PRE-TREATMENT: THE KEY ISSUE IN VINASSE VALORIZATION

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1 INTRODUCTION

The agricultural food industry uses large amounts of water per production unit, although its effluents rarely pose serious environmental problems, as they usually consist of biodegradable organic matter. There are, however, significant exceptions to this rule, such as the alcohol and olive oil production industries (Pulgar, 1983). Their effluents contain high DBO₅ concentration; poorly biodegradable substances or antibacterial activity compounds like phenols and lignin residues (Moreno et al., 1990).

Anaerobic digestion has been the usual biological procedure for purifying wastewater from agricultural food industries containing high organic load, as their aerobic treatment would be incomplete and expensive (Basu et al., 1975; Metcalf and Eddy, 1991). Integrating biological and chemical procedures, with the purpose of removing or altering the structure of refractory and/or toxic substances, seems to be a good option (Heinzle et al., 1995). In fact, preliminary ozone oxidation has been found to increase the wastewater biodegradability.

The homogeneous and heterogeneous photocatalytic systems (UV radiation/O₃/H₂O₂ and O₃/UV/TiO₂) have been studied due to their ability to photo-catalyse the complete mineralization of a wide range of organic substrates, including amides, aromatics, dyes and pesticides (Mansilla et al., 1997; Mokrini et al., 1997; Beltran et al., 1999). The complete mineralization of poorly biodegradable compounds is not selective enough, in fact the necessary ozone generation cost to generate CO₂ would be unviable. However, a shorter treatment time could be suitable for changing the molecular structure of phenol compounds to more biodegradable substances, reducing the process cost.

The aim of this study was to enhance the organic matter degradation by anaerobic digestion, after a light ozone treatment, of vinasse, which is a poor biodegradable agricultural effluent from sugar cane distillery.

2 MATERIALS AND METHODS

2.1 Experimental set-up and procedure

Ozonation pre-treatment was carried out in a 1L Pirex reactor in which a pure oxygen stream containing 34 g O₃/m³ (0ºC and 1atm) was conducted through a porous plate diffuser. The reactor was provided with a magnetic stirred system. The outlet gas stream was measured and continuously registered by an ozone analyser and a data acquisition system. The selected pre-treatment time was 15 minutes.

The experimental anaerobic digestion set-up, used at laboratory scale, consisted of two 1L CSTR connected to a thermostatic jacket containing water, which allowed maintaining the reactors temperature as 35ºC (mesophilic conditions). All of the experiments were carried out in batch mode. The volume of methane produced during the process was measured after removing the CO₂ contained in the biogas.

The vinasse used is produced in SOTRAMEG Company (Kenitra, Moroco), which chemical composition is shown in Table 1.

The innoculum was selected on the basis of its high methanogenic activity, showing values ranging from 0.87 to 0.99 g COD/g volatile suspended solid (VSS)-d. The experiments were carried out using an innoculum concentration of 10 g VSS/L. The start-up was developed by adding a synthetic solution composed of glucose (50 g/L), sodium acetate (25 g/L) and lactic acid (20.8 mL/L), over a 21-day period. Subsequently, the acclimatisation was carried out by increasing the added load with pre-treated vinasse to 1 g COD/L over a 16-day period. Once this preliminary acclimatisation step was completed, a series of batch mesophilic experiments were carried out using the pre-treated vinasse until reaching a final concentration of 3 g COD/L. Each assay lasted a maximum of 24 hours; the time interval required to completely biomethanize each load. The volume of methane was measured as a function of
time and samples were taken and analyzed before and after feeding. Each load was carried out at least in duplicate and the results expressed as means.

All analyses were carried out in accordance with the Standard Methods of the American Public Health Association (APHA, 1989).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Untreated Vinasse</th>
<th>Pre-treated Vinasse (Ozonation 15 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>3.75 ± 0.08</td>
<td>3.54 ± 0.10</td>
</tr>
<tr>
<td>COD total (mg/L)</td>
<td>68,560 ± 8,170</td>
<td>66,100 ± 8,170</td>
</tr>
<tr>
<td>COD soluble (mg/L)</td>
<td>55,830 ± 2,120</td>
<td>54,020 ± 1,000</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>29,700 ±100</td>
<td>33,350 ±130</td>
</tr>
<tr>
<td>TOC soluble (mg/L)</td>
<td>20,160 ± 50</td>
<td>19,760 ± 70</td>
</tr>
<tr>
<td>MS (mg/L)</td>
<td>30,990 ± 1,170</td>
<td>n.d.</td>
</tr>
<tr>
<td>VS (mg/L)</td>
<td>46,390 ± 790</td>
<td>n.d.</td>
</tr>
<tr>
<td>MSS (mg/L)</td>
<td>5,300 ± 370</td>
<td>n.d.</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>15,860 ± 650</td>
<td>n.d.</td>
</tr>
<tr>
<td>VA (mg acetic acid/L)</td>
<td>1,500 ± 115</td>
<td>2,610 ± 60</td>
</tr>
<tr>
<td>Phenols compound (mg caffeic acid/L)</td>
<td>446 ± 10</td>
<td>267 ± 10</td>
</tr>
</tbody>
</table>


3 RESULTS AND DISCUSSION

3.1 Ozonation pre-treatment and aerobic biodegradability

Figure 1 shows the ozone effect on the reduction percentage of phenols compounds with the ozonation time. As can be seen the phenols removal –although it practically has shown no influence over COD concentration (Table 1) – produced a positive influence upon the vinasse aerobic biodegradability. The BOD/COD ratio is a variable which indicates the biodegradable organic fraction in a wastewater. This ratio enhanced with the slight oxidation with ozone. As higher the ozonation time was, higher the BOD/COD ratio was, in spite of 15 minutes were chosen as pre-treatment time due to economic reasons.

Some chemical variables remained approximately constant during the pre-treatment, including pH, COD and TOC, although the enhancement of volatile acidity (from 1,500 to 2,610 mg acetic acid/L) seems to indicate the transformation of complex compounds into short chain acids –substances much more biodegradable than the previous ones.

3.2 Anaerobic digestion viability

In order to evaluate the anaerobic biodegradability, growing loads of vinasse and pre-treated vinasse were added into batch reactors, and the stability evolution, methane production yield and COD removal percentage were studied. It was remarkable that the variation of the VA/Alk ratio –stability index-, was slightly higher for untreated vinasses, 0.26 while it was 0.23 values for pre-treated vinasse respectively. pH values were lower for untreated vinasses (7.02<pH<7.54) than pre-treated vinasse (7.40<pH<7.72) This result indicated worse maintenance conditions in the anaerobic process stability. 0.30 is the value considers as the threshold of instability; this value was lower in both cases. It was also interesting the VSS concentration decrease when both wastes were fed, although the decrease was 10% higher for the untreated vinasse (Figure 2). As the inoculum adaptation period was appropriate, this marked VSS reduction could be attributed to higher phenols accumulation in the reactors loaded with untreated vinasse, which produces cellular death.
Pre-processing of manure and organic waste for energy production

FIGURE 1 Variation of phenol reduction percentage and BOD/COD ratio with ozonation time.

FIGURE 2 Evolution of VSS reduction percentage with the anaerobic digestion treatment.

FIGURE 3 Untreated and pre-treated vinasses specific methane production rate.

For organic loading rates ranging from 1.00 to 3.00 g COD/L·d, the methane yield remained relatively stable around 0.25 L CH₄/g COD added for untreated vinasses and 0.28 L CH₄/g COD added for pre-treated vinasses, measured at 0ºC and 1 atm in both cases. Moreover, Figure 3 shows the specific methane production rate obtained with pre-treated vinasse, which was found to be 43.85 mL CH₄/g VSS·g COD·d, while it was 30.78 mL
CH₄/g VSS·g COD·d without pre-treatment in spite of the COD removal was around 80% in both cases. Authors described this positive effect over the kinetics (Borja et al., 1995).

4 CONCLUSIONS

Vinasse chemical characterisation shows values in the range of 60,000-70,000 mg COD/L, being approximately 40-50% aerobically biodegradable (BOD₅). A short oxidation pre-treatment with ozone produced a decrease in phenols concentration that, although just supposed a light reduction of total organic carbon, increased the aerobic and anaerobic biodegradability and the biodegradation rate.

The methane production increase, which is a useful product due to its caloric power (Lower Caloric Power): 35,793 kJ/m³, equivalent to 9.96 kWh/m³. This fact together with the enhancement of the biodegradability ratio justifies the advantage of carrying out the pre-treatment. Treated wastewater contains less non biodegradable organic compounds, minimizing the necessity of applying a post-treatment to fulfill the environmental legislation. The main consequence of the degradation rate increase is the reduction of the anaerobic reactor volume, with the consequent investment reduction.

So important as obtaining the highest yield is to carry out the anaerobic digestion under stable conditions. In that sense, pre-treated vinasses have maintained the stability representative variables more than untreated vinasses.

In conclusion, the results were found to depend on the pre-treatment, being the anaerobic digestion process more adequate after ozonation.

ACKNOWLEDGEMENTS

The authors are very grateful to AECID for funding the project PCI-A/018624/08 between Córdoba and Kenitra Universities. We also wish to express our gratitude to the Company SOTRAMEG (Kenitra, Morocco) for permitting to do research into this field and to the Spanish Ministry of Science and Innovation for funding José Ángel Siles López through Project CTM2005-01293 and Grant BES-2006-14074 (Co-financed by the European Social Fund).

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