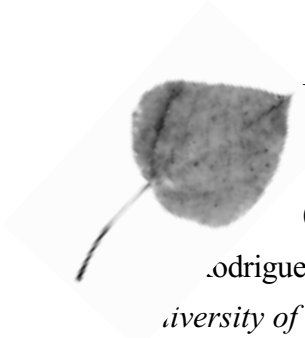

REMOVAL OF HEAVY METALS AND PATHOGENS DURING BIPHASIC FERMENTATION OF SOLID WASTES

.odriguez, J.B. Richardson, and S. Ghosh

.iversity of Utah, Department of Civil Engineering, Salt Lake City, UT 84112; Phone: (801)581-5152, Fax: (801)581-6937

ABSTRACT

Research was conducted to study the effects of biphasic anaerobic fermentation upon an organic fraction of municipal solid waste, and to observe the fate of heavy metals and pathogenic organisms in the acidogenic and methanogenic environments of the biphasic process. The high-solids (16 wt % solids) substrate was packed in a bench-scale, anaerobic, solid-state fermenter with amounts of lead nitrate and cadmium chloride which corresponded to limits for these metals as per EPA 503 Regulations for biosolids (840 mg Pb/kg TS and 85 mg Cd/kg TS). Solid-state, hydrolytic-acidogenic fermentation was induced by an anaerobic digester innoculum; recirculation of the percolated culture (leachate) from bottom to the top of the solid bed accelerated the production of volatile fatty acids (VFAs) which reached concentrations of 18,000 mg/L at an ambient temperature of 23 ^{o}C. Solid-state fermentation was characterized by a low culture pH of 4 – 5, production of soluble COD, and generation of high-CO2 head gases. Leachate VFAs were recycled to a methane fermenter where they were gasified to methane (75-80 mol%). Dissolved lead and cadmium concentrations were significantly reduced during two-phase operation. Destruction of fecal coliforms was observed in nine days of acid-phase operation, which suggests that digested solids may comply with EPA 503 Regulations for pathogens and metals.

Key words: *anaerobic digestion, biphasic fermentation, acidogenic, methanogenic, heavy metals, pathogen removal*

INTRODUCTION

Increasing population and decreasing space for landfills have spawned research involving the treatment of municipal solid waste (MSW). An estimated 208 million tons of municipal solid waste is disposed of annually in the United States. Municipal landfills often contain lead acid and nickel cadmium which may leach into underlying aquifers. According to the USEPA, 250,000 metric tons of lead and 2400 metric tons of cadmium will be codisposed with MSW in the U.S. (USEPA, 1996).

Concentrations of these heavy metals are pervasive in landfill leachate and have been known to percolate into groundwater supplies. Since roughly 50% of the populace relies on groundwater for potable water, contamination of these resources would be disastrous. Current treatment technologies for hazardous landfill leachate are physical and/or chemical processes that tend to be costly. However, previous research has shown that biological processes may be used to effectively treat solid waste. New trends encourage reuse, recycling with, and treatment with energy recovery as opposed to land disposal. Recently, simulated municipal solid waste containing known amounts of lead and cadmium (SMSW) was stabilized using a two-phase anaerobic fermentation process, well-suited to produce high-grade methane (75-80%). Results also suggest that metals partitioned into the methane phase. Complete destruction of fecal coliforms was observed in a separate exepriment after a short period of acid-phase operation.

Recent USEPA Biosolids Rules (USEPA, 1994) categorize sewage sludge solids (biosolids) generated in wastewater treatment plants as Class A, B, or C soil amendments. For Class A solids, ceiling limits for lead and cadmium are 840 mg/kg and 85 mg/kg, respectively. Fecal coliform counts should be less than 1000 MPN/g TS. Finally, at least 38% of the volatile matter content must be stabilized (USEPA, 1994). It should be noted that few of the physico-chemical and/or biological processes used until now meet the stringent Class A requirements (Ponugoti et al.., 1997; Stukenberg et al.., 1994).

Two-phase fermentation of MSW is an economical treatment technology which enhances the biologically mediated hydrolysis and gasification of solid waste into methane gas, a potential source of energy. Other advantages include higher methane yields when contrasted with single-phase processes. Sorption of some heavy metals such as lead in the acid phase may also be enhanced (Leighton and Forster, 1997). Anaerobic digestion was found to achieve significant pathogen destruction (Ponugoti et al., 1997). Two-phase operation allows for a lower pH in the acid phase which will further contribute to the destruction of pathogens to comply with EPA 503 Regulations for Class A biosolids.

EXPERIMENTAL DESIGN

Three bench-scale experiments were performed on 1.22 kg of organic simulated MSW to separately investigate the fate of lead and cadmium, pathogen destruction, and waste stabilization using a two-phase process. The experiments are described as:

System 1: Energy production and stabilization of MSW by biphasic fermentation

System 2: Fate of lead and cadmium metals during biphasic fermentation

System 3: Destruction of pathogens during solid-state acid fermentation

System 1

A cylindrical, jacketed, cone-bottomed 14-L capacity (8-L waste volume) vessel of Plexiglass construction, maintained at an ambient temperature of 25 ^{o}C, was used to simulate a solid-bed landfill bioreactor. The reactor was hermetically sealed to maintain anaerobic conditions. Gas was collected from a port on the reactor head plate and measured by a tritube manometric device. The operation of the manometer was controlled by an electro-mechanical, liquid-level controller which was connected to a gas counter.

A cylindrical, upflow, Plexiglass methane-phase reactor was randomly filled with plastic Pall rings. The packing material had a 90% void volume. The reactor had a culture volume of 8 L, maintained at 35 ^{o}C. Gas production was monitored as previously described.

System 2

The experimental apparatus consisted of a solid-bed reactor containing a solid waste volume of 8 L, as in System 2. The packed-bed, methane-phase reactor was constructed as described in System 1, but had a culture volume of 1.3 L.

System 3

A 10-L cylindrical Plexiglass reactor, maintained at an ambient temperature of 23°C, was used to contain an 8-L waste volume (primary sludge).

SYSTEM OPERATION

System 1

Anaerobic fermentation was operated until incremental gas production from the two reactors was negligible (after 524 days). The 524 time interval is categorized according to various operating modes:

Period I (Day 1-152): Solid-bed reactor was operated with recirculation of 900 ml/minute once a day to promote hydrolysis and acidification of complex organics. Leachate recirculation was stopped after leachate VFAs reached 13,000 mgHAc/l.

Period II (Day 152-335): Solid-bed leachate was recycled once a day to the upflow methane-phase reactor, the effluent of which was again sprayed over the solid bed. By this mode of operation, leacahte VFA was gasified to alleviate inhibition of the fermentative, acetogenic, and methanogenic organisms. Three different recycling rates of 128, 256, 384 ml/day were investigated during this period.

Period III (Day 335-524): On day 335, the inter-phase recycling was stopped since gas production from the methanogenic reactor was negligible. Period III featured methane production of the solid bed and was operated by leachate recirculation as during Period I until gas production from the solid bed ceased.

System 2

The heavy metals were added with the innoculum as salts for complete dissolution: 1.60 g $Pb(NO3)2$, and 0.170 g $CdCl2$. Total lead and cadmium concentrations in the solid bed, volatile fatty acids (VFAs), gas composition, as well as COD profiles will be compared with previous experiments which contained no significant amounts of heavy metals. Total operating time for system 2 will likely be 200 days; however, System 2 has run for only 13 days which may be divided into two periods:

Period I (Day 1-100): Solid-bed acid fermentation was investigated whereby the solid-bed reactor operated with recirculation of leachate culture about the solid bed was performed at 900 ml/minute every day for 25 days (as in System 1). Thereafter, recircualtion was increased by a factor of 12 to 900 ml/minute every two hours.

Period II (Day 101-130): After day 100, solid-bed leachate recirculation was maintained, but part of the leacahte was recycled to the methane-phase reactor when the leachate pH dropped below 5.8, until leachate pH was observed to rise above 5.8.

System 3

Solid-state acid fermentation was operated by recirculation of 1.5 L of leachate around the solid-bed reactor during seven minutes, repeated every four hours.

RESULTS AND DISCUSSION

System 1

Hydrolysis and acidification, as quantified by soluble COD and VFA concentrations, respectively, were the predominant reactions during solid-bed fermentation (Period I) in System 1 (Figure 2). Rapid soluble COD increased to 60,000 mg/l on Day 60 which corresponded to hydrolysis of 28% of the initial VS. VFA accounted for one half of the hydrolysate COD. The solid bed produced a negligible amount of methane during Period I, indicating inhibition of methanogenesis at low pH between 4 and 5. The major gases produced were CO2, H2, and N2, summing up to 35 liters or only 10 vol% of the total gas generated during the 524-day fermentation period. Hydrolysis and acidification were also inhibited for 60 days as the VFA concentration reached 13,000 mg/l at pH 5 around Day 85, corresponding to a soluble COD concentration of 50,000 mg/l.

The application of leachate inter-phase recycling after Day 152 (Figure 2) quickly alleviated inhibition of hydrolysis, acidification, and methanogensis. Solid-bed VFAs reached a maximum concentration of 17,000 mg/l. Methane production started after Day 152 in the methane-phase reactor (Figure 3); methane reactor gas contained 70-80% mol% methane. Methane production started in the solid-bed reactor (Figure 3) as the pH increased to 6.8; methane content in the reactor gas slowly increased from zero on Day 152 to 55 mol% at the end of the experiment. Gas and methane yields computed at the end of 524 days of fermentation were 0.34 and 0.17 standard cubic meters (SCM) per initial kg VS. Of the total methane produced, 47% was produced in the methane reactor, while the remaining 53% was produced in the solid-bed reactor. Ideally, application of such a two-phase process should produce a greater fraction of methane gas in the methane reactor.

Carbohydrate, protein, and lipid reductions amounted to 90%, 37%, and 49%, respectively. As expected, lignin was not degraded. The system achieved a 54% substrate VS reduction corresponding to a destruction of almost 100% of the biodegradable VS in 1.4 years as compared with 20-30 years in a landfill. With this VS reduction (>38%), the residue would comply with the low-vector-attraction reduction criteria (USEPA, 1994).

System 2

Hydrolysis and acidification in the solid-bed were not greatly inhibited by the presence of lead and cadmium. Soluble COD increased to a maximum of 49,000 mg/l in 30 days (figure 4), thereafter remaining nearly constant throughout Period I, until Day 100. After Day 25, a recirculation rate 12 times greater was initiated which did not cause elevations in VFAs or COD. VFA concentra-

tions reached 16,000 mg/l as acetic acid at pH 5 on Day 80 and remained constant for the duration of Period I. Compared with System 1, Period I, maximum COD values were 18% less and maximum VFA concentrations were 23% greater. One explanation would be that acetic acid was used as a carbon source by denitrifiers during the 150-day Period I of System 1, and probably denitrification was not as pervasive during the 100-day Period I of System 2. Major gases in the solid-bed headspace of System 2 were CO2, H2, and N2 as in System 1, yet total gas produced in the solid bed was negligible.

During solid-bed acid fermentation, cadmium and lead partitioned somewhat to the solid bed. Review of salient literature indicates that this sorption of metals has been previously observed (Lin, 1993). Sorption of lead and cadmium occurred in this experiment regardless of pH. A poor correlation of metals solubility is illustrated in Figure 6. On Day 60, amounts of metals dissolved in the leachate at pH 5 were only 28% of the cadmium and 2% of the lead that were originally added to the solid waste. This observation is consistent with previous research as well.

However, recycling of solid-bed leachate to the methane-phase reactor after Day 100 clearly reduced metals concentrations beyond what had already been attenuated by the solid bed (Figure 6). The mechanism of metals removal by the methane phase may readily be attributed to precipitation in the more alkaline methane phase (pH=7-9) and/or biological complexation by methanogens. Ultimately, lead and cadmium were remediated near drinking water limits for these metals, after only 30 days of two-phase recycle. At the conclusion of the experiment, samples from the biosolids of both reactors will be analyzed to assess the fraction of metals that partitioned to each phase.

System 3

An acid-phase digester was innoculated with primary sludge diluted 1:7 with distilled water to an initial fecal coliform count of $5.65X10^{11}$ MPN/L and operated at an ambient temperature of 23 ^{o}C. Similar trends of VFA and COD concentrations as seen in Systems 1 and 2 were observed. On Day 9 (Figure 7), total VFA production was 10,000 mg/l as acetic acid, at a pH of 4. On the same day, pathogen counts of leacahte from the reactor were 0 MPN/L, suggesting complete destruction of coliform bacteria. On Day 14, pathogen counts were repeated and were again 0 MPN/L. Therefore, phase separation provided a hostile environment with a low pH and ORP by which pathogens may be destroyed. Further research should be conducted on the destruction of more resilient organisms such as viruses and helminth ova as required by EPA 503 Regulations.

CONCLUSIONS

In conclusion, biphasic fermentation of MSW is an economically feasible technology by which to rapidly stabilize wastes for energy recovery and land application while complying with EPA 503 Regulations. Bench-scale experiments indicate that high methane yields are possible from a two-phase process. Additional benefits include sorption of metals found in leachate down to concentra-

tions near drinking water limits as well as destruction of pathogens such as fecal coliform bacteria. Bench-scale systems were operated in which MSW was stabilized and gasified in a two-phase fermentative process. Approximately 47% of the methane was produced in the methane phase. A separate two-phase experiment was operated where concentrations of lead and cadmium were remediated from fluctuating concentrations of 2-4 mg/l down to 0.88 and 0.07 for lead and cadmium, respectively, after 30 days of two-phase operation. Further research is warranted in improving the fraction of methane derived from the process, as well as determining whether or not this process will successfully destroy helminth ova to meet EPA 503 regulations for Class A biosolids.

ACKNOWLEDGMENTS

This work was supported by a grant from the New Energy and Industrial Technology Development Organization (NEDO), Government of Japan. Laboratory assistance provided by Messrs. Tuanchi Liu and Yuji Kato is gratefully acknowledged.

REFERENCES

Bilitewski, B., G. Härdtle, K. Marek, A. Weissbach and H. Boeddicker, 1994. Waste Management, Springer-Verlag.

Chandler, J. A., W. J. Jewell, J. M. Gossett, P. J. Vansoset and J. B. Robertson, 1980. Predicting Methane Fermentation Biodegradability, Biotechnol. Bioeng. Symp., 10, pp. 93-107.

Chiu-Yue L., 1993. Effect of Heavy Metals on Acidogenesis in Anaerobic Digestion, Water Research Vol. 27, No. 1, pp. 147-152.

De Baere, L., P. Van Meenen, S. Deboosere and W. Verstraete, 1987. Anaerobic Fermentation of Refuse, Resources and Conservation, 14, pp. 295-308.

Ghosh, S., M. P. Henry and A. Sajjad, 1987. Stabilization of Sewage Sludge by Two-phase Anaerobic Digestion, EPA/600/S2-87/040.

Leighton, J. R., and C. F. Forster, 1997. The Adsorption of Heavy Metals in an Acidogenic Thermophilic Anaerobic Reactor, Wat. Res., 31 (12), pp. 2969-2972.

Oleszkiewicz, J. A., and H. M. Poggi-Varaldo, 1997. High-solids Anaerobic Digestion of Mixed Municipal Wastes for Fuels and Chemicals, J. Environ. Eng., 123 (11), pp. 1087-1092.

Pepper, I. L., C. P. Gerba and J. W. Brendecke, 1995. Environmental Microbiology. A Laboratory Manual, Academic Press, Inc.

Ponugoti, P. R., M. F. Dahab and R. Surampalli, 1997. Effects of Different Biosolids Treatment Systems on Pathogen and Pathogen Indicator Reduction, Water Environ. Res., 69 (7), pp. 1195-1206.

Standard Methods for the Examination of Water and Wastewater, 1992. APHA, AWWA and WEF, Washington DC, USA, 18th ed.

Stukenberg, J. R., G. Shimp, Sr., J. Sandino, J. H. Clark and J. T. Crosse, 1994. Compliance Outlook: Meeting 40 CFR Part 503, Class B Pathogen Reduction Criteria with Anaerobic Digestion, Water Environ. Res., 66 (3), pp. 255-263.

US EPA, 1994. A Plain English Guide to the EPA Part 503 Biosolids Rule, EPA/832/R-93/003.

US EPA, 1996. Characterization of MSW in the US: 1996 Update, Franklin Assoc.

Figure 1. Schematic diagram of solid-state biphasic fermentation.

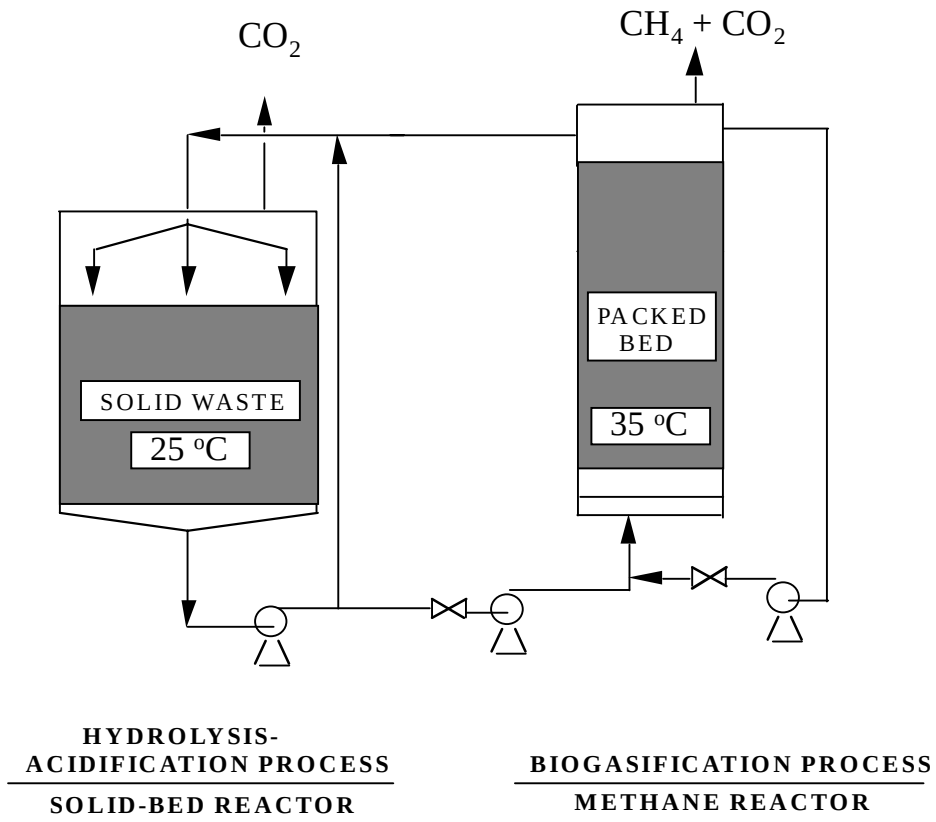

Figure 2. Time profiles of solid-bed leachate soluble chemical oxygen demand (COD), COD equivalent of VFA, and pH or solid-bed and methane-phase reactors, during 524 days of solid-state biphasic fermentation.

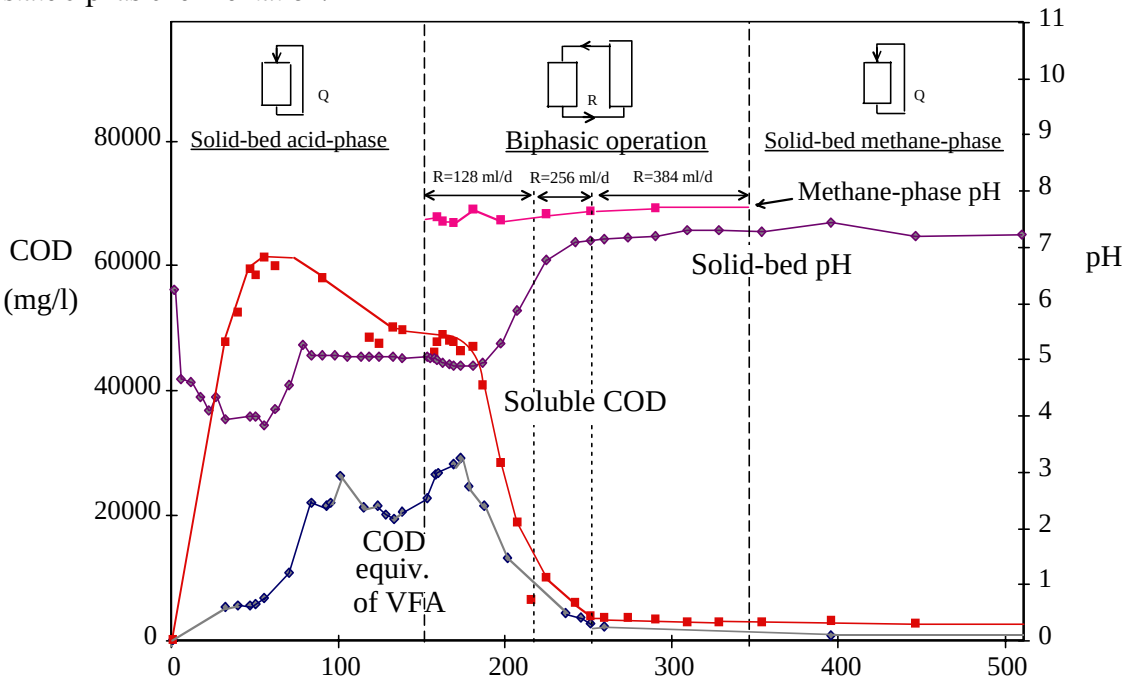

Figure 3. Cumulative methane production from solid-bed and methane-phase reactors during 524 days of solid-state biphasic fermentation.

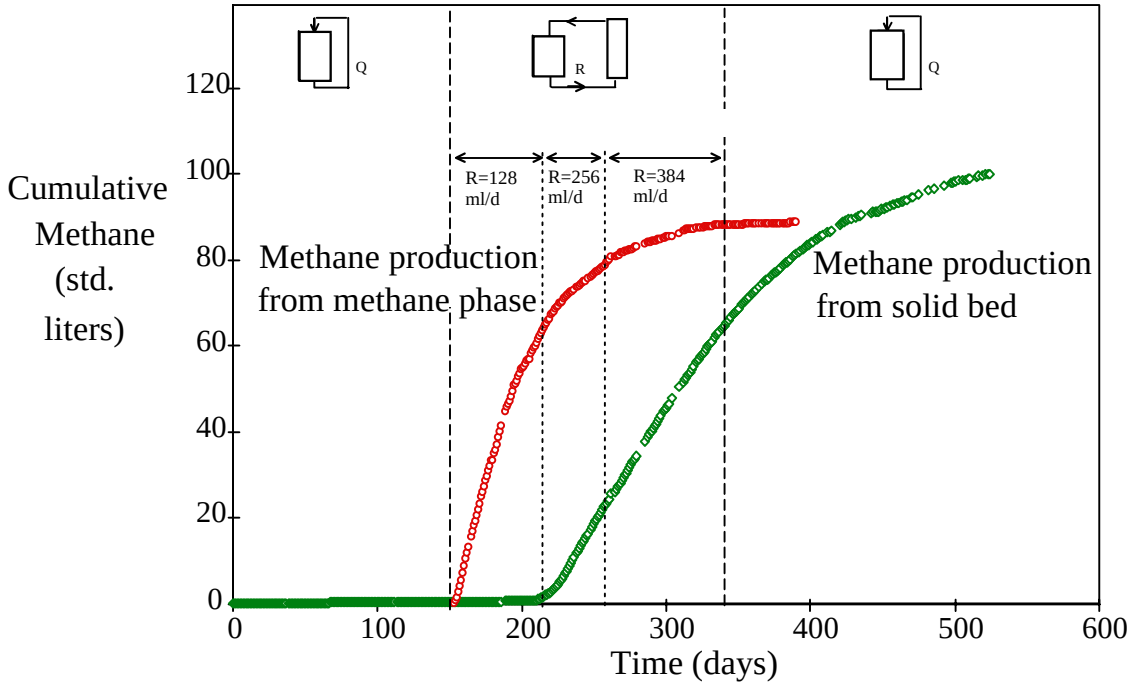

Figure 4. Leachate total and soluble COD and pH profiles, during 100 days of solid-state acid fermentation in presence of lead and cadmium.

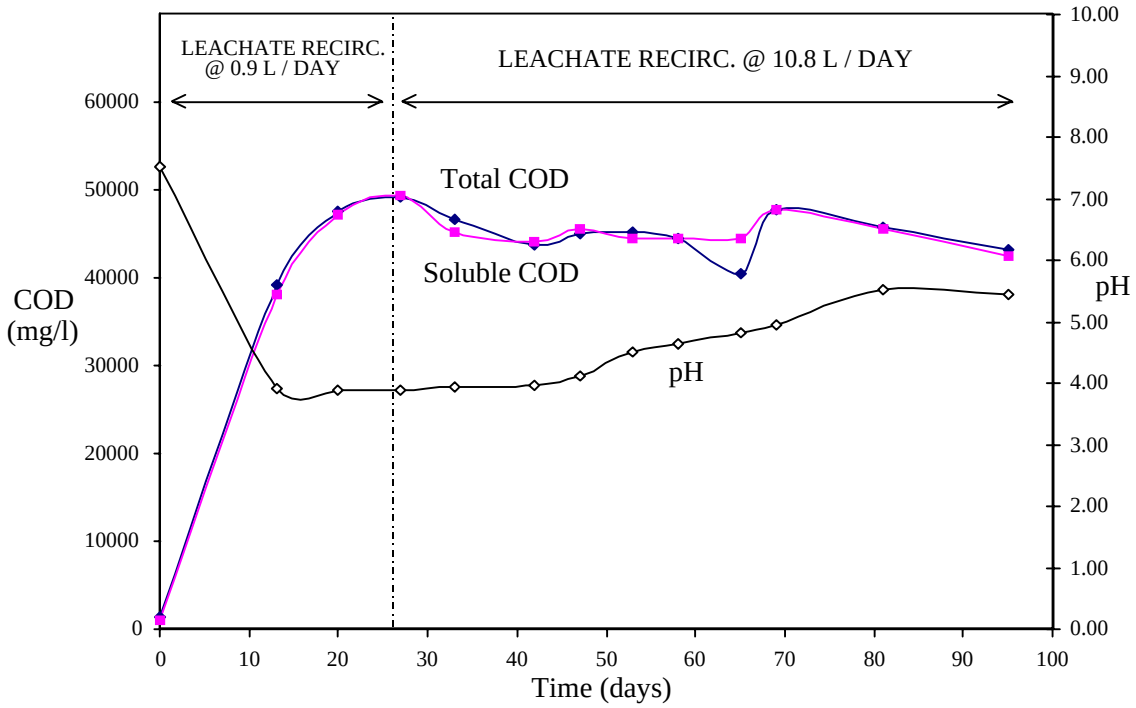

Figure 5. Volatile fatty acids (VFA) profiles during 100 days of solid-state acid fermentation in presence of lead and cadmium.

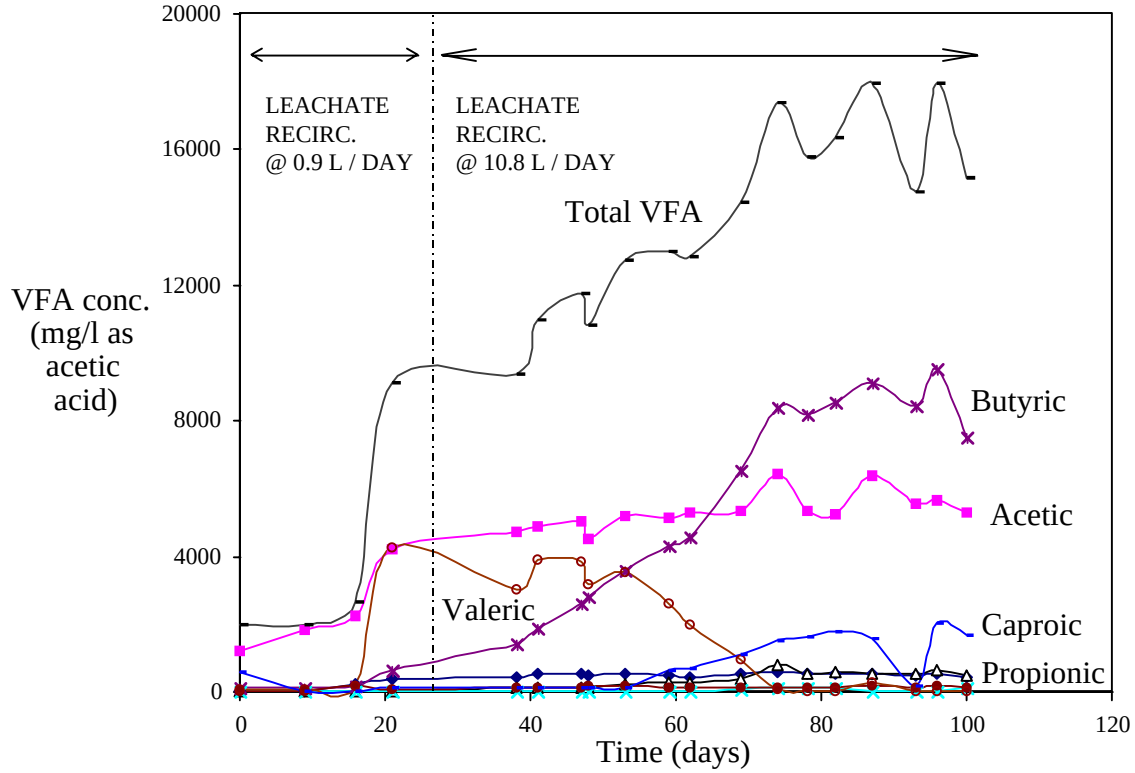

Figure 6. Cadmium and lead profiles during solid-state acid fermentation.

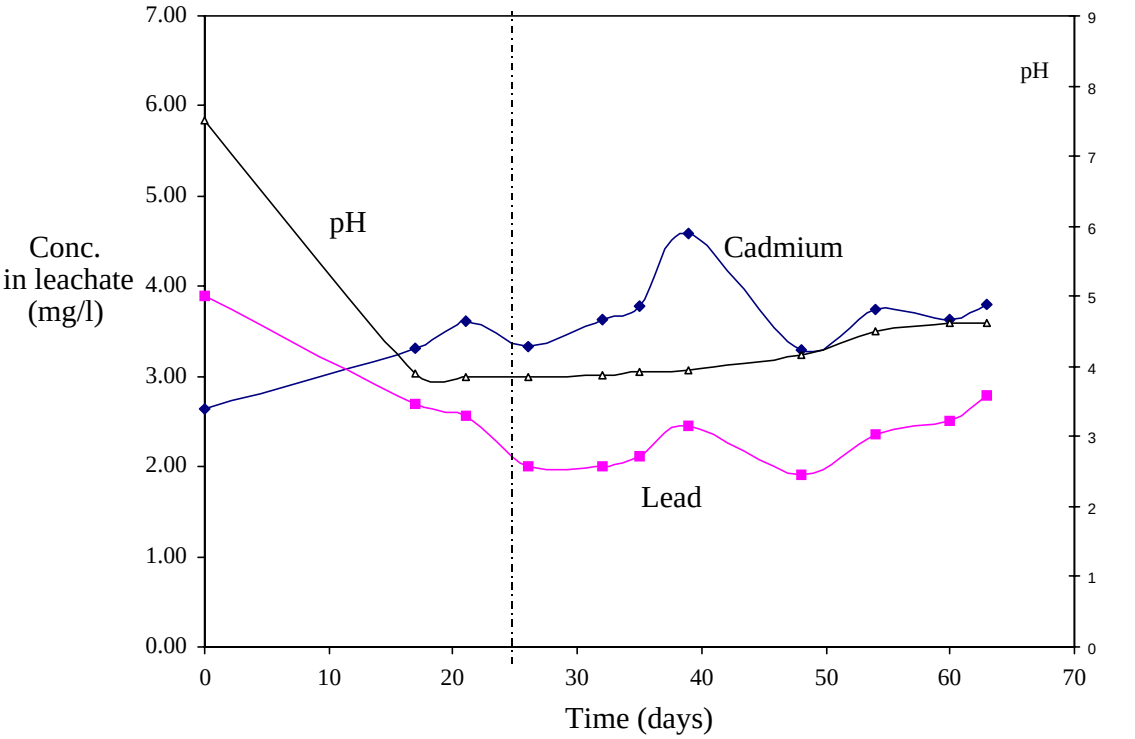

Figure 7. Pathogen content, volatile fatty acids (VFA) and pH profiles of solid-bed leachate during solid-state acid fermentation.