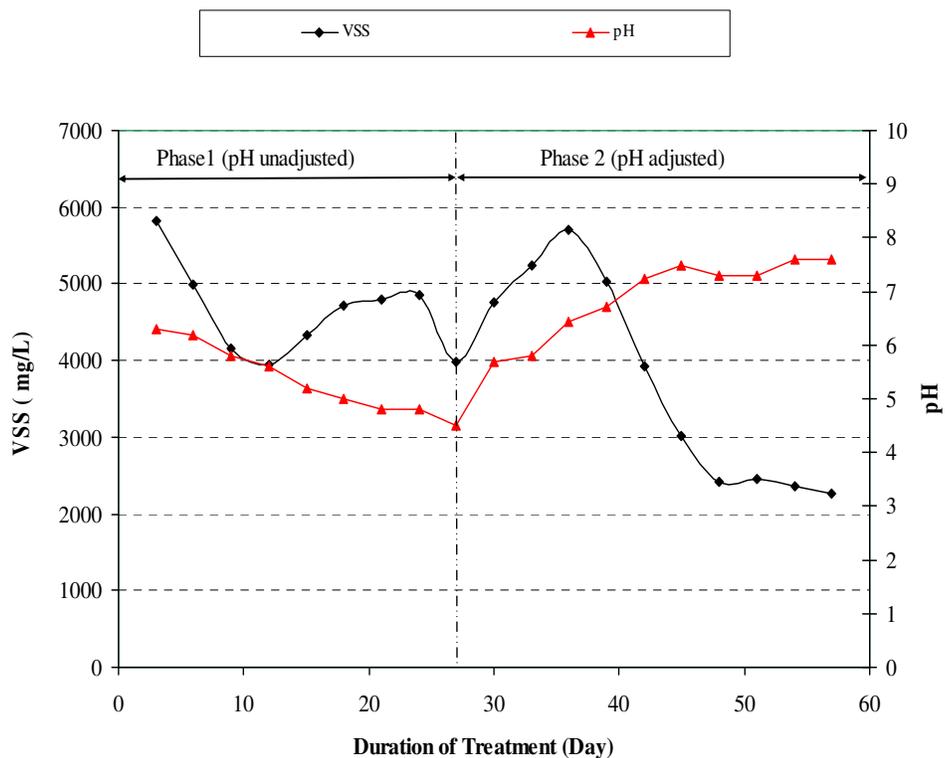


Figure 8. Variation of VSS and pH vs. duration of treatment (day).

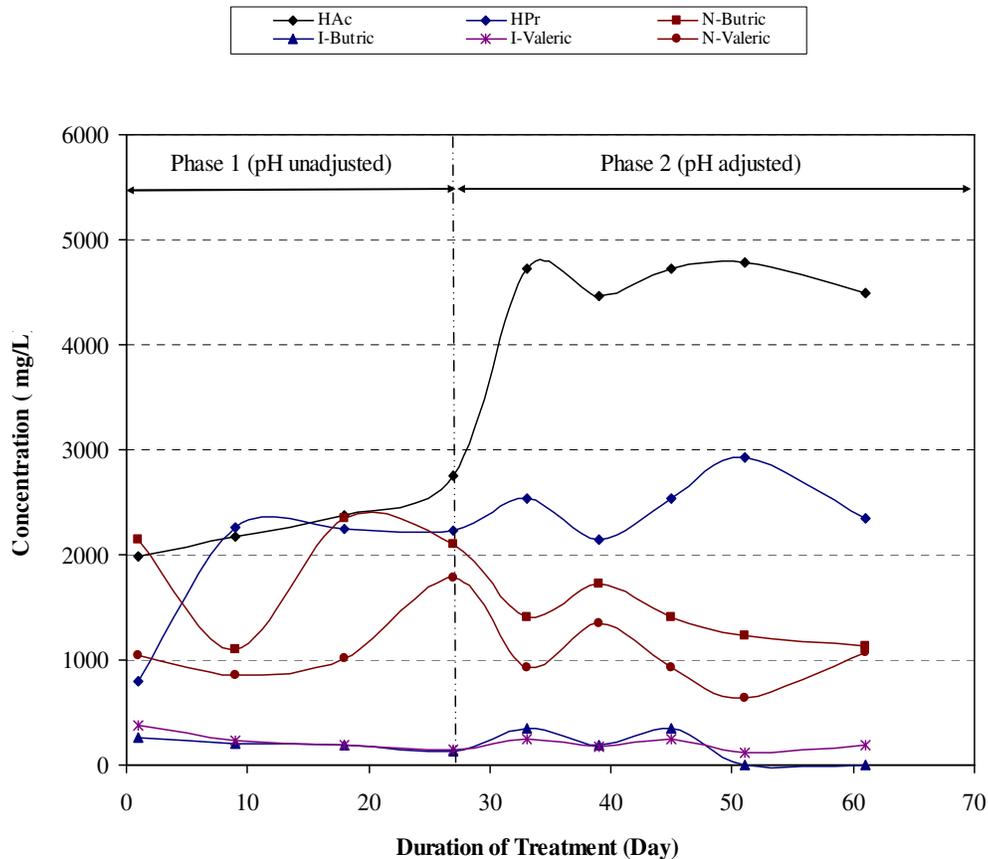


Figure 9. Variation of VFAs vs. duration of treatment (day).

ment was effective to increase the VSS concentration but it did not last for longer time (day 37 to 56). The declining of biomass from day 37 to 56 might due to the following reasons:

1. Shortage of biodegradable substrate for biomass to grow.
2. Death of microorganisms due to the toxicity compounds presented in the reactor.
3. Since no biomass was allowed to settle in the operation (continuous mixing), a lot of biomass was washout as confirmed by the reduction in VSS value inside the bioreactor. This was also experienced by Yacob et al. (2006) in which good mixing of the reactor has caused the beneficial biomass to washout during the routine loading of raw POME. Cail and Bardford (1985a, b) reported by operating in a mix and settle mode it is possible to accumulate and retain high biomass concentration in the reactor.
4. The other possible reason maybe because of toxicity resulted using extra NaOH to adjust the pH that has increased the concentration of Na^+ in the reactor. According to Kim et al. (1994) the use of NaOH to control the pH during the fermentation would cause cells lysis due to the toxicity and that was observed at the end of the Phase 2

operation in the present study.

The distribution of residual VFA in the reactor is depicted in Figure 9 which shows the accumulation of HAc, HPr and n-butyric acid (n-HBu) in the ratio of about 1.2:1:1 for Phase 1 on a COD basis, respectively. It was found that n-HBu concentration in the some period of time was higher than acetic acid concentration or any other type of fatty acids in Phase 1. This may indicate that the conversion from n-butyric acid to acetic acid might become the rate controlling step of biodegradation process.

In Phase 2, it was aimed to increase the pH from acidic zone to the acceptable range of methanogens growth (6.8 - 7.5) to gain more efficiency in anaerobic digestion. At the first day of Phase 2, acetic acid concentration was 1.7 times higher than what was reported at the end of Phase 1 (2760 mg/L). Propionic acid had a little increase around 300 mg/L. Decrease in n-butyric acid was also observed at approximately 964 mg/L. It was expected that microbial populations inside the bioreactor can adapt with the new environmental condition. VFAs, HAc and HPr, started to increase and reached the maximum values of 4778 and 2931 mg/L, respectively, with total volatile fatty acid (TVFA) of 9695 mg/L at day 51 (pH 7.3). They were then decreased to 4500 and 2350 mg/L,

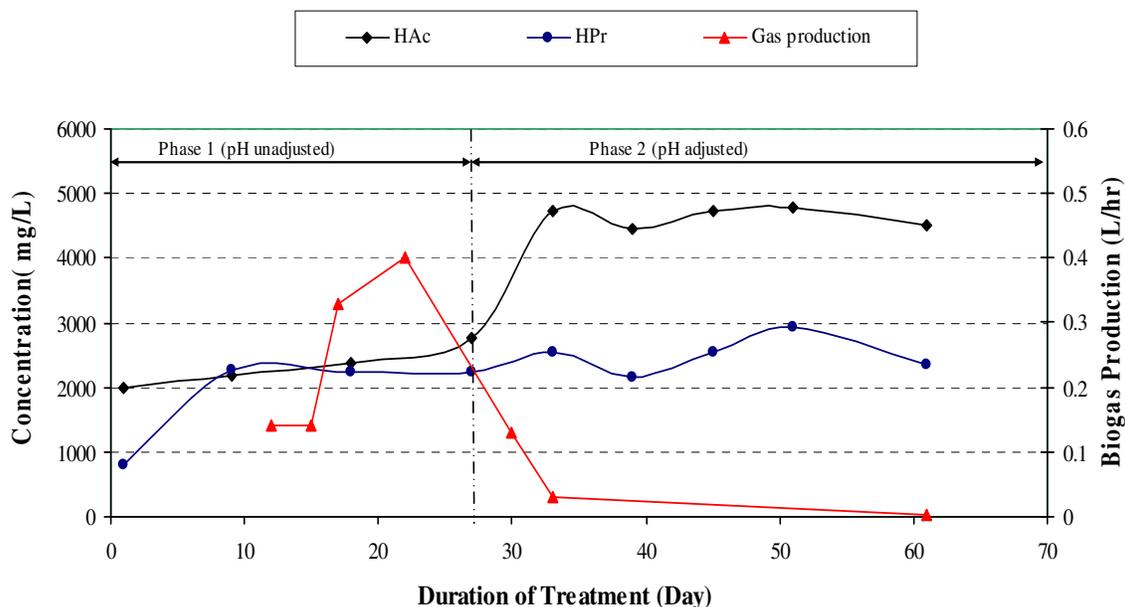


Figure 10. Variation of acetic acid and propionic acid vs. biogas production.

Table 4. Biogas component percentage for day 33 and 61 of Phase 2.

Type of biogas production	Day 33 (Phase 2-pH adjusted) pH 5.8	Day 61 (Phase 2-pH adjusted) pH 7.6
Hydrogen (%H ₂)	46.92	0
Methane (%CH ₄)	15.54	99.99
Carbon dioxide (%CO ₂)	37.53	0

respectively with TVFA of 9243 mg/L. Since the first day of Phase 2 till end of the experiment, TVFA had 10% reduction in concentration that is too low to establish the balance between the acetogenic and methanogenic phase which indicated an imbalance in the bioreactor leading to the accumulation of high amount of acids, especially acetic acid. Therefore, methanogenesis bacteria might not be able to survive in the bioreactor. The distribution of residual VFA in the reactor showed HAc, HPr and n-HBu accumulated in the ratio of about 3.4:2:1 for Phase 2 on a COD basis, respectively. Acetic acid accumulated rapidly in the reactor and reached more than 39% increment in comparison to day 27, while propionic increased to 5% and n-butyric reduced to 46% in Phase 2.

Figure 10 clearly shows that acetic acid gradually started to increase from its initial value of 1988 to 2760 mg/L at day 27, at the end of Phase 1, while propionic acid rose up dramatically from 800 to 2260 mg/L at day 9. The level of propionic acid was maintained constant until end of Phase 1, which was 2236 mg/L. Biogas production started from low level of 0.14 L/h and reached rapidly the maximum value of 0.33 and 0.4 L/h at day 19 and 22, respectively. Obvious reduction in biogas production was

observed since day 22 until end of anaerobic treatment in Phase 2, while sensible increment in volatile fatty acids was considerable.

Biogas production decreased drastically to 0.11 L/h at day 29 at pH 5.7 and after that gradually decreased until end of the experiment which was 0.0864 L/h at day 61 (pH 7.6). In Phase 2 by adding the NaOH into the bioreactor, both acids increased to 4778 and 2931 at day 51 and pH 7.3 and slowly decreased to 4500 and 2350 mg/L at day 61 (pH 7.6). High increase in VFA concentration in the bioreactor indicated the slow conversion of VFA by the methanogens bacteria.

As it is obvious, accumulation of acetic acid was the major reason to cause bioreactor inhibition and consequently low amount of biogas production. Table 4 shows the biogas components percentage at day 33 and 61 in Phase 2 (first and end of Phase 2).

The major biogas components in the first sample (day 33) were mainly CH₄, CO₂ and H₂. It has been seen in this section that methanogens bacteria can survive at pH < 6 (5.8). The decrease in the methane content in day 33 was due to the increase in the carbon dioxide content which was a result of the chemical equilibrium between the CO₂ partial pressure in the reactor gas components,

bicarbonate and pH of the liquor (McCarty, 1964). The decline in methane concentration in the biogas mixture also can be attributed to the loss of biomass and high concentration of organic matter introduced into the system. In other words the equilibrium of microbial population and as well as production and conversion of organic acids into methane had been disturbed.

Volume of gas production for day 33 and 61 were 0.03 and 0.0036 L/h, respectively. It can be understood that anaerobic treatment was fully inhibited. As it has been shown in Table 4, hydrogen production has the highest value of 49.92% among the other produced gases and methane production percentage was 15.54 at day 33 (pH 5.8). In day 61 it has been determined that neither H₂ nor CO₂ were detectable and only produced gas was methane. Almost all of CO₂ was dissolved and its partial pressure was too low. Generally, the rate of methane production was too low in both days and methanogenic activity was effectively inhibited in the bioreactor. Major reason could have been accumulation of VFAs and also adding more alkaline into the reactor in order to raise the pH to the suitable level of anaerobic treatment 6.8 – 7.5. Main biogas produced was methane and the amount of CO₂ concentration was zero or negligible. The reason might due to the dissolving of CO₂ in supernatant and also introducing more NaOH as an alkaline caused the CO₂ to be more dissolved and absorbed from the gas compositions as normally gas production during the fermentation is collected after passing through distilled water and NaOH solution 3 N to remove the carbon dioxide produced during fermentation (Rincón et al., 2008).

Conclusion

In this study it was found that using POME sludge as source of anaerobic microbial has effectively removed the COD from leachate. The efficiency of COD removal was 37 and 52.7%, for Phase 1 and 2, respectively for the semi-continuous leachate treatment. In this research it has also been observed that acetic acid plays the indispensable role in anaerobic treatment of fresh leachate in which high level of HAc concentration resulted in imbalance between the acetogenic and methanogenic bacteria and subsequently led to low production of biogas and less COD removal. The results of this study are significant for wastewater treatment process. Semi-continuous reactor failure is characterized by an increase in the VFA concentrations and there is now considerable evidence which shows this can be detrimental to the degradation of both acetic and propionic acids.

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