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Project Summary

Thermophilic Anaerobic Biodegradation of Phenolics

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This report presents the results of a series of anaerobic microbial acclimation and treatment performance tests conducted with synthetic phenolic substrates. The research is a feasibility level assessment of substituting anaerobic biodegradation of phenolics for solvent extraction. The tests demonstrated the feasibility of biodegrading phenol and p-cresol to methane under thermophilic anaerobic conditions. The experimental data indicate that anaerobic biodegradation of phenolics under thermophilic conditions involves a dual system of bioaccumulation and biodegradation. Phenolics and unknown metabolites were accumulated in the anaerobic flocs of sludge, and these compounds were apparently slowly degraded over time. Despite periodic upsets, treatment improved as the phenolic loadings were incrementally increased during the experiments. This indicates that, although acclimation of thermophilic anaerobic bacteria to phenolics is difficult, it can be accomplished using normal microbial cultivation techniques. Moreover, degradation intermediates identified during thermophilic anaerobic treatment of phenolics were similar to those found in effluents from anaerobic treatment systems that operate at lower temperatures.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Fixed-bed coal gasification wastewaters are generally high in biochemical oxygen demand. The largest fraction of the carbonaceous biochemical oxygen demand characteristic of these wastewaters can be attributed to the presence of phenolics. In addition to phenols, the wastewaters contain appreciable levels of cresols, xylenols, and aromatic heterocyclic compounds with nitrogen contained in the ring.

The chemistry of fixed-bed gasifier wastewaters offers the potential for a biological treatment alternative to solvent extraction pretreatment of high phenolic wastewaters. A conventional wastewater treatment system for fixed-bed coal gasification quench condensates consists of tar/oil separation, solvent extraction (phenolics removal), steam stripping (ammonia and acid gas removal), aerobic biodegradation, and assorted tertiary treatments (specific to discharge or reuse requirements). This system is energy intensive and presents both health and safety (worker exposure to solvents) and hazardous materials handling (phenolic by-product) considerations.

This research is a feasibility level assessment of substituting anaerobic biodegradation of phenolics for solvent extraction. This alternative treatment system would consist of tar/oil separation, steam stripping, anaerobic biodegradation, aerobic biodegradation, and assorted tertiary treatments. Anaerobic biodegradation would eliminate many of the health and safety concerns posed by solvent extraction treatment while also producing methane as a by-product. Methane may be generated in sufficient quantity to meet the power requirements of the entire alternative wastewater treatment train.

The anaerobic treatment system would provide simultaneous storage, equalization, and treatment of steam-stripped quench condensates and other process wastewaters. Since the process would receive wastewaters at temperatures in excess of 95°C, the anaerobic biodegradations should occur in the thermophilic temperature range (49 to 57°C) to minimize cooling requirements. These temperatures are consistent with equilibrium bioreactor temperatures estimated from heat balances on the anaerobic process. Operation in the thermophilic range would thus remove much of the cooling requirement typical of most mesophilic microbial treatment processes. (Traditionally, hot wastewaters are cooled by retention in large aerated impoundment ponds. This practice also permits the uncontrolled release of volatile compounds to the atmosphere.) A thermophilic anaerobic treatment process would restrict the release of volatile compounds because the emissions are controlled during treatment. The major gaseous emissions from the process are methane and carbon dioxide. The thermophilic temperature range should also optimize the rate of microbial conversion.

Objectives

The purpose of this research was to study the feasibility of biodegrading phenolics to methane by thermophilic anaerobic treatment. The study was a feasibility level assessment which examined techniques for culturing thermophilic bacteria, acclimating these microorganisms to phenolics, and assessing toxicity thresholds for simple phenol. The study was conducted with bench-scale test reactors using synthetic substrates composed of phenol, p-cresol, organic acids, and basal salts. Both continuous-feed and batch treatment tests were conducted and treatment performance monitored. Where possible, degradation intermediates were identified. These data provide the basis for assessing the feasibility of thermophilic anaerobic biodegradation of phenolics.

Results and Conclusions

The report presents the results of a series of anaerobic microbial acclimation and treatment performance tests conducted with synthetic phenolic substrates. These tests were designed to demonstrate the feasibility of biodegrading phenolics under thermophilic anaerobic conditions. Two types of experiments were conducted:

- microbial seed acclimation tests using mixed cultures of anaerobic microorganisms grown under thermophilic conditions, and
- treatment performance tests using acclimated microorganisms subjected to both continuous and batch biodegradation conditions.

The experimental results are discussed relative to the feasibility of achieving thermophilic anaerobic biodegradation of phenolics characteristic of most fixed-bed coal gasification wastewaters.

Microbial Seed Acclimation Testing

Mesophilic anaerobes from a municipal sewage sludge digester were used to seed two test bioreactors. These sludges were fed a mixture of phenol and organic acids and were subjected to mixed liquor temperatures between 52 and 55°C. These two bioreactors were operated throughout the acclimation period at different substrate loadings. Although the bioreactors were loaded similarly, they performed differently because of differences in the nature of the microbial cultures developed during seed acclimation.

The microorganisms showed an inherent ability for thermophilic anaerobic biodegradation of phenol early in the acclimation cycle. After three hydraulic residence times, a flocculent microbial mass developed that settled well and produced an effluent that was low in phenol. Overall chemical oxygen demand (COD) reduction lagged phenol removal: optimum COD removal was not obtained until after about six hydraulic residence times. Methane was detected in the off gas from the bioreactor whenever these gases were sampled during the acclimation period.

Although the bioreactors consistently reduced the phenol concentration in the wastewater, the apparent level of methane produced did not keep pace with the rate of phenol removal during the early stages of the acclimation. However, this was not unexpected because methane-forming bacteria are usually slow to develop in most anaerobic treatment processes. The bioreactors also maintained relatively low concentrations of volatile cell mass throughout the test, and the apparent rate of growth of new biosludge was negligible.

Performance Testing

Performance testing consisted of two continuous-feed biodegradation experiments with similar populations of acclimated thermophilic anaerobic bacteria. Each experiment was designed to track the change in phenol, p-cresol, acetic acid, and propionic acid in a test reactor. Treatment performance data for one test are presented in Table 1. This reactor was fed phenol at 1000 mg/L, p-cresol at 50 mg/L, and volatile organic acid as equal quantities of acetic and propionic acids (i.e., 200 to 400 mg/L). The bioreactor was operated with an hydraulic residence time of 20 days and a mean cell residence time of about 60 days. The system maintained a mass loading of 0.04 mg phenol/mg total volatile suspended solids (TVSS)/day throughout the test run.

Test data indicate relatively uniform treatment performance with the removal of cresol and acetic acid. However, variable effluent qualities for phenol and propionic acid may be the result of several system specific factors. The mass loading of phenol to the bioreactor could change the equilibrium concentration within the mixed liquor by no more than 50 mg/L for each day of operation. Therefore, an apparent rise in the mixed liquor phenol concentration of between 78 and 230 mg/L over a single day of bioreactor operation must be the result of factors other than the normal changes in biochemical reaction rate typical of microbial processes. One such condition is the accumulation of phenol within the flocs of sludge before actual biodegradation occurs. This accumulation probably results from sorption of phenol to the activated sludges because of the lipophilic properties of the flocs. Therefore, the biofloc may carry much higher concentrations of phenol than actually are measured in the liquid of the reactor. From time to time, desorption may occur, liberating phenol and unknown metabolites to the reactor liquid. These compounds would be quickly taken up by the biomass and biodegraded in the normal course of process operation. However, point-in-time measurements will show effluent quality variability as reported by the test data. The accumulation and eventual biodegradation of degradable pollutants on flocs is a common occurrence in activated sludge treatment. Whether this phenomenon presents problems specific to thermophilic anaerobic treatment of phenolics cannot be assessed from the experimental data.

Conclusions

The following conclusions result from the study of thermophilic anaerobic

Table 1. *Thermophilic Performance Test*

	Influent					Effluent[a]				
Test Day	Phenol (mg/L)	Cresol (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	COD (mg/L)	Phenol (mg/L)	Cresol (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	COD (mg/L)
1	–[b]	50	300	280	3040	<5	<5	<5	97	170
4	–	–	370	310	3100	–	–	<5	–	–
5	1030	31	–	–	2970	<5	<5	<5	96	231
6	–	–	–	–	3120	79	<5	<5	–	234
7	–	–	–	–	–	<5	<5	<5	94	124
8	1070	38	350	440	–	–	–	<5	–	–
10	–	–	–	–	–	230	<5	<5	103	570
11	970	48	230	230	2440	<5	<5	<5	110	190
12	–	–	320	490	–	55	<5	<5	86	115
13	–	–	310	240	3140	10	<5	<5	110	150
14	–	–	170	160	–	6.2	<5	–	–	126
15	–	–	97	115	2890	<5	<5	<5	88	134
16	–	–	–	–	–	<5	<5	<5	108	153
17	–	–	–	–	–	75	<5	36	95	282
18	1000	47	250	300	2570	190	–	–	–	–
19	–	–	–	–	–	120	<5	84	16	350
20	1000	48	200	590	2960	<5	<5	6	90	210
22	–	14	<5	<5	2680	16	<5	<5	100	204
25	1020	31	–	95		<5	<5	<5	80	102
27	–	<5	–	–	2810	133	<5	–	–	224

[a]Reactor total volatile suspended solids (TVSS) equals 1400 mg/L during test.
[b]Blank (–) means parameter not analyzed.

degradation of synthetic phenolic substrates:

- Experimental results indicate that phenol and p-cresol can be metabolized to methane under thermophilic anaerobic conditions. This microbial treatment process was sustained for a period of 6 months with continued improvement in treatment performance. A phenolic toxicity threshold for the microbial process was not evident when the degradations were performed with acclimated microorganisms. Relatively short acclimation periods were required to achieve consistent treatment performance (i.e., greater than 90 percent removal of phenol) at low substrate concentrations. However, extended periods of acclimation (i.e., greater than six hydraulic residence times) were required to achieve acceptable treatment at higher substrate (phenolic) loadings. Generally, acceptable treatment occurred coincident with the development of a flocculated biomass. However, the presence of dispersed microorganisms signalled poor treatability. These observations indicate that stable treatment performance could be maintained with conventional microbial acclimation techniques.
- The experimental data indicate that thermophilic anaerobic biodegradation of phenolics involves a dual system of bioaccumulation and biodegradation. Phenolics and unknown metabolites are accumulated in the anaerobic flocs, and these compounds are released to the liquid at various times during treatment. Process control would specify a condition that optimizes the degradation of toxics in the liquid phase while maintaining an equivalent level of treatment for the sludges. Operating under this condition would minimize the production of new cell mass.
- Although the test bioreactors experienced upset conditions in the early stages of the acclimation study, phenolic wastes were continuously fed to the systems throughout the upset periods. Despite these periodic upsets, system performance improved as the waste loadings were incrementally increased during the experiments. This indicates that, although acclimation of thermophilic anaerobic bacteria to phenolics is difficult, it can be accomplished using normal microbial cultivation techniques.
- The experimental observations indicate that proportional increases in reactor biomass relative to pollutant loading will not guarantee that the individual phenolic compounds and intermediates will be uniformly degraded. This would imply that system kinetics may not fit a conventional microbial substrate utilization model.
- The experimental data indicate that degradation intermediates identified during thermophilic anaerobic treatment of phenolics were similar to those found in effluents from anaerobic treatment systems that operate at lower temperatures.

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The complete report, entitled "Thermophilic Anaerobic Biodegradation of Phenolics," (Order No. PB 86-122 603/AS; Cost: $11.95, subject to change) will be available only from:
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