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EFFECT OF SULFIDE, CHROMIUM, AND PHOSPHATE IONS ON METHANE PRODUCTION BY AN ANAEROBIC SLUDGE ACCLIMATED TO TANNERY BEAMHOUSE EFFLUENT

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INTRODUCTION

Leather tannery effluent is a difficult waste to treat biologically due to the presence of various components which may be at levels that are toxic to many microorganisms. Typical effluent concentrations for these constituents have been evaluated by the EPA in their proposed guidelines for the leather industry [1]:

Table I. Tannery wastewater constituents in mg/l

Constituent	Concentration Range	Geometric Mean
Chemical oxygen demand (COD)	182-27200	4640
Sulfide (S^{2-})	0.8-198	64
Ammonia (NH_3)	17-380	104
Phenol	0.14-110	1.0
Chromium (Cr)	3-345	76

Our laboratory has developed a bench-scale anaerobic reactor that removes 40-75% of the COD from tannery waste feed while producing recoverable methane gas (CH_4) [2]. The feed stock consisted solely of diluted beamhouse wastewaters (BW) which comes from the section of the tannery where hides are soaked, unhaired, and relimed prior to tanning. This particular wastewater stream contains an average of 30,000-45,000 mg/l COD and

2,000-4,000 mg/l S^{2-} , but no other toxic componen. BW was used since it typically contains most of the COD found in tannery effluent, and because the Cr found in other tannery waste streams was originally listed by the EPA as a hazardous waste, necessitating different treatment methods. However, in 1981, the EPA removed Cr (III) from the list of specific hazardous chemicals. As a result, waste containing Cr could now be treated biologically without the necessity of placing the resulting sludge in secured landfills. We therefore decided to change the feed to total tannery wastewater (TTW), which contains all the tannery wastewater streams, including Cr, to see if the anaerobic reactor could continue to perform adequately. Samples of the anaerobic sludge from the reactor were first tested to see how it was affected by the different constituents of TTW.

The purpose of this series of studies was to determine how anaerobic sludge from the mother reactor could react to, and how treatment would be affected by, the potentially toxic constituents commonly found in total tannery effluents. This was accomplished by performing a series of bioassay tests with anaerobic biomass from the mother reactor in the presence of suspected toxic materials.

Owen et al. [3], have developed a bioassay technique for measuring the biodegradability of feed constituents subjected to anaerobic treatment processes. In their procedure, serum bottles containing samples, anaerobes, nutrients, and feed are incubated, and gas production and composition are monitored. From the results of these bottle tests, one can calculate biochemical methane potential (BMP), which is a measure of the biodegradability of the sample based on CH_4 production. The theoretical value, $0.350m^3 CH_4/kg COD$, is used to calculate efficiency of conversion of organic matter to methane. By testing components of tannery waste in this manner, the usefulness and limitations of anaerobic tannery waste treatment can be investigated [4]. Our bioassays dealt with the effects of S^{2-} , phosphate (PO_4), chloride (Cl), ammonia (NH_3), sulfate (SO_4), phenol, and trivalent Cr, all components likely to be found in TTW.

MATERIALS AND METHODS

Anaerobic microorganisms were obtained from the mother reactor, which consists of a 28 l glass tank which is constantly stirred and maintained at 37°C [2]. Feed stock with a COD concentration of 4,000-6,000 mg/l continuously enters this complete mix system at 12-16 l/day and

the effluent overflow goes into a 7ℓ settling tank. Settleable sludge is recirculated into the large tank at 100 ℓ/day. Gas production is measured by water displacement, and is usually between 250 and 450 ml/hr. Methane accounts for 75-85% of the gas, and most of the balance is CO₂.

The bottle tests were conducted with 125 ml borosilicate glass serum bottles (actual volume is 160 ml with 20 mm butyl rubber stoppers and tear-off aluminum seals in place). The bottles were filled with a mixture of 70% N₂ and 30% CO₂ prior to sealing. Defined media solution was prepared, containing COD source (BW), resazurin (an indicator which turns blue if oxygen enters the system), (NH₄)₄ HPO₄, NH₄Cl, NaHCO₃, and Ca, Mg, K, Mn, Co, B, Cu, Mo, Zn, and Fe ions as described by Owen [3]. The concentration of these ions was too low to interfere with the S⁻ tests. One hundred ml of sludge was anaerobically transferred from the reactor to a bottle containing 900 ml of defined media that had been flushed with the N₂-CO₂. Ninety ml of the mixture was then syringed into each serum bottle, along with 10 ml of a solution of the waste component being examined. Sodium salts were used as the sources of SO₄, NH₃, Cl, and S⁻. A pH 7.4 mixture of KH₂PO₄ and K₂HPO₄ was used for PO₄ tests. Tanolin R, a tanning material containing 23.5% Cr₂O₃, was the source of Cr and did not contribute an appreciable COD. (Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned). Concentrations of chemicals tested are described as the amount added, and are not necessarily the total concentrations. The COD available to the microorganisms in each bottle ranged from 373-527 mg, equivalent to concentrations of 3,730-5,270 mg/ℓ. The bottles were incubated at 37°C.

Gas volume measurements were taken by piercing the stopper with a syringe needle and noting the displacement of the syringe barrel. Gas composition was determined by a gas chromatograph equipped with a molecular sieve column [2], and from this the amount of CH₄ produced was calculated. The BMP value was found by dividing the net m³ CH₄ by the Kg COD removed and conversion efficiency of organic material to CH₄ was calculated by dividing BMP by the theoretical BMP value of 0.350.

RESULTS AND DISCUSSION

Reproducibility in the tests was excellent. At least five different concentrations of each sample were analyzed, and although only one bottle was used for each concentration, there was little scatter seen in the data.

A series of control bottles, containing combinations of BW and TTW as the COD source, were used in biodegradability tests. After 3 weeks, it was apparent that 100% BW or a 75% BW—25% TTW mixture were less efficient energy sources for converting organics to CH₄ than mixtures containing a 50:50 or 25:75 ratio (Figure 1).

Inhibition by S⁻ is obvious in Figure 2, which shows a 35% decrease in CH₄ production as the S⁻ concentration was increased from 100 mg/ℓ to 1,500 mg/ℓ. It should be noted that the anaerobes were able to generate CH₄ even in the presence of this concentration of sulfide. This effect was observed in the reactor [2] and is presumably due to acclimation of the methanogenic microorganisms to sulfide ions. This result is contrary to most published information on the effect of sulfide in anaerobic waste treatment systems.

Bottle tests were performed to be certain that PO₄ was not limiting CH₄ production. There was no improvement in CH₄ generation over a range of 50-1,000 mg/ℓ P and there was a decrease at the highest level (Figure 3).

Based on the results of the bottle tests, the mother reactor feed stock was changed to half TTW and half diluted BW. Methane generation immediately increased as did the COD conversion efficiency. Bioassays with Cl, NH₃, SO₄, phenol, and Cr were then done to see if any of these could be inhibiting CH₄ production in the reactor. BW was used as sole COD source. The increase in conversion efficiency can be seen by comparing Figures 1-3 with Figures 4-8.

CH₄ production at 500 mg/ℓ Cl was basically the same as at 0 mg/ℓ (Figure 4). There was also little difference between tests at 25 and 500 mg/ℓ NH₃ (Figure 5). A slight effect was seen between SO₄ concentrations of 100 and 500 mg/ℓ (Figure 6), but generation of CH₄ was still high. The most striking result was the lack of inhibition by phenol (Figure 7). The anaerobes were unaffected by levels of up to 100 mg/ℓ, and a 500 mg/ℓ sample actually showed increased CH₄ production. It is possible that the organisms were acclimated to phenol and were able to use it as a COD source. Cr was the only chemical

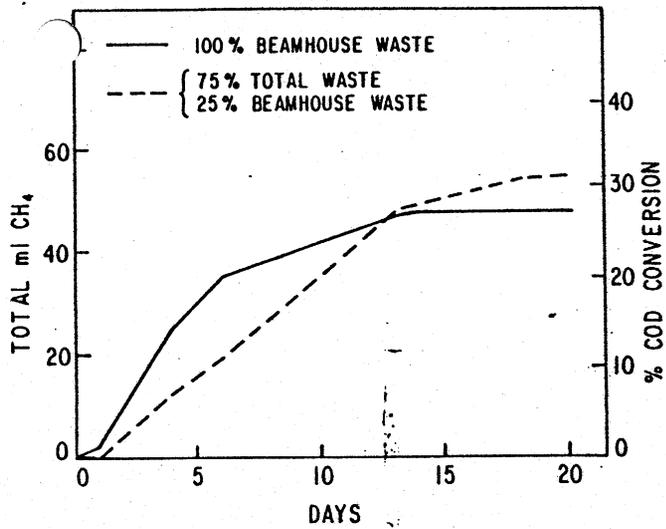


Figure 1. Effect of feed composition on CH₄ production

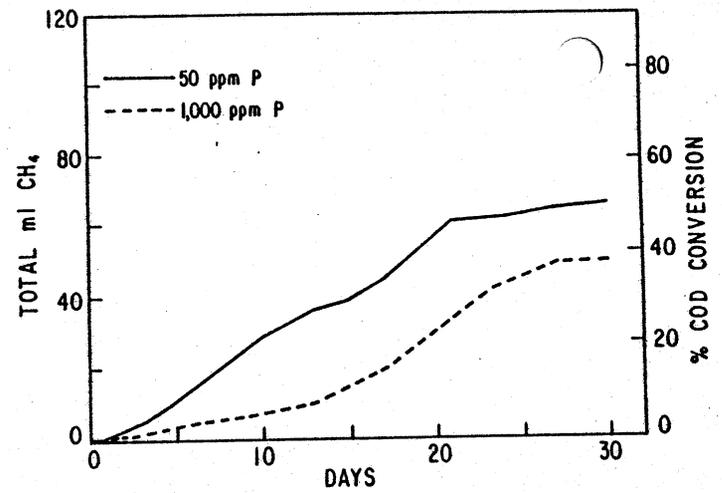


Figure 3. Effect of PO₄ on CH₄ production

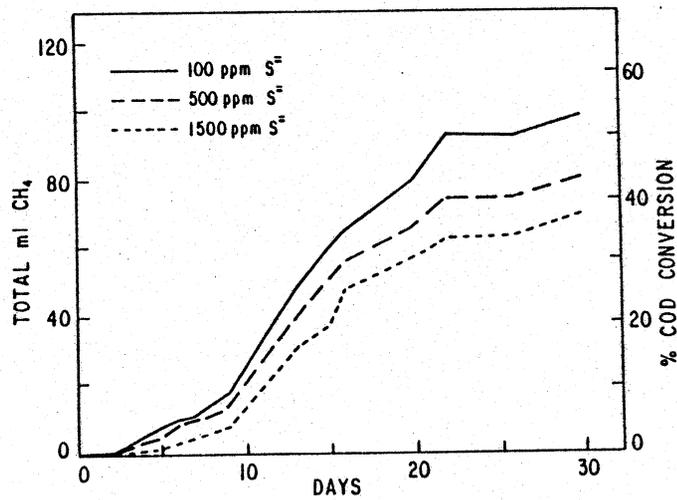


Figure 2. Effect of S²⁻ on CH₄ production

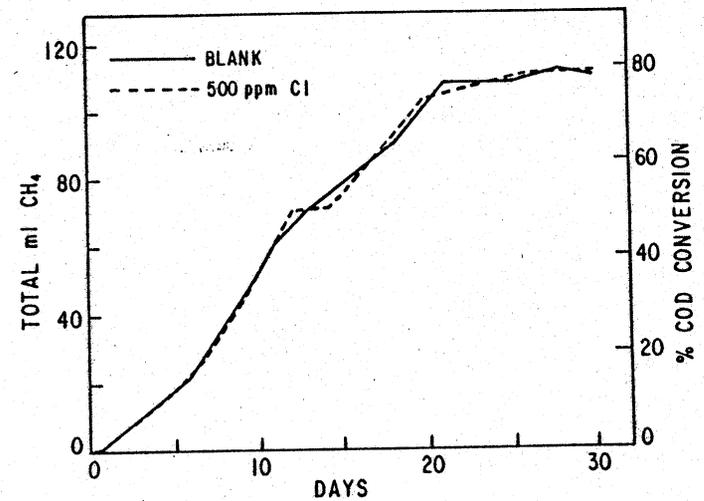


Figure 4. Effect of Cl on CH₄ production

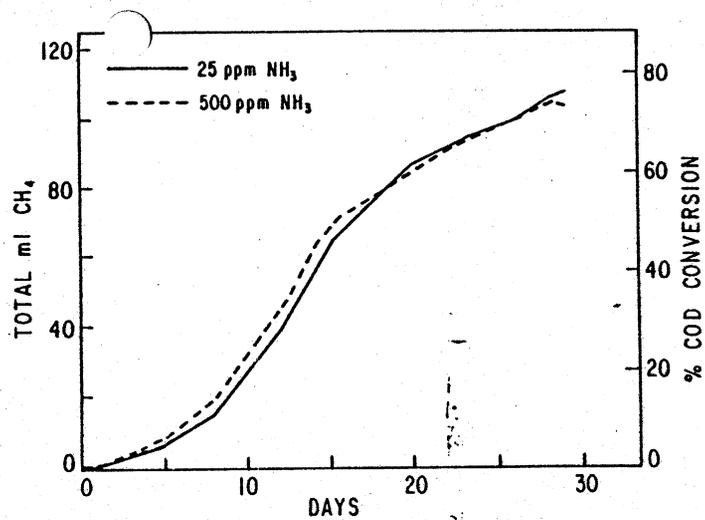


Figure 5. Effect of NH₃ on CH₄ production

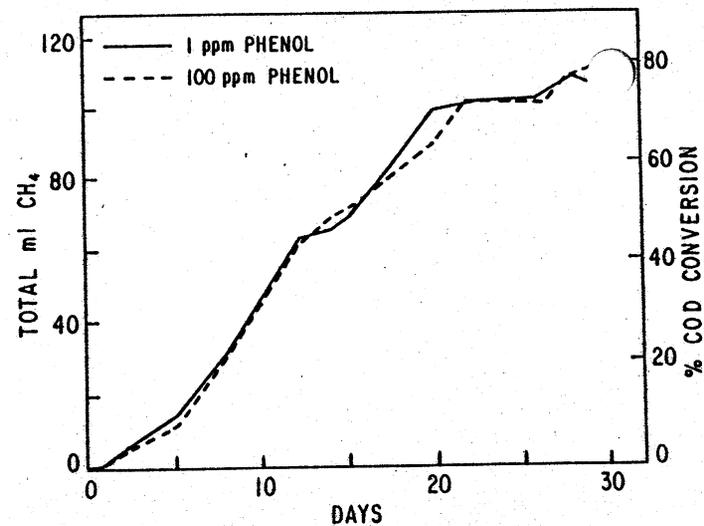


Figure 7. Effect of phenol on CH₄ production

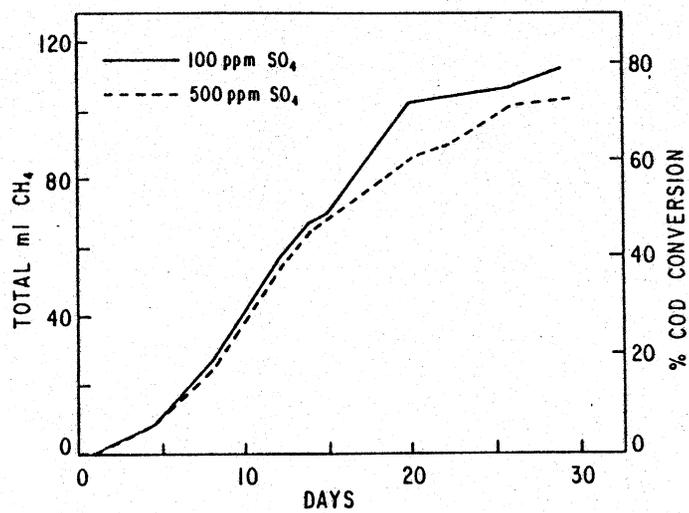


Figure 6. Effect of SO₄ on CH₄ production

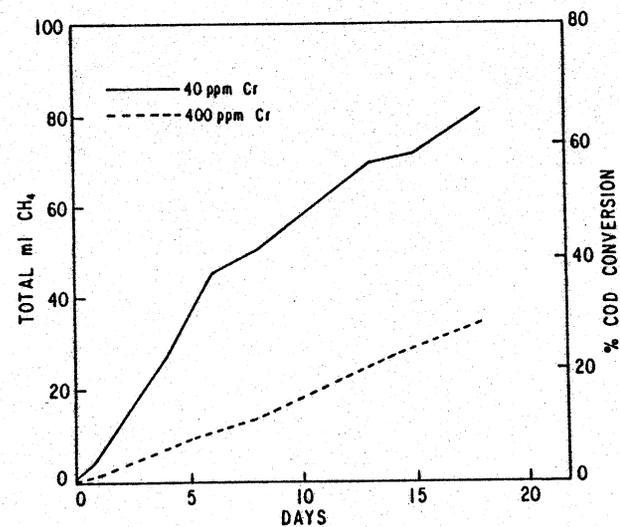


Figure 8. Effect of Cr on CH₄ production

tested, besides S^{2-} , which inhibited CH_4 production (Figure 8). However, at concentrations normally found in tanneries, the inhibition was small. The Cr concentration in the TTW used for the reactor feed stock was 31 mg/l.

CONCLUSIONS

Bioassays were performed on anaerobic sludge acclimated to tannery wastewaters in a bench-scale anaerobic contact reactor. These assays were done to determine the effects of various constituents normally found in total tannery wastewater effluents on methane production by these organisms. Sulfide and chromium were found to inhibit the methane production, but only at levels much higher than those usually observed in tannery wastewaters.

The results of this work demonstrate that a complete mix single cell recycle anaerobic contact sludge can be acclimated to produce methane even in the presence of high levels of trivalent chromium (50% inhibition at 400 mg/l) and sulfide (20% inhibition at 800 mg/l). This strongly suggests that the anaerobic process can be used to effectively treat total tannery wastewaters, normally considered a difficult waste to treat biologically because of the presence of these substances. Demonstration that anaerobic sludges can be acclimated to these constituents may greatly expand the number of industrial wastes which can be considered for anaerobic contact treatment.

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