Effect of Mixture of Surfactants and Adsorbents on Anaerobic Digestion of Water Hyacinth-Cattle Dung

DATTA MADAMWAR,1,* ANAMI PATEL,1 VIKRAM PATEL,1 AND N. V. SHASTRI2

¹Department of Biosciences, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India; and ²Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India

Received February 4, 1992; Accepted June 8, 1992

ABSTRACT

In an effort to improve the anaerobic digestion of water hyacinth-cattle dung with enriched methane content, the effects of mixtures of surfactant-surfactant, adsorbent-adsorbent and surfactant-adsorbent have been studied in various combinations. Among the combinations tested, bentonite and gelatin, gelatin and Tegoprens 43, sodium lauryl sulfate and Tegoprens 42, and Tegoprens 47 and Tegoprens 63 showed more than a 100% increase in gas production with higher methane yield.

Index Entries: Water hyacinth; cattle dung; anaerobic digestion; surfactant; adsorbent; energy.

INTRODUCTION

There has been increased interest in recent years to apply anaerobic digestion to the production of biogas from the renewable carbon source of biomass and wastes. Cattle dung (CD) has so far been the major resource for biogas production (1-3). In recent years water hyacinth (WH) has come to be used as a replacement for cattle dung, mainly because of the latter's limited availability (4-6). The WH also has relatively low nutrient

^{*}Author to whom all correspondence and reprint requests should be addressed.

164 Madamwar et al.

requirements and very high growth rates with an excellent pollutant removal and methane generation potential that makes it amenable to utilization in integrated pollution control and energy conversion systems in rural areas. There is also a growing interest in maximizing the extraction of methane for energy recovery from WH. Unfortunately, operating experiences with anaerobic digesters and their cost effectiveness has not been consistently good.

Earlier studies have shown that the addition of surfactant, particularly nonionic, results in exceptionally high performance stability and increased rate of decomposition (7). Similar studies with adsorbents showed increased gas production with higher methane content when they were incorporated into anaerobic digesters (8). In both cases positive effects are shown mainly because of their surface property that provides a more favorable environment for bacteria (enzyme)-substrate system. Their chemical nature also suggests that when they are mixed in different combinations (surfactant-surfactant, adsorbent-absorbent and surfactant-adsorbent), they may have an effect on biomethanation. Therefore, it was necessary to conduct a study on the effects of mixtures of surfactants and adsorbents in different combinations on anaerobic digestion of WH-CD with the ultimate aim to improve the digestion process.

MATERIALS AND METHODS

Resources

All chemicals used were of analytical grade. All Tegoprens were obtained from Gold Schmidt AG, Essen, FRG. Cattle dung and water hyacinth were obtained locally.

Anaerobic Digestion

Several bench-scale anaerobic digesters were used. Each vessel consisted of a 10 L glass reaction bottle, having a working volume of 6 L and containing 7% (w/v) of total solids (TS). The digesters were intermittently stirred with magnetic stirrers and maintained at $37\pm1^{\circ}$ C. Gas was collected and measured by displacement of acidified saturated salt solution, making due correction for atmospheric pressure and temperature. The digesters were fed on a semicontinuous basis once per day using a freshly prepared mixture of powdered WH (dried at 60 °C and powdered to 50 mesh size) and CD in a ratio of 7:3 (w/w), with a retention time (RT) of 8 d (where the loading rate was 8.75 g TS/L of digester/day). This was found to be most suitable from a previous study (8). Prior to feeding, an equal quantity of sludge was withdrawn from the bottom of the digester. Surfactants and/or adsorbents were mixed with feed sludge.

A fresh digester was always started by preparing a mixture of the powdered WH and CD in the ratio of 7:3 (w/w) to give a final TS concentration of 7% (w/v), and using a 10% inoculum from the running biogas digester of the same type (containing only WH and CD in the ratio of 7:3 (w/w) and TS 7% (w/v) without surfactant and/or adsorbents). A steady-state condition was decided upon by a fairly constant mean gas production rate and constant BOD/COD values. Digesters were operated at least for 5 RTs. Experiments were carried out in triplicate for each mixture and for each combination, and average data are presented in Table 1.

Analysis

Gas composition was analyzed with a CIC gas-liquid chromatogram with stainless steel chromosorb 2 column and thermal conductivity detector (1). Feed and effluent slurry were routinely analyzed for pH, volatile acids, biological oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), and volatile solids (VS), as standard procedures (10).

RESULTS AND DISCUSSION

The impact of different surfactants like Tween 20, Tween 40, Tween 60, sodium lauryl sulfate, Tegoprens 42, Tegoprens 43, Tegoprens 47, Tegoprens 51, Tegoprens 52, Tegoprens 63, and adsorbents like gelatin, pectin, aluminum powder, bentonite, silica gel, polyvinyl alcohol, talcum powder, and powdered activated charcoal in different combinations on gas production in anaerobic digestion of water hyacinth-cattle dung were studied. An improvement in gas production (over 100%) was obtained with the addition of bentonite (5 g/L) and gelatin (7 g/L) into the digester. In addition to high gas production, the digester showed improved methane production presented as methane yield and methane production rate. As shown in Table 1, a maximum of about 0.304 L/g vs added methane yield and 9.14 L of digester/day methane production rate were observed at a dose of bentonite 5 g/L and gelatin 7 g/L, as compared with 0.129 L/g vs added methane yield and 0.646 L/L of digester/day methane production rate of control digester in which no surfactants or adsorbents were incorporated.

Concentration of organic acids in fermenter is a sensitive parameter used to determine fermenter stability (2). Table 1 shows the data on the levels of total volatile fatty acids present in the fermenters stabilized with different doses of surfactants and adsorbents. Average volatile fatty acids concentration ranged from 1.35 g/L in the digester with no surfactants and/or adsorbents to 0.47 g/L in bentonite and gelatin dosed digester.

 $Table\ 1 \\ Summary\ of\ Effluent\ Data\ During\ Steady-State\ Periods\ of\ Digesters\ Maintained\ at\ 37\pm1^{\circ}C\ in\ Presence\ of\ Surfactants\ and\ Adsorbants$

| | | Total | | | | | Volatile | | | | |
|-----------------------|-------------------------------|-------------------------|-------------------------|----------------------|------|------|----------|---------------|--|--|--|
| Dose | | gas | CH ₄ | CH₄ yield | BOD | COD | acid | %COD | | | |
| mg/L | | production ^a | production ^b | L/g vs added | g/L | g/L | g/L | removal | | | |
| Contr | ol | 1.01 | 3.87 | 0.129 ± 0.000070 | 17.3 | 27.2 | 1.35 | 62.01 | | | |
| Bentonite + Gelatin | | | | | | | | | | | |
| 500 | 100 | 1.05 | 3 <i>.</i> 78 | 0.126 ± 0.000003 | 18.7 | 26.4 | 1.26 | 63.12 | | | |
| 1000 | 2000 | 1.37 | 5.34 | 0.178 ± 0.000172 | 16.6 | 23.7 | 0.93 | 66.89 | | | |
| 3000 | 4000 | 1. <i>7</i> 7 | 7.00 | 0.233 ± 0.000027 | 15.4 | 22.3 | 0.63 | 68.85 | | | |
| 5000 | 7000 | 2.21 | 9.14 | 0.304 ± 0.000380 | 11.8 | 17.4 | 0.47 | 75.69 | | | |
| 500 | 7000 | 2.05 | 8. 4 8 | 0.283 ± 0.000217 | 12.4 | 16.7 | 0.50 | 76.67 | | | |
| 5000 | 100 | 1.25 | 4.95 | 0.165 ± 0.000025 | 16.8 | 24.2 | 0.97 | 66.20 | | | |
| Alum | Aluminium + Silica Gel | | | | | | | | | | |
| 100 | 500 | 1.01 | 3.81 | 0.127 ± 0.000004 | 19.9 | 27.2 | 8.33 | 62.01 | | | |
| 300 | 300 | 1.05 | 3.96 | 0.132 ± 0.000012 | 18.6 | 26.9 | 1.21 | 62.43 | | | |
| 500 | 500 | 1.05 | 4.03 | 0.134 ± 0.000243 | 18.2 | 27.1 | 1.24 | 62.15 | | | |
| 100 | 300 | 1.20 | 4.68 | 0.156 ± 0.000007 | 17.4 | 26.3 | 0.96 | 63.26 | | | |
| 300 | 100 | 1.13 | 4.40 | 0.147 ± 0.000012 | 17.2 | 26.8 | 0.97 | 62.57 | | | |
| 500 | 100 | 1.35 | 5.34 | 0.178 ± 0.000147 | 16.9 | 26.1 | 0.85 | 63.55 | | | |
| PVA | PVA ^c +Talc Powder | | | | | | | | | | |
| 100 | 50 | 1.15 | 4.4 8 | 0.149 ± 0.000003 | 18.9 | 26.3 | 1.20 | 63.27 | | | |
| 500 | 100 | 1.20 | 4.68 | 0.156 ± 0.000217 | 18.6 | 26.2 | 1.08 | 63.40 | | | |
| 1000 | 500 | 1.15 | 4.48 | 0.149 ± 0.000021 | 18.2 | 26.4 | 1.17 | 63.13 | | | |
| 2000 | 1000 | 1.13 | 1.34 | 0.144 ± 0.000172 | 18.1 | 26.6 | 1.21 | 62.84 | | | |
| 100 | 1000 | 1.10 | 4.22 | 0.140 ± 0.000009 | 18.8 | 26.8 | 1.28 | 62.57 | | | |
| 2000 | 50 | 1.05 | 4.03 | 0.134 ± 0.000211 | 18.9 | 27.0 | 1.31 | 62.29 | | | |
| Alum | inium | + Bentonite | | | | | | | | | |
| 10 | 500 | 1.02 | 3.91 | 0.130 ± 0.000064 | 19.9 | 27.2 | 1.34 | 62.01 | | | |
| 50 | 1000 | 1.02 | 3.91 | 0.130 ± 0.000084 | 19.4 | 27.3 | 1.36 | 61.87 | | | |
| 100 | 2000 | 1.06 | 4.13 | 0.138 ± 0.000091 | 18.3 | 26.9 | 1.26 | 62.43 | | | |
| 10 | 5000 | 1.05 | 4.03 | 0.134 ± 0.000037 | 18.6 | 27.0 | 1.27 | 62.29 | | | |
| 50 | 500 | 1.06 | 4.13 | 0.138 ± 0.000039 | 19.0 | 26.8 | 1.28 | 62.57 | | | |
| 100 | 1000 | 1.03 | 3.95 | 0.132 ± 0.000031 | 19.5 | 27.1 | 1.30 | 62.15 | | | |
| | | goprens 43 | | | | | | | | | |
| 2500 | 10 | 1.05 | 4.09 | 0.136 ± 0.000196 | 19.4 | 26.2 | 1.30 | 63.40 | | | |
| 5000 | 30 | 1.30 | 5.14 | 0.171 ± 0.000133 | 17.1 | 24.7 | 1.05 | 65.50 | | | |
| 7500 | 50 | 1.78 | 7.15 | 0.238 ± 0.000052 | 16.0 | 22.3 | 0.65 | 68.85 | | | |
| 10000 | | 2.09 | 8.65 | 0.288 ± 0.000012 | 12.5 | 17.7 | 0.40 | <i>7</i> 5.27 | | | |
| 2500 | 30 | 1.65 | 6.73 | 0.224 ± 0.000003 | 15.1 | 22.9 | 0.72 | 62.01 | | | |
| 5000 | 50 | 1.48 | 5.94 | 0.198 ± 0.000012 | 17.7 | 24.0 | 0.81 | 66.48 | | | |
| Pectin + Tegoprens 52 | | | | | | | | | | | |
| 500 | 25 | 1.72 | 6.91 | 0.230 ± 0.000237 | 16.4 | 22.5 | 0.65 | 68.57 | | | |
| 1000 | 50 | 1.74 | 7.00 | 0.233 ± 0.000157 | 15.7 | 22.3 | 0.64 | 68.85 | | | |
| 1500 | <i>7</i> 5 | 1.88 | 7.66 | 0.255 ± 0.000237 | 14.4 | 21.8 | 0.61 | 69.55 | | | |
| 2000 | 100 | 1.81 | 7.27 | 0.242 ± 0.000367 | 14.5 | 22.2 | 0.63 | 68.99 | | | |
| 1000 | 25 | 1.68 | 6.75 | 0.225 ± 0.000048 | 15.5 | 22.6 | 0.71 | 68.43 | | | |
| 2000 | 50 | 1.84 | 7.50 | 0.250 ± 0.000133 | 15.1 | 21.8 | 0.68 | 67.55 | | | |

| | | Total | | | | | Volatile | | | | |
|---------------------------------|-----------------------|-------------------------|-------------------------|----------------------|-------------|------|----------|----------------|--|--|--|
| Dose | | gas | CH₄ | CH₄ yield | BOD | COD | acid | %COD | | | |
| mg/L | | production ^a | production ^b | L/g vs added | g/L | g/L | g/L | removal | | | |
| PAC ^d + Tegoprens 47 | | | | | | | | | | | |
| 1000 | 25 | 1.03 | 3.95 | 0.131 ± 0.000366 | 18.3 | 26.9 | 1.23 | 62.43 | | | |
| 2000 | 50 | 1.05 | 4.03 | 0.134 ± 0.000273 | 18.2 | 26.7 | 1.18 | 62.70 | | | |
| 3000 | <i>7</i> 5 | 1.05 | 4.03 | 0.134 ± 0.000199 | 18.2 | 26.8 | 1.15 | 62.57 | | | |
| 4000 | 100 | 1.06 | 4.13 | 0.138 ± 0.000453 | 17.1 | 26.3 | 0.98 | 63.27 | | | |
| 2000 | 25 | 1.20 | 4.75 | 0.158 ± 0.000421 | 16.7 | 26.1 | 0.93 | 63.55 | | | |
| 3000 | 50 | 1.06 | 4.13 | 0.138 ± 0.000147 | 17.6 | 26.2 | 1.01 | 63.40 | | | |
| Silica Gel+SLS ^e | | | | | | | | | | | |
| 100 | 100 | 0.81 | 2.43 | 0.081 ± 0.000337 | 19.7 | 28.2 | 2.13 | 60.61 | | | |
| 500 | 200 | 0.90 | 3.34 | 0.112 ± 0.000171 | 20.1 | 27.6 | 1.63 | 61. 4 5 | | | |
| 1000 | 300 | 0.90 | 3.34 | 0.112 ± 0.000259 | 20.2 | 27.7 | 1.68 | 61.31 | | | |
| 100 | 300 | 0.81 | 2.43 | 0.081 ± 0.000256 | 19.4 | 28.1 | 2.09 | 60. <i>7</i> 5 | | | |
| 500 | 100 | 0.93 | 2.45 | 0.115 ± 0.000364 | 18.2 | 27.5 | 1.45 | 61.59 | | | |
| 1000 | 200 | 0.82 | 2.95 | 0.098 ± 0.000268 | 19.4 | 28.1 | 2.08 | 60.68 | | | |
| | Tween 60+Tegoprens 43 | | | | | | | | | | |
| 10 | 10 | 1.29 | 5.02 | 0.167 ± 0.000133 | 17.5 | 24.7 | 1.10 | 65.50 | | | |
| 20 | 20 | 1.37 | 5.34 | 0.178 ± 0.000403 | 16.9 | 23.8 | 0.97 | 66.76 | | | |
| 50 | 50 | 1.95 | 7.83 | 0.261 ± 0.000313 | 14.8 | 21.4 | 0.40 | <i>7</i> 7.11 | | | |
| 10 | 50 | 1.77 | 7.11 | 0.237 ± 0.000252 | 15.1 | 22.2 | 0.52 | 68.99 | | | |
| 20 | 10 | 1.52 | 6.01 | 0.200 ± 0.000121 | 15.8 | 23.8 | 0.81 | 67.17 | | | |
| 50 | 10 | 1.22 | 4.75 | 0.158 ± 0.000316 | 15.8 | 24.3 | 1.13 | 66.06 | | | |
| Twee | n 80+ | Tegoprens 51 | | | | | | | | | |
| 50 | 50 | 1.15 | 4.41 | 0.147 ± 0.000171 | 17.5 | 24.7 | 1.08 | 65.50 | | | |
| 100 | 100 | 1.27 | 4.95 | 0.165 ± 0.000496 | 17.0 | 24.0 | 0.93 | 66.48 | | | |
| 200 | 200 | 1.90 | 7.63 | 0.254 ± 0.000409 | 14.9 | 21.6 | 0.57 | 69.83 | | | |
| 300 | 300 | 1.81 | 7.16 | 0.239 ± 0.000247 | 15.0 | 22.1 | 0.63 | 69.13 | | | |
| 100 | 300 | 1.34 | 5.22 | 0.174 ± 0.000508 | 16.2 | 23.8 | 0.94 | 66.76 | | | |
| 300 | 100 | 1.01 | 3.87 | 0.129 ± 0.000283 | 16.7 | 25.4 | 1.43 | 64.52 | | | |
| SLS ^e - | - Tego | prens 42 | | | | | | <u> </u> | | | |
| 50 | 50 | 1.06 | 4.13 | 0.137 ± 0.000157 | 18.6 | 27.0 | 1.08 | 62.29 | | | |
| 100 | 100 | 1.25 | 4.95 | 0.165 ± 0.000223 | 17.6 | 26.3 | 0.83 | 63.26 | | | |
| 150 | 150 | 2.00 | 8.16 | 0.272 ± 0.000084 | 10.1 | 15.8 | 0.54 | <i>7</i> 7.93 | | | |
| 200 | 200 | 2.20 | 9.10 | 0.303 ± 0.000139 | 9.4 | 14.3 | 0.43 | 80.03 | | | |
| 50 | 100 | 1.70 | 6.83 | 0.227 ± 0.000417 | 15.4 | 22.7 | 0.68 | 68.29 | | | |
| 100 | 50 | 1.52 | 6.11 | 0.203 ± 0.000412 | 17.8 | 25.1 | 0.74 | 64.94 | | | |
| Tegoprens 47+Tegoprens 63 | | | | | | | | | | | |
| 50 | 50 | 1.56 | 6.27 | 0.209 ± 0.000252 | 16.1 | 22.7 | 0.83 | 68.29 | | | |
| <i>7</i> 5 | 75 | 1.89 | 7.71 | 0.257 ± 0.000388 | 13.4 | 19.1 | 0.51 | 73.32 | | | |
| 100 | 100 | 2.14 | 8.85 | 0.295 ± 0.000559 | 11.2 | 15.6 | 0.48 | 78.21 | | | |
| 50 | 100 | 2.16 | 8.94 | 0.298 ± 0.000169 | 10.1 | 14.9 | 0.44 | 79.19 | | | |
| 75 100 | 50 | 1.94 | 8.02 | 0.267 ± 0.000127 | 12.3 | 18.4 | 0.56 | 74.30 | | | |
| 100 | <i>7</i> 5 | 2.10 | 8.69 | 0.289 ± 0.000163 | 11.2 | 16.2 | 0.46 | 77.37 | | | |

^aL/L of digester/day.
^bL/digester/day.
^cPVA=Polyvinyl alcohol.
^dPAC=Powdered activated charcoal.
^eSLS=Sodium Lauryl Sulphate.

168 Madamwar et al.

This indicates that volatile fatty acids are consumed at a faster rate than that in the control experiments. Presence of surfactant and/or adsorbent in the digester enhances the methane forming step of the digestion process, which is the slowest and most rate limiting (11).

Methanogenic bacteria catabolize mainly acetate, carbon dioxide, and hydrogen to the terminal products. The maintenance of a very low concentration of hydrogen in the digester by methanogens is essential for efficient fermentation because it maintains low production of propionate and other reduced products (12). Thus, only a slight increase in hydrogen will lead to the accumulation of propionate and carbon dioxide. In previous studies propionate and carbon dioxide were found to be accumulating in larger quantities in a control digester (data not given), however, the addition of bentonite and gelatin reduced the amount of propionate and carbon dioxide.

Présence of bentonite and gelatin gave minimum value of BOD (11.8 g/L) and COD (17.4 g/L), indicating greater biodegradation with high process performance (13). The value of BOD and COD in a control digester were 17.3 g/L and 27.2 g/L respectively. This indicates that microbial degradation of organic matter is at a much higher rate in a bentonite and gelatin dosed digester than in a control digester.

Bacterial efficiency can also be judged by the values of %COD removal (13). Table 1 also gives data of %COD removal. This shows that the presence of bentonite and gelatin improves the bacterial efficiency, and thereby increases biodegradation.

Studies with other combinations of surfactants and/or absorbents (Table 1) also showed improved gas production with higher methane yield and methane production rate. They are also responsible for lower volatile acid content and lower values of BOD and COD, indicating better process performance, high process stability, and high rate of biodegradation in the presence of surfactants and/or adsorbents.

It is shown that surfactants have unusual properties of polymeric form (micelles) and they show catalysis of organic reactions. Surfactants also increase the rate of enzymatic cellulose saccharification (14). Addition of adsorbents in general improve the digestion performance, although a clear mechanism of their action cannot be given. However, from the analysis of the data and the other investigator's experience with adsorption, certain possibilities can be envisaged.

Adsorbents may be providing adsorption sites where substrates can accumulate, thereby providing high localized substrate concentration. These areas of adsorption provide a more favorable environment for the bacteria substrate system, while adsorption and orientation of the surfactant molecules at the solid-liquid interphase could render the substrate readily wettable by the enzymes produced by bacteria. Therefore, the presence of surfactants and/or adsorbents may provide a more favorable environment for the bacteria (enzyme)-substrate system, and improve

the digester performance and quality of gas with a higher fuel value. Some adsorbents such as gelatin may have an additional effect, such as stimulating fatty acid degrading bacteria, by serving as a good nitrogen source. This may be why the effect of gelatin with bentonite is much better than any other combinations.

ACKNOWLEDGMENT

Thanks are due to the DNES, New Delhi, India, for financial support.

REFERENCES

- 1. Robbins, J. E., Gerhardt, S. A., and Kappel, T. J. (1989), *Biol. Wastes* 27, 1-14.
- 2. Varel, V. H., Hashimoto, A. G., and Chen, Y. R. (1980), Appl. Environ. Microbiol. 40, 217-222.
- 3. Smith, R. J., Hein, M. E., and Greiner, T. H. (1979), J. Anim. Sci. 48, 202-218.
- 4. Saraswat, N. and Khanna, P. (1986), Biotechnol. Bioeng. 28, 240-246.
- Wolverton, B. C. and McDonald, R. C. (1976), New Scientist (USA) 71(1013), 318–329.
- 6. Obeid, M. (1975), in: *Aquatic Weeds in the Sudan*, Obeid, M., ed., National Council Res., Sudan and US National Academy Science, Washington, DC, pp. 101–103.
- 7. Madamwar, D. B., Patel, A., and Patel, V. (1991), Bioresource Technology 37, 157-160.
- 8. Patel, V., Patel, A., and Madamwar, D. (1992), Bioresource Technology 40, 179-181.
- 9. Madamwar, D. B., Patel, A., and Patel, V. (1990), J. Ferment. Bioeng. 70, 340-342.
- 10. APHA, (1976), Standard Methods for the Examination of Water and Waste Water, 14th ed., American Public Health Association, Washington, DC.
- 11. Handki, K. and Nagase, K. (1981), Biotechnol. Bioeng. 23, 1591-1640.
- 12. McInerney, M. J. and Bryant, M. P. (1981), in: Biomass Conversion Process for Energy and Fuel, Sofer, S. S., and Zaborsky, O. R., eds., Plenum, New York, pp. 277-298.
- 13. Hills, D. J. and Roberts, W. D. (1981), Agric. Wastes 3, 179-189.
- 14. Castanan, M. and Chavles, W. R. (1981), Biotechnol. Bioeng. 23, 1365-1372.