Optimization Of the Anaerobic Digestion Of Solid Waste By Addition of Leachate

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EXECUTIVE SUMMARY

The GEEB Team of the University of Reunion directed this research towards the optimization of the anaerobic digestion of solid and liquid waste by injection of leachate. The objectives are to assess the performances of this type of process (to accelerate the process of biological breakdown) and to require a better control of the physicochemical mechanisms involved. During anaerobic digestion, the reactional medium desiccates and induces a deceleration of the process. The injection of leachate methanogene makes it possible to humidify the medium and to maintain the medium reactional under ideal physicochemical and biochemical conditions and to bring an additional organic load. In this paper, the optimization of the process of Co-digestion is presented through an experimental and a theoretical study. The experimentation is carried out on 10L laboratory bioreactors and is based on obtaining leachate methanogene by using liquid waste (STEP mud, liquid pig manure, residuary liquor) and solids. Several parameters are studied: the total volume of the mixture (5 or 10 L), the volume and the state of each waste in the mixture (always a solid waste and a liquid waste). A sample of leachate is taken every 8 days and a liquid addition of waste of the same quantity is carried out in the bioreactor. The experimentation is stopped when it is no longer possible to distinguish waste and leachate. Then, the leachate is characterized from a physicochemical point of view by spectrometric techniques: Ntotal, AGV, NO2-, NH4+, TOC, PO4³-, K+, COD, BOD, DM, VM but also pH. Lastly, they will be reinjected in a Co-digestion. The experimental data obtained will be used as inputs parameters of the numerical mathematical model (biphasic: Acidogenesis and Methanogenesis). Simulations obtained make it possible to follow the behavior of the medium through the organic load (COD, TOC) and the biogas produced with or without addition of leachate.
INTRODUCTION

The process of anaerobic digestion of solid waste co-digested with other organics sludges (e.g. primary sewage sludge, PSS) has the potential to contribute significantly to the renewable energy budget and also to the reduction of landfill or other undesirable waste disposal routes.

Many mathematical models are available in the literature (Hill and Barth, 1977; Simeonov 1995). Generally, their parameters were obtained as some average constants and they are not good enough for real time control design of the process. The physical, chemical and biochemical Parameters of the process were optimized (Bernard, 2001) (IWA, 2002) in order to improve the simulation, but very few studies approached the optimization of the process by addition of an catalyst. In fact, the use of leachate as catalyst could accelerate the achievement of a more stable state and also install favourable conditions for biodegradation. For landfills, the idea was expressed more than 30 years ago, (Pohland and Kang, 1975; Leckie et al., 1979; Ham and Booker, 1982) and several studies were recently published to evaluate the effect of leachate recycling (Bayard et al., 2005; Sponza and Agdag, 2004; Jianguo et al., 2007; Francois et al., 2007).

Thus, the state of the art reported above, clearly shows the valorization of the leachate approached primarily in the optimization of the production of biogas in landfills [Moletta, 2006]. As a whole, the recirculation of the leachate in the solid mass was used to improve the biological breakdown and thus the stabilization of the solid mass of waste within a discharge because of improvement the humidification rate. The results obtained made it possible to control and quantify the diffusion of the leachate injected in order to have an optimal moisture (40 to 70%, (Reinhart D.R and Towsend TG, 1998) on the whole of waste. The studies out of digesters remain anecdotic and were undertaken by Nedwell [Nedwell, 1996] through the use of the leachate in anaerobic digestion in order to reduce the production of the sulfides which inhibits the méthanogenesis (reduction in the production of biogas) during digestion and supports the formation of metals. That was accompanied by detailed work on the treatment by the leachate (reduction of the load) by discharges by comparing two techniques UASB and SBR [Kennedy, 2000]. The idea is thus to optimize a methanisation in a digester with the injection of the leachate in the medium.

The present work investigated the optimization of methanisation in digesters by injection leachate in mixes of organic wastes. This paper was aimed at determining the feasibility of the mesophilic anaerobic digestion of mixture of source separated (pig manure, organic waste, stillage, the slurry) by injecting leachate and to simulate the biogas production through the follow up of the behavior physicochemicals and biochemicals parameters and so provide a data base for analysis and mathematical development.
MATERIALS AND METHODS / EXPERIMENTAL

Experimentation

The experiment consisted of performing the monitoring of leachate obtained by a mixture of biodegradable waste in a bioreactor. Subsequently, these leachates were characterized from a physical chemical point of view to serve as "catalyst" in a co-digestion.

A set of seven types of waste were selected for this study:
- 3 liquids: STEP mud, manure and sugar cane distillery waste.
- 4 solid: canteen waste, grass, compost Beef / pork and compost grass / plant / chicken manure

Choice of waste

Taking into account that the biodegradability of a solid waste is facilitated with the addition of a liquid waste (Boullagui et al 2004) we used the sludge to their neutral pH (Zhang et al 2008), pig manure for its potential methanogenic (Castaing et al. 2002) and sugar cane distillery waste on both the quantity produced on Reunion Island.

The choice of solid farm waste made the world and communities represent a very significant waste producers on the island.

Operating conditions

Part Bioreactor

We did not modified the temperature parameter, since the reactors remained outside in the sunlight: transition from 25 ° C overnight at 30 ° C during the day.

We selected two volumes for bioreactors: 5 or 10 L.

Several mixes were made, but in all cases we have always opted for a mixture 50% liquid waste / 50% solid waste.

The leachates were collected every seven days and the amount recovered was filled by adding an equal volume of liquid waste.

Experimental Analysis / Part physico-chemical

The following physicochemical parameters: COD, BOD5, potassium, ammonium, nitrite, volatile fatty acids, total nitrogen and phosphorus, pH were obtained using a spectrometer DR5000 society HACH LANGE using the test protocols vats.

Physico – chemical characteristics of the leachate are show in Table 1.

<table>
<thead>
<tr>
<th>K⁺ (mg/L)</th>
<th>NO₂⁻ (mg/L)</th>
<th>Pt (mg/L)</th>
<th>PO₄³⁻ (mg/L)</th>
<th>NH₄⁺ (mg/L)</th>
<th>Ntotal (mg/L)</th>
<th>pH</th>
<th>DCO (g/L)</th>
<th>DBO (mg/L)</th>
<th>AGV (mg/L)</th>
<th>COT (mg/L)</th>
<th>DCO/DBO</th>
<th>C/N</th>
<th>C/N/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1062</td>
<td>0,3</td>
<td>169</td>
<td>123</td>
<td>230</td>
<td>318</td>
<td>5,05</td>
<td>8,09</td>
<td>600</td>
<td>5910</td>
<td>6800</td>
<td>13,48</td>
<td>21,38</td>
<td>0,13</td>
</tr>
</tbody>
</table>

Table 1: Physico-chemical characteristics of the leachate
Choosing the mixture for co-digestion and leachate:
The mixture used for co-digestion was as follows:
- 47.5% of pig manure
- 17.5% of organic waste
- 17.5% stillage
- 17.5% of the slurry

The composition of this mixture was determined by the nature and quantities of waste on the island. In addition, the carbon to nitrogen (C/N) of this mixture with a value of 5.62 shows a high production of ammonium inhibition of the process if it is not compensated, it was decided to choose a grass leachate/mud with a high C/N = 21.4.

Protocol for monitoring the digestion:
- Checking the temperature of the digester at a set time once a day to ensure the homogeneity of it in time and mesophilic bacteria.
- Dilution: daily digest of recovery and reintroduction of the same volume of leachates (water charge determined by the biodegradation of grass and mud in a reactor of 5 L) from t0 to t2, then addition of leachate and sludge from the CILAM t3 to t6, adding that the mud from t7 to t10, finally adding the initial mixing until the end of the process of co-digestion. These changes made according to the pH can be inhibitory if it is not between 6.5 and 7.5.
- The experimental system includes a water meter for measuring the volume of biogas produced, it must confront the daily volume of water.
- The magnetic stirring bar magnet was performed on alternate days.

MODELING

The simulated model rests on Anaerobic Model n°2 developed by the INRA of Narbonne and the INRIA of Sophia - Antipolis in 2001 [Bernard.O, 2001]. This model is much simpler than ADM1 [IWA, 2002], to make control and optimization.

Biochemical process

Modeling includes two processes and two bacterial populations. The first stage is that of the acidogenesis modelled by a bacterial population acido-acétogenesis of X1 concentration which breaks up the carbonaceous substrate S1 into volatile fatty-acids (VFA which becomes S2) and into carbon dioxide. One can consider in this model that the VFA are only in not ionized form and behaves like the acetic acid. The two substrates are present in the power supply of the engine. The modelled chemical reactions are the following [Figure 2]:

\[ k_s S_1 \overset{r_1}{\rightarrow} X_1 + k_2 S_2 + k_4 CO_2 \]  
avec la vitesse de réaction \( r_1 = \mu_1 X_1 \)

The growth of the bacteria acidogenes follows kinetics of Monod:

\[ \mu_1(S_1) = \mu_{\text{max}} \frac{S_1}{S_1 + K_{S1}} \]

The second stage is that of the méthanogenesis modelled by a population of bacteria methanogens of X2 concentration which transform the VFA (S2 substrate, coming from the food and/or resulting from the acidogénèse) into methane and carbon dioxide according to the following chemical reaction:

\[ k_s S_2 \overset{r_2}{\rightarrow} X_2 + k_5 CO_2 + k_6 CH_4 \]  
avec la vitesse de réaction \( r_2 = \mu_2 X_2 \)
The growth of the bacteria methanogenes follows kinetics of Haldane:

\[
\mu_2(S_2) = \frac{\mu_{2\text{max}} \cdot S_2}{S_2 + K_{S_2} + \left(\frac{S_2}{K_{i_2}}\right)}
\]

The inhibition of the methanogenesis by the accumulation of VFA is thus modelled.

**Dynamical Model**

\[
\begin{align*}
\frac{dX_1}{dt} &= (\mu_1 - \alpha D) X_1 \\
\frac{dX_2}{dt} &= (\mu_2 - \alpha D) X_2 \\
\frac{dZ}{dt} &= D (Z_i - Z) \\
\frac{dS_1}{dt} &= D (S_{i_1} - S_1) - k_1 \mu_1 X_1 \\
\frac{dS_2}{dt} &= D (S_{i_2} - S_2) + k_2 \mu_1 X_1 - k_3 \mu_2 X_2 \\
\frac{dC}{dt} &= D (C_i - C) - q_C + k_4 \mu_1 X_1 + k_5 \mu_2 X_2
\end{align*}
\]

avec

\[
q_C = K_{n_C} (C + S_2 - Z - K_{n_C} P_C)
\]

\[
P_C = \frac{\varphi - \sqrt{\varphi^2 - 4 K_{n_C} P_C (C + S_2 - Z)}}{2 K_{n_C}}
\]

et

\[
\varphi = C + S_2 - Z + K_{n_C} P_C + \frac{k_6}{K_{n_S}} \mu_2 X_2
\]

*S1in [gDCO.l-1], S2in [mmole.l-1], Cin [mmole.l-1] and Zin [mmole.l-1] are respectively the concentrations in S1, S2, C and Z of the influent.*

The \(\alpha\) term represents degree of agitation of the bioreactor with \(0 \leq \alpha \leq 1\).

\(\alpha = 1\) implies that the digester is completely agitated

\(\alpha = 0\) implies that the digester is perfectly with fixed bed.

With these equations are added the following expression giving the molar flow of the methane, which we rewrite below:

\[q_M = k_6 \mu_2 X_2\]

like that formulating the pH within the digester.

\[
pH = -\log_{10} \left( K_b \frac{C - Z + S_2}{Z - S_2} \right)
\]

In order to be able to carry out numerical simulations using this model, it is essential to also know the analytical expressions of the specific rates of the bacterial growths \(\mu_1\) and \(\mu_2\). In order to consider the possible accumulation of VFA, the model of Haldane was selected for the kinetics of growth of the bacteria methanogens:
\[ \mu_2(S_2) = \mu_{2\text{max}} \frac{S_2}{S_2 + K_{s2} + \left(\frac{S_2}{K_{i2}}\right)^2} \]

The parameters of the model are shown in the table 3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Signification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mu_{1\text{max}} ) ([\text{j}^{-1}])</td>
<td>Growth rate maximum of the bacteria acidogenes</td>
<td>1,468</td>
</tr>
<tr>
<td>( K_{s1} ) ([\text{g.L}^{-1}])</td>
<td>Constant of half saturation associated with the substrate acidogene S1</td>
<td>7,1</td>
</tr>
<tr>
<td>( \mu_{2\text{max}} ) ([\text{j}^{-1}])</td>
<td>Growth rate maximum of the bacteria methanogenes</td>
<td>0,3811</td>
</tr>
<tr>
<td>( K_{s2} ) ([\text{mmol.L}^{-1}])</td>
<td>Constant of half saturation associated with the substrate methanogene S2</td>
<td>9,28</td>
</tr>
<tr>
<td>( K_{i2} ) ([\text{mmol.L}^{-1}])</td>
<td>Constant of inhibition associated with the S2 substrate.</td>
<td>256</td>
</tr>
<tr>
<td>( K_{\text{L}a} ) ([\text{j}^{-1}])</td>
<td>rate of transfer Liquid/gas</td>
<td>1.638</td>
</tr>
</tbody>
</table>

Table 2 : tableau d’estimation des paramètres cinétiques du modèle

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Signification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_1 ) ([\text{s.u}])</td>
<td>Efficiency for the degradation of the DCO</td>
<td>28.02</td>
</tr>
<tr>
<td>( K_2 ) ([\text{mmol.g}^{-1}])</td>
<td>Efficiency for the production of AGV</td>
<td>209.2</td>
</tr>
<tr>
<td>( K_3 ) ([\text{mmol.g}^{-1}])</td>
<td>Efficiency for the consumption of AGV</td>
<td>154.2</td>
</tr>
<tr>
<td>( K_4 ) ([\text{mmol.g}^{-1}])</td>
<td>Efficiency for the production of CO_2</td>
<td>38.61</td>
</tr>
<tr>
<td>( K_5 ) ([\text{mmol.g}^{-1}])</td>
<td>Efficiency for the production of CO_2</td>
<td>73.25</td>
</tr>
<tr>
<td>( K_6 ) ([\text{mmol.g}^{-1}])</td>
<td>Efficiency for the production of methane</td>
<td>212.3</td>
</tr>
</tbody>
</table>

Table 3 : tableau d’estimation des coefficients de rendement du modèle

This model is of the interest to reproduce to 97.8% the variability of the real system [Bernard, 2006]. Its robustness makes its use possible for varied enough experimental conditions [Steyer, 2003].
RESULTS AND DISCUSSION

Model solution

<table>
<thead>
<tr>
<th>DCO (mg.L⁻¹)</th>
<th>AGV (mg.L⁻¹)</th>
<th>Nt (mg.L⁻¹)</th>
<th>NO₂⁻ (mg.L⁻¹)</th>
<th>pH</th>
<th>DBO (mg.L⁻¹)</th>
<th>NH4+ (mg.L⁻¹)</th>
<th>Pt (mg.L⁻¹)</th>
<th>DCO/DBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>32500</td>
<td>3870</td>
<td>1480</td>
<td>2,63</td>
<td>6,97</td>
<td>12880</td>
<td>650</td>
<td>28,5</td>
<td>2,5</td>
</tr>
</tbody>
</table>

Table 4: Initial values

Equations were solved numerically using the fourth order Rung Kutta method. Initial values were those observed on day 1 of the experiment. The initial values of some variables were assumed within a reasonable range of those quoted in the literature. Further initial values are shown in table 4. The coded model was used to simulate pH, biogas, VFA, methane (CH₄) and the behavior of bacteria during the anaerobic digestion with and without leachate. Inputs model obtained from the experimental reactor. The model requires influent values for substrate and COD loading.

![Figure 2: pH behaviour in the digester](image)

![Figure 3: Effect of pH on bioconversion yield (methane)](image)
Figure 4: growth rate of bacteria methanogen

Figure 5: VFA concentration

Figure 6: growth rate of bacteria acidogen
The model assumes a 15 lag time, as suggested by the observed data, after which methane production is in the growth phase. We note the injection of leachate makes it possible to reach an methane concentration more important and regular during the Time Retention Hydraulic (figure 7), nevertheless the addition did not affect the flow of biogas. The presence of leachate at the beginning of the process, in phase acidogenesis, has a positive effect on the pH (figure 2) and the growth of the bacteria (figures 4 and 6). The methane yields (figure 3) obtained during this set of tests with the catalyst are higher than those without leachate. This different yield is mainly due to methane production during the acidogenesis phase. This is due to a better acclimatization and moisturizing of the medium. But even when the medium with leachate was acclimatized, a lag period was present, probably due to the negative effect exerted by the higher initial substrate concentration. The stabilization of the pH influences, positively, the bioconversion in acidogenesis phase [Becarri, 1996]. pH also affects acid distribution. Acetic and butyric acids are the prevailing products at alkaline and acid pH, respectively (data not shown). Figure 5 also shows that VFA’S production is characterized by two different kinetic steps, the second one starting after a plateau has been reached for the first one. The second step occurred at the same time as methane production was revealed. This second step is higher with the leachate than without catalyst. This “secondary” VFA’s production could reasonably arise from the lipid degradation that, as is usually reported in literature [Colberg, 1988], is promoted by H₂, scavenging from methane bacteria.

CONCLUSION

We note that the injection of leachate has brought favourable conditions (pH 7.1, 35°C, acclimatized inoculum). The mixture composed of four different wastes are degraded with a high conversion yield to methane (30%) instead of 16%. A little methanogenic activity is established in acidogenic conditions. This activity might be hypothesized as a basic condition for allowing lipid degradation in acidogenesis.
Moreover, acidogene biomass is remarkably more sensitive to the effect of leachate injection than methanogene biomass. However, no significant changes on lag periods were observed in the hydrolysis phase.

REFERENCES


