FACTORS INHIBITING ANAEROBIC DEGRADATION IN A LANDFILL

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SUMMARY : The landfill "Hooge Maey" is, despites the fact it originates from the sixties, in the acetogenic phase. The physico-chemical analysis of the leachate showed no absence of trace-elements and no presence of toxic compounds, only high concentrations of total ammoniacal nitrogen (TAN) (3421 mg/L) and volatile fatty acids (VFA) (3140 mg/L, mainly propionic acid). It appears that the high amount of TAN inhibited the methanogenic population and resulted in an accumulation of VFA, which became a further factor of inhibition of the whole landfill maturation. Both the leachate as the solid waste from the landfill were in lab tests subjected to different types of methanogenic inocula. Inocula not adatpted to high concentrations of TAN gave no gas production. On the other hand, high TAN adapted inocula resulted in a significant gas production of good quality. Furthermore, a major part of the propionic acid was converted to acetate. Hence, bioaugmentation of the landfill with a TAN adapted inoculum can generate methanogenic conditions. Moreover, the addition with a lignosulphonate based supplement also promoted methanogenesis of the landfill wastes.

1. INTRODUCTION

The landfill "Hooge Maey" represents the largest landfilling capacity in Flanders. In order to obtain continuity of the legal license, elaborate remediation activities have to be carried out. One of them is the removal of about one million m³ of leachate, rich in COD and VFA, present in the waste body. Although landfilling activities have been going on since the sixties, a substantial part of the landfill is still pertaining to the acetogenic bioconversion phase. The absence of the methanogenic phase results in a highly loaded leachate for the waste water treatment plant and in a poor biogas production. Currently, research is being carried out on both lab-scale and pilot-scale experiments to identify the reason for this slow performance of the overall anaerobic process.

2. EXPERIMENTAL SETUP

2.1 Physico-chemical characterization of the leachate

In order to have a balanced view of the elements present in the landfill, a physico-chemical characterization was made of the leachate. The results are shown in Table 1.

Table 1 – Physico-chemical parameters (mg/L) of the leachate from the landfill “Hooge Maey”.

COD	26120	SO_4^{2-}-S	52
BOD	6000	S^{2-}-S	20
VVZ	3140	Na^+	5840
pH	8.4	K^+	1777
TAN-N	3421	Mg^{2+}	59
TON-N	0	Ca^{2+}	41
Kj-N	3635	Cl^-	4933
PO_4^{3-}-P	23		

The VFA were further characterized as shown in Table 2.

Table 2 – Absolute (mg/L) and relative concentrations of the most important VFA.

	Absolute (mg/L)	Relative (%)
Total amount of VFA	3140	
Acetate	631	20
Propionic acid	1754	56
Iso butyric acid	278	9
Iso valeric acid	323	10

The results of Table 1 show that there is a large amount of salts present in the leachate. Sodium, the cation with the highest inhibition capacity of all cations (De Baere et al., 1984) is emphatically present, but not in those amounts that stress situations can be suspected. The amount of sulphate/sulfide was rather low in the leachate, therefore sulphate reducing bacteria (SRB) were not expected to be predominant in the landfill. It is known that SRB can compete very efficiently for hydrogen and substrates yielding hydrogen with methanogenic bacteria; on the other hand they do not compete effectively for acetate (Isa et al., 1986a; Isa et al., 1986b). Kroiss and Wabnegg (1983) found that a free H_2S of 50 mg/L inhibits acetotrophic methanogens by about 50%, while complete inhibition occurred at a free H_2S level of ca. 200 mg/L. It is clear that in our specific case, inhibition due to H_2S is an unlikely cause of the absence of methanogenesis.

The overall ratios for nutrients were far from optimal. For anaerobic processes, a ratio for COD/N/P of 100/1.25/0.25 is generally accepted as optimal. In this specific case, a ratio of 100/13.92/0.09 was determined (Table 1). This suggests that the available phosphorous was slightly insufficient, but that the amount of nitrogen was high. Furthermore 94% of all nitrogen was present as TAN. As known, the TAN can be present as ammonium ion and free ammonia. Free ammonium is an inhibitor of the methanogenic process. The equilibrium of the ratio ammonium ion/free ammonia is function of both temperature and pH. Under mesophilic conditions and at a pH of 7 only 1.1% of TAN is present as free ammonia. When the pH increases to 8, already 11.3% of TAN is present as free ammonia. This means that in the leachate of the landfill Hooge Maey (pH 8.4), about 1 g of free ammonia/L is present. De Baere et al. (1984) showed that 50 – 80 mg of free ammonia/L can result in a decrease of the methanogenic activity of 50%. De Baere et al. (1984) reported that high concentrations of TAN result in an overall decrease of the methanogenic process, characterized by an accumulation of residual VFA. In the leachate of the landfill, high concentrations of VFA are indeed present (Table 2). Furthermore, about 80% of them were higher VFA (mainly propionic acid), with only 20% present as acetate. Propionic acid is, moreover, not only a recalcitrant intermediate, it executes at levels of g/L a bacteriostatic activity (De Baere et al., 1986) and becomes a factor of inhibition for the overall methanogenic process. James et al. (1998) also reported that even when the pH is not acidic, high concentrations of VFA can inhibit the methanogenisis indirectly.

Overall, the results of the Hooge Maey leachate indicate that, both the high concentration of TAN and the resulting high concentrations of higher VFA are the main causes of the poor methanogenic process performance. Nevertheless, it is reported that methanogenic populations can adapt to high concentrations of TAN, even at high pH-values. Van Velsen and Lettinga (1979) and Angelidaki (1992) reported that in digested manure, methanogenic bacteria are adapted to TAN concentrations of 3 g/L and more.

2.2 Inoculation experiments

To investigate if the high concentration of TAN was indeed the parameter limiting the methanogenic process, both leachate and solid waste from the landfill was collected and subjected to different types of anaerobic sludge. The methanogenic sludges could be divided into two categories. The first category contained sludges which were not adapted to high concentrations of TAN. The second category of sludges was adapted to TAN stress. Furthermore, a supplement developed to stimulate methanogenic processes was tested for its applicability in landfill sites. The supplement contains several components such as e.g. lignosulphonates. The latter slowly release sulphate and sulphite which can act as electron acceptor. Moreover, the humic acids are also considered to be able to function as electron sinks and thus to activate anaerobic conversions (Field, 2001). The supplement also contains a balanced mix of trace elements and vitamins. When the leachate was inoculated with methanogenic sludge, a volume of 10% inoculum was added. The supplement was dosed at 1 g/L leachate. In case of inoculation of the solid waste fraction, about 30 kg of solids was inoculated with 10 L of liquid, consisting of 10% inoculation material and 90% tap water. The COD, VFA, pH and the qualitative and quantitative aspects of the biogas production were analyzed. The experiments were performed under mesophilic conditions.

3. RESULTS AND DISCUSSION

3.1 Experiments on leachate from the landfill “Hooge Maey”

3.1.1 Inoculation with non TAN adapted methanogenic sludge

Two types of non TAN adapted granulated methanogenic sludge were tested. The activity of the sludge was verified by means of adding sodium acetate (NaAc), which resulted in a significant gas production. Nevertheless, by adding the inoculum to the leachate, no gas production was observed. It was tried to adapt the inoculum to the leachate by means a gradual exposure to leachate. Even under those conditions, there was no gas production observed.

3.1.2 Inoculation with TAN adapted methanogenic sludge

Three different types of such TAN adapted methanogenic sludge were applied to inoculate the leachate. All three sludges had a highly TAN loaded history in common. All three inocula were tested separately, and also as a mixed inoculum. None of them was significantly different from the other. The figures and values given below are in the case of the mixed inoculum. Figure 1 shows the biogas production during a period of 35 days following after bioaugmentation.

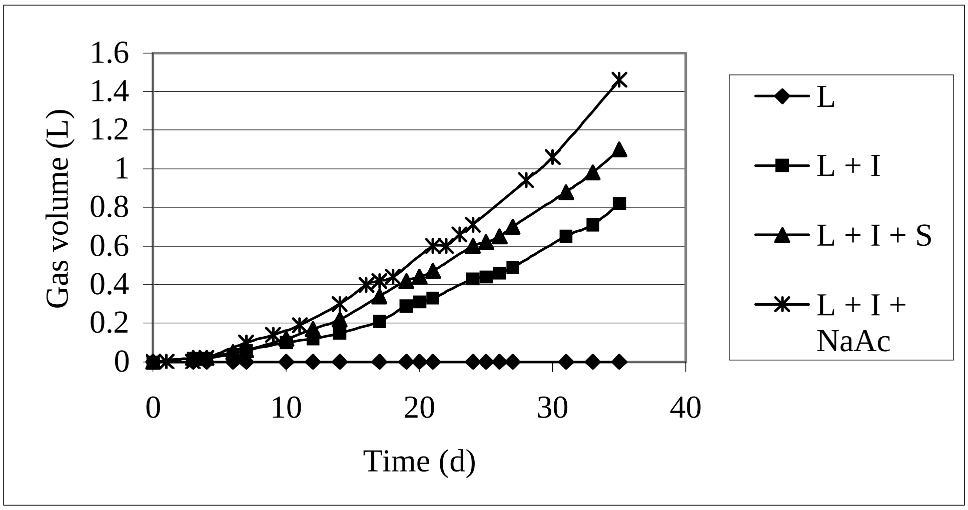

Figure 1 - Quantitative biogas production over a period of 35 days after bioaugmentation; L = leachate; I = mixed inoculum and S = supplement

Figure 1 clearly shows the positive effect of a TAN-adapted inoculum on the biogas production, whereas a non-adapted inoculum had no result at all. Interestingly, the supplement also enhanced the gas production, which must be related to additional electron acceptor capacity, which it represents. Yet, overall, the methanogenic process was slow : a total of about 1 L of biogas per L leachate was measured after one month. Hence, if the landfill is considered as reactor, the total amount of gas thus putatively produced can be estimated at, at least, 30.000 m^3/d for the one million m^3 of leachate present in the waste body. In this estimation, the biogas production of the solid waste is not included. The quality of the gas was remarkably high : respectively 76% and 79% of the biogas consisted of methane for inoculation of the leachate and inoculation in combination with the supplement. Calculation of the biogas production with respect to the removal of COD, resulted in a biogas production of 0.21 $L/gCOD_{removed}$ and 0.31 $L/gCOD_{removed}$, for inoculation of the leachate, and inoculation in combination with the additive, respectively. Theoretically, 0.5 $L/gCOD_{removed}$ is possible. The evolution of COD and VFA are respectively shown in Figures 2 and 3.

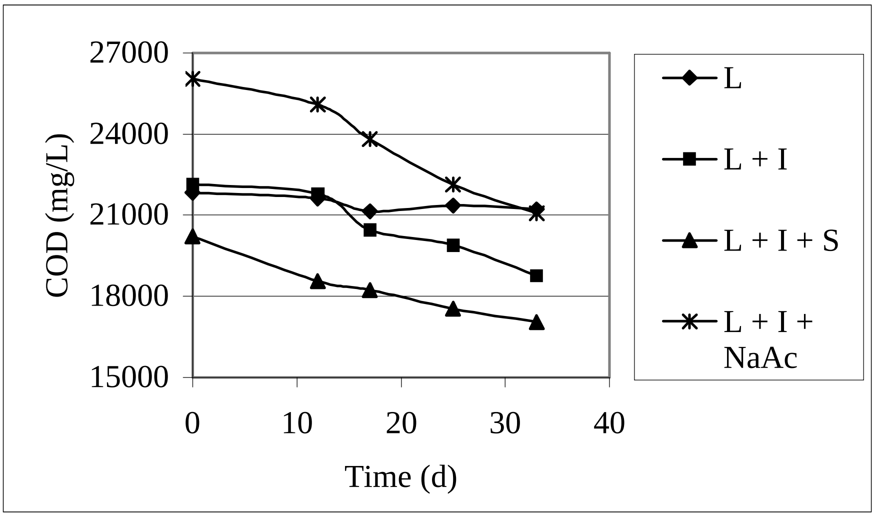

Figure 2 - Evolution of COD over a period of 33 days after bioaugmentation; L = leachate; I = mixed inoculum and S = supplement.

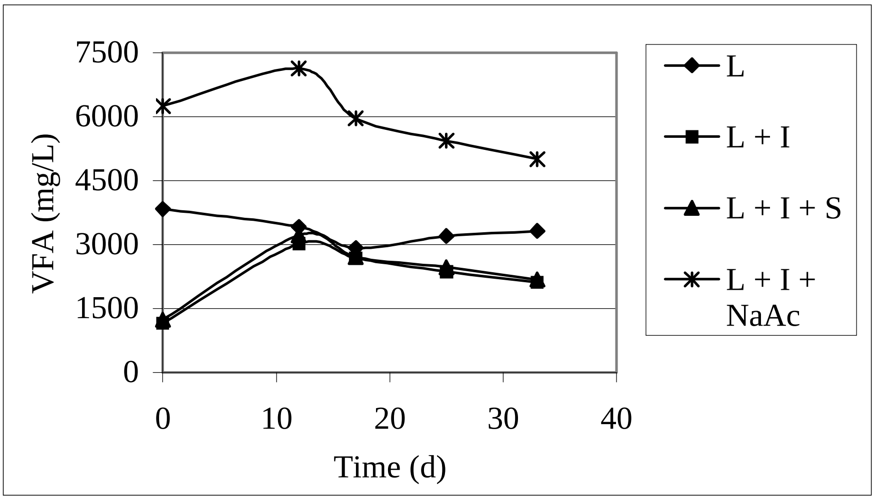

Figure 3 - Evolution of VFA over a period of 33 days after bioaugmentation; L = leachate; I = mixed inoculum and S = supplement.

The lower soluble levels of COD observed for the (L + I + S) combination in Figure 2 suggest that the supplement may bring about a coagulation respectively sorption of some of the higher molecular organics to the waste matrix. This aspect warrants further examination. After inoculation, during the first period, there was a slight increase in VFA (Figure 3). This suggests that this is due to the conversion of a certain part of the COD by acidogenic bacteria to VFA, the initial step in the methanogenisis process. After two weeks, a slow decrease in the concentration of VFA was noted. This is due to of the formation of biogas from the VFA. The decrease in VFA was not spectacular, but it is known that the overall methanogenic process is rather slow. On the other hand, there was a significant difference in the amount of VFA before and after inoculation. This is shown in Table 3.

Table 3 – Absolute (mg/L) and relative concentrations of the most important VFA before inoculation and 33 days after inoculation.

	VFA before inoculation		**VFA 33 days after inoculation**	
	Absolute (mg/L)	Relative (%)	Absolute (mg/L)	Relative (%)
Total amount of VFA	3140		2178	
Acetate	631	20	1788	82
Propionic acid	1754	56	274	13
Iso butyric acid	278	9	46	2
Iso valeric acid	323	10	37	2

Table 3 clearly shows that, despite the rather small decrease in the total amount of VFA (31%), there is a major shift in the different types of VFA. Before inoculation, 80% of the total amount of VFA consisted of higher VFA, which potentially inhibit the further reaction mechanism of the methanogenisis. After inoculation, the major part of those higher VFA are converted to acetate. This indicates that the acetogenic stage of the process is no longer inhibited. The acetate can easily be converted during the methanogenic stage to methane and CO_2. It should be mentioned that during the whole test period, the pH did not significantly change (results not shown).

3.2 Experiments on solid waste from the landfill "Hooge Maey"

The same setup was tested on solid waste. In 60 L barrels, about 30 kg of one year old solid waste from the landfill was kept. Three different types of highly TAN loaded inoculum were added to the barrels. 1 L inoculum was diluted with 9 L tap water. The control consisted of 10 L tap water. The biogas production is shown in Figure 4.

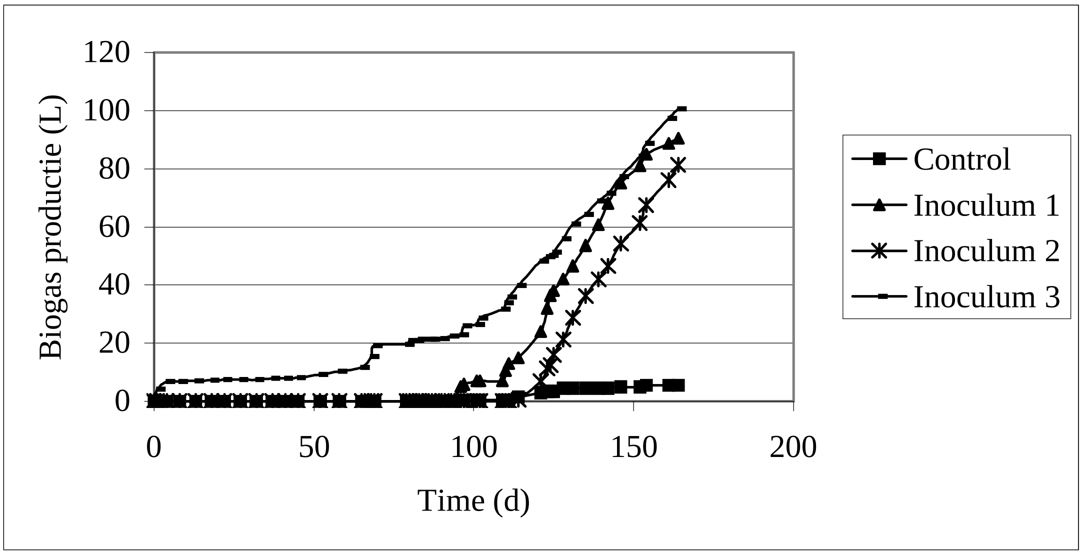

Figure 4 - Cumulative biogas production of one year old solid waste with three different types of TAN adapted inocula.

Figure 4 shows that the initiation of the methanogenic stage is possible with TAN adapted inocula. A lag phase of about 3 to 4 months was necessary before the solid waste became methanogenic. In the startup, the quality of the biogas was rather poor (20% methane), but after 160 days of treatment, the quality increased to acceptable values (59% – 61% methane). Some 165 days after inoculation, a total biogas volume of about 80 – 100 L was obtained. As seen in Figure 4, one can expect that this is only the initial phase. Based on those experiments, one can not predict the efficiency of the methanogenic process, but it is clearly shown that solid waste that was non methanogenic due to high TAN and VFA concentrations, could be bioaugmented by means of a properly adapted inoculum.

3.3 Experiments on pilot-scale in the landfill

Currently, large-scale pilot scale experiments are carried out in situ on the landfill. It is known that recirculation of leachate in waste bodies of landfills can improve the methanogenic process. In this context, a comparative study is carried out. On a specific part of the landfill, an area of about 1.5 ha with a depth of about 30 m, is continuously recirculated with leachate. Another similar area is recirculated with the same amounts of leachate, but with addition of 10% of TAN adapted methanogenic inoculum. At this moment, results are not yet available about the biogas volumes and qualities from these test areas.

4. CONCLUSIONS

Despite landfilling activities since the sixties, methanogenic populations in the Hooge Maey landfill still did not succeed to adapt to high concentrations of TAN. No other inhibitors or deficits in trace elements were identified. Inoculation of the leachate with 10% of inoculum with a high TAN loaded history, resulted within one month to a major change in the kinetics of the different stages of the methanogenic process. Whereas the leachate before inoculation, contained 3140 mg VFA/L, after one month of inoculation, the total amount of VFA decreased by 31% (2178 mg VFA/L). Furthermore, before inoculation, the acetogenic stage was clearly inhibited, resulting in high concentrations of higher VFA (80% of the total amount of VFA). After one month of inoculation, the acetogenic stage was obviously no longer inhibited, the major part of the higher VFA being converted to acetate. Although the inoculation of the leachate with TAN adapted inoculum was sufficient to counteract the inhibiting factors in the methanogenic process, the addition of a supplement resulted in an even better overall process performance. Inoculation of the leachate with the same volume of inoculum, which was not adapted to high amounts of TAN, showed no positive results in any of these stages. The study demonstrated that the solid waste itself could be initiated to produce biogas. After a lag phase of 3 to 4 months, TAN adapted inocula initiated successfully the methanogenisis. Within 1.5 months after the lagphase, 30 kg of solid waste produced about 100 L of biogas consisting of 65% methane. Furthermore, it was shown that the biogas production did not level off, hence a higher conversion with time can be expected. Further research on both recirculation of leachate in the body of the landfill and recirculation of leachate in the body with 10% TAN adapted inoculum , is currently ongoing.

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