Treatment of a Leachate produced in a co-disposal landfill (containing both municipal and toxic solid waste) using the anaerobic digestion method. The effect of heavy metals in the process.

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Abstract

General/ purpose
The leachate produced from a highly bioreactive landfill is low in biochemical oxygen demand (BOD₅) as a result of the conversion of cellulosic and protein wastes to CO₂ and CH₄. However at containment site i.e. hydrogeologically secure, the leachate often contains very high concentrations of dissolved organic substances mainly short chain volatile acids (acetic, propionic, butyric etc) which give rise to characteristically high BOD and COD and are derived from anaerobic liquefaction of organic material present in domestic waste. Depending on the nature and age of a particular landfill leachates may also contain significant quantities of toxic materials that can upset biological treatment. Because of the complex nature of the substrate likely to be used in the anaerobic digestion process, one can expect an equally complex microbial ecosystem.

Most research has concentrated on the response of the methanogens to various stimuli or inhibitory factors and in this study it was concentrated on the effects of heavy metals.

Experimental procedure/ Methods of analysis
Two anaerobic bench scale reactors were employed (one as a control), at a mesophilic temperature, to examine the treatability of a specific leachate produced in a co-disposal landfill of municipal and toxic waste. The leachate was introduced at an OLR of 0.2 Kg COD/m³d (equivalent to a COD of 6,000 mg/l) until the feeding of the digester reached the aimed OLR of 1 KG COD/ m³d (equivalent to a COD 30,000 mg/l). The volatile acids were completely utilised and the CH₄:CO₂ ratio was 80:20% respectively.

Further, the effects of an enhanced concentration of zinc, a metal of concern at the site, on the performance of the anaerobic digestion was determined as 50 mg/l of Zn fed as zinc nitrate, (Zn₂(NO₃).6H₂O) was pulse fed into the digester. The postulated role of sulphide in preventing heavy metal toxicity of the anaerobic digestion process was put into test.

The methods of analysis used are those of Standard methods.

Results/ Conclusions
The leachate treated proved to be an amenable waste to the anaerobic treatment with a 96% removal of COD. No ill effects due to the presence of heavy metals or other inhibitory substances (ammonia etc) present in the leachate were detected, the free volatile acids were effectively removed and the CH₄:CO₂ ratio was 80:20% respectively and a gas yield of 0.20 m³ CH₄/ Kg COD removed . With the introduction of a heavy metal (Zn) as an external source pulse fed to the system, inhibition of methanogenesis occurred instantaneously at remarkably low levels of heavy metal concentration existing in the soluble phase. It was proved that when a precipitating agent such as sulphide is used, toxicity will result when the total equivalent concentration of the toxic heavy metals present, exceeds the equivalent concentration of sulphides present. The supply of equivalent amounts of
sulphide following increased quantities of Zn, pulse fed into the system, prevented heavy metal toxicity and failure of the process.

1. LITERATURE REVIEW

Heavy Metal Toxicity of the anaerobic process

The heavy metals have been blamed for many digester failures. In several investigations a certain heavy metal is reported to exert toxic effects on the anaerobic waste treatment process, while in another case high concentrations are reported to be non toxic. The magnitude of the toxicity observed or reported was a function of several factors including concentration, antagonism, synergism, complex formation and acclimatization.

Mc Carty [7], recognises that low, but soluble concentrations of copper, zinc and nickel salts are quite toxic, Iron and aluminium salts are non toxic because of their low solubility. He further states that that when heavy metals combine with sulphides, which themselves are quite toxic to digestion, sulphide salts are formed which are extremely insoluble and as such have no detrimental effects to the organisms responsible for the anaerobic process.

Mosey [9], states that heavy metals cause digestion failure only when the concentrations of their free ions exceeds a certain threshold concentration which is directly related to the concentration of divalent sulphide ions ($S^{2-}$) present in the digesting sludge. Since soluble sulphides can be quite corrosive and high concentrations are also toxic (150 mg/l), excessive amounts should be avoided. Such problems might be minimised by adding an iron containing compound along with the sulphides. Ferrous iron has been found to be non-toxic to digestion even in the absence of sulphides. Iron is the most soluble sulphide of the heavy metals. Thus, the sulphide formed during digestion would be available first for the precipitation of heavy metals and only then would iron be precipitated. Consequently, sulphide bound as iron sulphide would constitute a sulphide reservoir. As a consequence to this finding it is not necessary to consider iron in evaluating the possibility of heavy metal effects on anaerobic digestion.

Patterson and Hao [10] investigated the interaction of heavy metals in feed sludge and concluded the following:

The added heavy metals were essentially completely taken up by the digester feed solids. Specifically, Cu (99%), Pb (99%), Cd (96%), and Ni (71%). Addition of each metal to the digester feed resulted in an increment in both the soluble and total concentration of that metal. However, addition of one metal resulted in a release of other metals present at background levels in the sludge phase, back into the soluble phase. These results reveal that the metal distribution for each metal is a function not only of that individual metal, but of other metals present, and their concentrations.

Mosey [9], states that in the most usual cases where a mixture of heavy metals is present and where the concentration of each individual metal is quite often clearly insufficient by itself to cause inhibition, the combined effect should be studied since it may be inhibitory. He further proposes a formula to determine the additive effects of the heavy metals on an equivalent weight basis.

The formula given below is expected to cause inhibition when K is greater than 400 meq/kg. Since digester failures have been reported at lesser K values, in so far as conditions to protect the anaerobic sludge treatment are needed, then the value of K should not exceed 200 meq/Kg.

$$ K = \frac{Zn/32.7 + Ni/29.4 + Pb/103.6 + Cd/56.2 + Cu/47.4}{\text{Solids Concentration (kg/l)}} $$

In this formula, the total concentration of each metal in the digester should be considered and “solids concentration” is the dry solids content in the digested sludge expressed as Kg/l.

Theis and Hayes [5] examined the relationship between hydrogen ion concentration and metal distribution. Increasing the pH decreases the solubility of the metals in solution, thus fewer metals become associated with
the biomass. Even a normally operating system, well acclimated to the heavy metal feedings, could experience difficulty from a small depression of pH, as for instance a small organic shock loading.

The affinity between metal and soil is also of importance. Copper ions form a highly insoluble precipitate and yet is rapidly taken up as pH is lowered. In contrast chromium which is comparatively soluble, shows little variation because of its lower tendency to complex with the bacterial fraction.

Parkin et al (1983) [3] have shown that methane bacteria may not necessarily be dead when gas production ceases. High values Solids Retention Time (SRT) allow for recovery from temporary slugs of toxicity by preventing washout of biomass prior to recovery. Thus, the entire contents of the system need not be discarded and the process started up from the beginning with seed sludge which is a very expensive and time consuming procedure, however if the contaminated liquid can be removed recovery will be accelerated.

**The effects of sulphides**

Sulphide is an anion that occurs in many wastes or can be produced by biological action on the wastes such as reduction of sulphur containing inorganic compounds, or from the degradation of sulphur containing organic materials such as proteins. Sulphides in a digester can be present in a soluble or an insoluble form, depending upon the cations they associate with. Several of the common metal sulphides are extremely insoluble and thus heavy metal cations precipitate and remove sulphides from solution. The removing soluble sulphide forms a weak acid which ionises in aqueous solution the extent depending on the pH. Thus it is possible to have H$_2$S, HS$^-$ and S$^{2-}$ in solution. At near neutral pH required for anaerobic treatment only the first dissociation of hydrogen sulphide is of importance as follows

$$\text{H}_2\text{S}_{(aq)} \rightarrow \text{H}^+ + \text{HS}^-$$

Because of the limited solubility of hydrogen sulphide, a certain portion of that formed will escape with digester gas produced. The resulting equilibrium between hydrogen sulphide remaining in the digester supernatant liquor (H$_2$S$_{aq}$) and that in the gas above (H$_2$S$_{g}$) is governed by Henry’s law. Lawrence et al [3] found soluble sulphide extremely toxic to anaerobic digestion, causing complete cessation of gas production above a threshold value of 200mg/l.

**Carbonate precipitation**

Another set of processes known to be capable of removing sufficient heavy metal ions from solution to prevent inhibition of anaerobic digestion, involves the interactions of metals with the carbon dioxide/carbonate system Mosey [9]. The activity of carbonate ions present in digesting sludge is controlled by the pH of the sludge and the partial pressure of the carbon dioxide in the digester gases. The heavy metals each form hydroxides, carbonates and under the conditions of digestion the precipitated salts are likely to be ZnCO$_3$, Cd CO$_3$, Cu CO$_3$, Pb CO$_3$. If inhibition is affected by the concentration of carbonate ions it should depend on the pH value of the sludge, i.e. inhibition should decrease markedly when pH increases.

2. RESULTS AND DISCUSSION

**Laboratory apparatus**

Two anaerobic bench scale reactors were employed (one as a control), at a mesophilic temperature. The digesters were two 6 litters pyrex aspirator bottles with multisocket lids. The lid had four openings, the centre one facilitating an entrance for a glass rod stirrer driven by a variable speed motor. One opening was used for sludge removal via a glass pipe, another opening used for feeding had a 250 ml funnel with a feed pipe adjustment. The fourth opening had a gas outlet with a syringe cap for gas analysis purposes with a further connection to a 6 Litre glass bottle filled with water. The gas production was determined on the principle of water displacement. The digesters were partially immersed in a water bath maintained at 35°C.

The digesters were used to examine the treatability of a specific leachate produced in a co-disposal landfill of municipal and toxic waste.

The efficiency of the process to remove the organic fraction and particulate elements such as heavy metals were closely monitored.
Experimental procedure
The daily procedure consisted of the following operations.
A portion of the MLSS was removed from the digesters, the amount of which was determined by the operating OLR or the strength of the feed. Thirty millilitres of the sludge were occasionally retained for suspended solids determination, while the remaining sludge was centrifuged at 3200 rpm for a period of thirty minutes. The portion of the centrifuged supernatant equivalent to the volume of the daily feed was retained for routine analysis while the biomass together with the remaining supernatant and the feed were returned to the digester. This procedure ensured that no sludge was wasted and that the MLSS was always maintained at the 5 litre level.

The digester was first acclimatised and then leachate from the site was introduced with the following characteristics:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.75</td>
</tr>
<tr>
<td>COD</td>
<td>31,000</td>
</tr>
<tr>
<td>BOD</td>
<td>12,000</td>
</tr>
<tr>
<td>TOC</td>
<td>6,000</td>
</tr>
<tr>
<td>Organic-N</td>
<td>47.6</td>
</tr>
<tr>
<td>Total-N</td>
<td>644</td>
</tr>
<tr>
<td>NH3-N</td>
<td>596.4</td>
</tr>
<tr>
<td>PO4-P</td>
<td>10</td>
</tr>
</tbody>
</table>

The units are in mg/l

The analysis which valued the digester’s performance and the prevalence of steady state conditions were pH, gas chromatography, gas production, volatile acids performance on a daily basis and COD, suspended solids, alkalinity, BOD, ammonia nitrogen, phosphorus were performed at regular intervals. Heavy metal analysis were further carried out for the influent effluent and sludge in both total and soluble phase.

The leachate was introduced at an OLR of 0.2 Kg COD/m°3d (equivalent to a COD of 6,000 mg/l) until the feeding of the digester reached the aimed OLR of 1 KG COD/m°3d (equivalent to a COD 30,000 mg/l). The volatile acids were completely utilised and the CH4:CO2 ratio was 80:20% respectively.

Further, the effects of an enhanced concentration of zinc, a metal of concern at the site, on the performance of the anaerobic digestion was determined as 50 mg/l of Zn fed as zinc nitrate, (Zn2(NO3).6H2O) was pulse fed into the digester.

The postulated role of sulphide in preventing heavy metal toxicity of the anaerobic digestion process was put into test with successive additions of Zinc and sulphide but with sufficient intervals in their separate introduction, 50, 100 and 200 mg/l of Zinc were successfully pulse fed into the digester.

The efficiency of the anaerobic digestion to produce methane gas was closely monitored through all the phases of the experiment.

The whole procedure can therefore be subdivided into four stages

STAGE I : ACCLIMATION OF THE DIGESTER

Digester were started up by filling them with 3 litres of sieved anaerobic sludge from a sewage treatment plant. The digesters were gradually fed on synthetic feed. The aim was to establish a healthy methanogenic bacterial population and to provide the background waste COD and accompanying nutrients. The organic loading rate was increased in steps by altering the concentration of the organic load in the feed. Recognising the prime importance in maintaining stable digesting conditions, the OLR was only increased if all the monitoring parameters permitted so. The average increase was 0.1-0.2 Kg COD/ m°3 day.

The COD removal efficiency was 96% , alkalinity was 4,000 mg/l as CaCO3 , pH 7.4

At this stage one digester was kept as a control and maintained on the synthetic feed while the other one was fed on the leachate.

STAGE II: BIODEGRADATION OF LEACHATE

As soon as leachate was introduced at an OLR interval of 0.2 Kg COD/m°3d (equivalent to a COD of 6,000mg/l) up to the OLR of 1 Kg COD/m°3d (equivalent to a COD of 30,000) the function of the system and the anaerobic process improved. The volatile acids were completely utilised and the CH4:CO2 ratio was 80:20 respectively.
At the end of this phase which lasted 23 days, the control had also been stabilised and the following comparisons in the performance of the two digesters can be made:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Digester 1 (leachate fed)</th>
<th>Digester 2 (control)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0</td>
<td>7.6</td>
</tr>
<tr>
<td>COD removal (%)</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>Gas composition (%) (CH₄:CO₂)</td>
<td>80:20</td>
<td>60:40</td>
</tr>
<tr>
<td>Volume of gas (lt)</td>
<td>1,000</td>
<td>1,500</td>
</tr>
<tr>
<td>Gas yield (m³ CH₄/ Kg COD removed)</td>
<td>0.20</td>
<td>0.30</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>5,000</td>
<td>5,800</td>
</tr>
<tr>
<td>NH₃-N (mg/l)</td>
<td>1,000</td>
<td>1,500</td>
</tr>
</tbody>
</table>

The gas yield for the leachate feed is considerably lower than the control but this is to be expected since the COD:BOD ratio of the leachate was calculated to be 0.35. This indicates the presence of non-biodegradable material in the leachate.

A considerable increase in percentage methane was further observed in digester 1 with the corresponding decrease in CO₂. This is characteristic of the substrate supplied. Pomerey (1933) has presented evidence showing that the CH₄:CO₂ ratios for the gas produced from carbohydrates, fats and proteins is 1.0, 2.3, and 5.3 respectively. This is consistent with the results since the synthetic feed is mainly of a carbohydrate nature whereas the leachate is supplied from a municipal landfill and according to reported literature it should contain substantial quantities of lipids. It has been reported that domestic sewage can contain as much as 25.2 per cent lipids on a dry weight basis.

The difference in alkalinity between the two digesters is reflected in the pH values and its level which is on the elevated side should provide an effective buffering capacity to the system.

The ammoniacal nitrogen introduced with the leachate which is of the level of 600 mg/l did not present an inhibition to the treatment.

The soluble heavy metals present in the leachate did not give any evidence of distress of the digestion although the quantities involved were measured to be quite small.

The two metals present in the highest quantities, Iron and Manganese although not known to be toxic to the anaerobic process, were shown to be taken up completely by the solids (insoluble precipitates) and not to exist in the soluble form which affects the bacterial cells.

Overall anaerobic digestion proved to be a very efficient way of degrading the leachate biologically in the laboratory. A 90% COD removal has been achieved with 80% of the gas yield in the form of methane.

Denitrification processes have also been noticed since the ammonia introduced with the daily feed did not increase the corresponding effluent concentration.

STAGE III: TOXICITY CAUSED BY HEAVY METALS

A quantity of 50 mg/l of Zn was introduced in the digester pulse fed as zinc nitrate, Zn(NO₃).6H₂O. The reported by Theis and Heis toxic limit for zinc is given as 600 mg/l [5]. An immediate reduction in gas production to virtually zero occurred due to the intoxication of the biomass. The volatile acids concentration rose from a total of 100 mmg/l as acetic acid to a value of 3500 mg/l within 10 days, with a gross accumulation of both acetic and propionic acids. The influent COD accumulated rapidly. The gas composition changed from 80% CH₄ and 16% CO₂ to 0% CH₄, 17% CO₂ and 73% N₂.
Analysis of the heavy metals present in total and soluble forms, before and after the zinc introduction were performed, as follows:

<table>
<thead>
<tr>
<th>Day</th>
<th>SOLUBLE (effluent) mg/l</th>
<th>TOTAL (sludge) mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>METAL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.18</td>
<td>0.48</td>
</tr>
<tr>
<td>Ni</td>
<td>0.11</td>
<td>0.25</td>
</tr>
<tr>
<td>Pb</td>
<td>0.50</td>
<td>0.87</td>
</tr>
<tr>
<td>Fe</td>
<td>0.61</td>
<td>0.92</td>
</tr>
<tr>
<td>Mn</td>
<td>0.20</td>
<td>0.50</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>Cr</td>
<td>0.19</td>
<td>0.28</td>
</tr>
<tr>
<td>Cu</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Day 76 the samples from the effluent (soluble) and from the sludge (total) phase were analysed before the pulse feeding of 50 mg/l of Zn and in Day 78 there were analysed after. The system was left with no further introduction of leachate (no feed) and complete analysis was performed again on the days 85, 95.

The above analysis were performed by Atomic Adsorption Spectrophotometry.

The results show that nearly all of the Zn added was essentially associated with the solid phase. However, an increase in the soluble phase not only of Zn but of all the other metals present in the digester, with the exception of Cu, was recorded. This is in agreement with Patterson’s findings (page 5 §8.3). By using the formula of Mosey (page 6 § 8.3), for the determination of the combined effect of metals in digestion, on an equivalent weight basis, and substituting the values of the concentration of the heavy metals, excluding the Fe which is reported to be non toxic, the k value was calculated to be 208 meq/ Kg which slightly exceeds the recommended value of K of 200 meq/kg.

The total heavy metal present in the digester before the addition of the Zn sums up to a value of 253.8 mg/l. The total value of sulphides were determined to be 65 mg/l. The question is why did not the digester fail before the pulse feeding of Zn.

According to the reaction,

\[ \text{M}^{2+} + \text{S}^{2-} \rightarrow \text{MS} \]

where \( \text{M}^{2+} \) is the divalent metal ion and \( \text{S}^{2-} \) the sulphur ion than one mole of sulphide is required per mole of heavy metal precipitation.

Taking into consideration that the heavy metals have molecular weights ranging between 58 to 65 while that of sulphur is 32, thus about half of sulphide is required to precipitate one mg/l of these heavy metals.

When examining the total heavy metal concentration before the first 50 mg/l of Zn was added (Day 76) it will be found to sum up to 253.8 mg/l of \( \text{M}^{2+} \). Determinations of total sulphides in the sludge gave the result of 65 mg/l of \( \text{S}^{2-} \), which is clearly highly inadequate in causing the precipitation of all the heavy metals present in the sludge. The question is then, why did the digester not fail long before the 50 mg/l pulse feeding of Zn.
If one closely examines the concentrations of the individual metals present, it will become apparent that 177.8 mg/l out of the total 253.8 mg/l of heavy metal present are iron (Fe) ions. Iron has been reported in the literature as being non toxic to digestion even in the absence of sulphide. Even if we assume that all of the sulphide present has been used for the precipitation of all other metals but iron this leaves just about the adequate amount 27 mg/l of sulphur to deal with the sudden load of Zn. This assumption can be made on the grounds that iron is the most soluble of all metals and thus will constitute a reservoir of sulphides to precipitate the other less soluble metals first. The safety margin in these calculations is clearly poor and indicates that there was an insufficient quantity of sulphur ions present to take care of the sudden dose of Zn. The results obtained indicate that the methanogenic bacteria were rapidly inhibited. Within five days the CH₄ fraction in the gas was reduced by 70%. The acid formers continued to convert the substrate into volatile acids which accumulated mainly on acetic and proprionic acids. There was not a noticeable fall in the pH value but the alkalinity was reduced by 600 mg/l as CaCO₃ which indicates that the buffering protection has been used.

The digester feeding was then discontinued. The volatile acids stabilised to a total value of 3500 ± 300 mg/l for a period of 20 days. Throughout this period a gradual increase in the percentage methane was noticed with a final composition of 56% CH₄ and 19% CO₂. Small and erratic gas production was recorded. The effluent COD also remained fairly constant at a value of 4700 mg/l. It is interesting that there is very little activity, if any by the acid formers.

The change in the gas composition is indicative of either bacterial re-growth or acclimatization or both. It is left upon the strengthening methanogenic population to complete the degradation of acidogenic products. This period is followed by a sudden drop of volatile acids to 2500 mg/l and the production of 0.3 l of gas. Thereafter, a regular gas production was established accompanied by a continuous reduction of volatile acids and COD.

A soluble zinc determination of the effluent shows it to be at the pre-inhibitory level (0.2 mg/l).

STAGE V: CONTROL OF SULPHIDES

It was decided to test the digester to another zinc pulse feeding but this time with subsequent sulphide supplementation. A total sulphides determination of the sludge showed the presence of 65 mg/l of S²⁻. Soluble sulphides were not possible to be determined. Firstly, 10 mg/l of Zn as Zn(NO₃)₂.6H₂O was introduced. By the next day inhibition of gas production had occurred. A sufficient quantity of sulphide to cause precipitation of the heavy metal, that is theoretically 5 mg/l of S²⁻, was introduced as sodium sulphide (Na₂S). A regular gas production was resumed. In this matter with, successive additions of Zinc and sulphide but with sufficient intervals in their separate introduction, 50, 100 and 200 mg/l of Zinc were successfully pulse fed into the digester. These results are in agreement with other researchers findings. The volatile acids were utilised all the way down from 1400 to 140 mg/l, unaffected by the presence of heavy metals. However, the % CH₄ was gradually reduced after the 100 mg/l Zn addition from 80% to 51%. A final soluble Zn determination showed the pre-inhibitory level of 0.2 mg/l indicating the complete recovery of the operation of the anaerobic process.

The above results are schematically shown in the graph shown below:
Reference List

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10. PATTERSON, J.W. and HAO, S.S.: Heavy Metals Interactions in the Anaerobic Digestion System