Enhancement of biomethanization by pretreatment of limed fleshings from tanneries

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This study presents effect of pretreatment using anaerobic inoculum (PT-AI) and thermo-chemical pretreatment (PT-TC) on solubilization of limed fleshings (LFs). Solubilization of LF in PT-AI (93.3%) was more than PT-TC. From biochemical methane potential (BMP) studies, LFs with PT-AI generated 0.16 m3 of CH4/kg CODtotal added, which was 2.7 and 1.5 times more than LFs pretreated with NaOH and KOH respectively.

Keywords: Anaerobic inoculum, Biochemical methane potential, Fleshings, Pretreatment, Tannery

Introduction

There are nearly 1500 tanneries in India processing 0.7 million tonnes (MT) of wet salted hides and skins per year. Every tonne of processed leather generates wastewater (30-50 m3) and solid wastes (300-500 kg), of which 200-300 kg are wet limed fleshings (LFs); India generates LFs (0.175 MT) per year. Organic content of LFs (80%, dry wt basis) cannot be disposed off in conventional landfills. Although, treatment options such as recovery of bio-energy using anaerobic digestion and co-digestion of fleshings with primary sludge1, cowdung4 and municipal solid waste5 are available, but co-digestions of LFs in anaerobic digesters require 35 days of solid retention time (SRT) and hence a large volume of reactor space3. Size reduction was done by mincing LFs mechanically before it was fed into anaerobic digester4. Mincing could not be done effectively as presence of lime and grit material lead to frequent failure of mechanical equipment, resulting in increase in operation and maintenance cost.

In present study, enhancement of biochemical methane potential (BMP) for LFs was studied after solubilization by thermo-chemical pretreatment (PT-TC) using alkalies [sodium hydroxide (NaOH) and potassium hydroxide (KOH)] at different concentrations under pressure with temperature and pretreatment using anaerobic inoculum (PT-AI).

Experimental Section

Characteristics of Limed Fleshings (LFs)

LF samples (30) were collected from tanning clusters of Melvisharam, Pallavaram, Ranipet, Vaniambadi and Ambur in Tamilnadu, India. Analysis7 of LF samples gave following values: pH, 12.0-12.5; moisture, 79-92%; and volatile solids (VS), 0.60-0.75; non-volatile solids (grit & lime); 0.26-0.40; CODtotal, 0.66-0.95; TKN, 0.05-0.15; ammonia N, 0.0013-0.0040; oil & grease, 0.036-0.104; and phosphorous as P, 0.0005-0.0020 g/g (w/w, dry basis).

Effect of pretreatment with Anaerobic Inoculum (PT-AI) on Solubilization of Lime Fleshings (LFs)

To study effect of PT-AI on solubilization of LFs, characteristics of inoculum obtained from upflow anaerobic sludge blanket (UASB) reactor were found as follows: pH, 7.75 ± 0.35; VS, 550 ± 110 mg/l; TS (total solids), 1000 ± 214 mg/l; CODtotal, 1250±353 mg/l; CODsoluble, 480±150 mg/l; TKN, 200±42.4 mg/l; ammonia N, 175±35.3 mg/l; and phosphorous, 2±1.4 mg/l. Solubilization of LFs was estimated by analyzing CODtotal and CODsoluble before and after pretreatment. Uncut LFs (1 kg; moisture, 85.5±6.3%; VS, 0.67±0.06 w/w) were mixed with anaerobic inoculum containing following VS concentrations from an UASB reactor:
0.6±0.06g (sample I); 1.2±0.12 g (sample II); and 1.8±0.18 g (sample III). Concentration of VS in inoculum, mixed with 1 kg of LF, was 550± 110 mg/l. VS (%) in inoculum taken for studies per kg of LF were 0.75, 1.5 and 2.25 respectively. A control with similar ratios was also taken up without inoculum but with distilled water. During study, pH, volatile fatty acids (VFA), COD_total and COD_soluble concentrations were monitored. Solubilization of LF is reported in terms of COD_soluble. Solubilized LFs were characterized and BMP studies were carried out.

Effect of Thermo-Chemical Pretreatment (PT-TC) on Solubilization of Lime Fleshings (LFS)

To study effect of thermo-chemical pretreatment (PT-TC) on LF solubilization, LF (1 kg) was mixed with NaOH and KOH solutions in the order of 1, 2, 3, 4 and 5%. Samples were subjected to a pressure (1 kg/cm²) and temperature (250°C) for 15 min and a control was also run with distilled water. Solubilization of LFs was estimated by analyzing COD_total and COD_soluble before and after pretreatment. After pretreatment, Solubilized LFs were characterized and BMP studies were carried out.

Experimental Set up for Biochemical Methane Potential (BMP) Assessment

BMP studies on LFs were carried out with seed sludge from UASB reactor treating tannery waste water. Assessment of BMP involved incubating LFs inoculated with anaerobic sludge for 30 days at 35°C with monitoring of methane gas production. A double-jacketed reactor (capacity, 2 l), used to assess BMP of LFs, contained airtight lid, a stirrer, a gas outlet and a sample port. A variable speed stirrer was connected to a timer so that stirrer rpm, stirring interval and duration of stirring could be controlled. Gas outlet from reactor was connected to a Marriot flask containing 6 N NaOH solution with methyl blue indicator. NaOH solution absorbs CO₂ and H₂S from biogas. A volume of NaOH equivalent to methane generated was displaced into a measuring cylinder.

Results and Discussion

Effect of Pretreatment with Anaerobic Inoculum (PT-AI) on Solubilization of Lime Fleshings (LFS)

During study, COD_soluble (Figs 1 & 2) and VFA (Fig. 3) were estimated and pH (Fig. 4) was measured. COD_total of LF (1 kg) was estimated as 134.4 g. Initial COD_total concentration of LF sample I, II and III after mixing with inoculum were estimated as 67200, 44800 and 33600 mg/l and COD_soluble concentration were 4254, 3595 and 2458 mg/l respectively. Initial COD_soluble concentration was due to dissolution of protein and organics from LF. During study period, COD_soluble fraction increased to a level of 41985 and 24528 mg/l from initial concentration of 3595 and 2458 mg/l respectively. At the end of 14th day, COD_soluble fraction in sample I was observed to be 59136 mg/l (13.9 times more than initial COD_soluble concentration of 4254 mg/l equivalent to 88% of COD_total of LF added). pH of sample I decreased to 9.2 from 12.1 at the end 14th day, due to production of VS as volatile fatty acids (VFA). VFA concentration in sample I on 14th day has increased to 150000 mg/l from initial VFA concentration of 600 mg/l, a 250% increase. In samples II and III, COD_soluble fraction increased to a level of 41985 and 24528 mg/l from initial concentration of 3595 and 2458 mg/l on 8th and 5th day respectively. This represents 11.5 and 10 times increase from initial COD_soluble concentration. It was also observed
that 93.3% of COD\textsubscript{total} added has come into COD\textsubscript{soluble} in sample II and 65% in sample III. COD\textsubscript{soluble} concentration decreased marginally in sample II and III after 8\textsuperscript{th} and 5\textsuperscript{th} day respectively, due to onset of methanogenic activity. pH observed on 8\textsuperscript{th} and 5\textsuperscript{th} day was 8.9 and 8.7 respectively. While in control after 8 days, 10.8, 14 and 14.1% of COD\textsubscript{soluble} was observed. COD\textsubscript{soluble} in sample II after 8 days was 93.3%. For same period, in samples I and II, same was observed to be only 50% and 65%. Solubilization (%) of LFs in term of COD\textsubscript{soluble} in sample II was 93.3%, whereas in control it was 14% only, which is 6.7 times less. Similar observations were made in samples I and III (Table 1). 

VFA profiles (Fig. 3) per kg of LF added in sample I, II and III showed similar trend as that of COD\textsubscript{soluble}. Gradual increase in VFA production was observed in sample I till 14\textsuperscript{th} day, whereas in samples II and III VFA production reached maximum on 8\textsuperscript{th} and 7\textsuperscript{th} day respectively. VFA produced per kg of LF in sample I was 21.84 g, whereas in samples II and III it was 46.8 g and 30.72 g respectively on 8\textsuperscript{th} day. Decrease in VFA after peaking on 7\textsuperscript{th} and 8\textsuperscript{th} day is due to onset methanogenic activity. Similar observations are reported for pretreatment of waste activated sludge by biological hydrolysis wherein a VFA concentration of 762 mg/l was obtained when a COD concentration of 6620 mg/l was present.

pH of LF samples after addition of inoculum were 12.1, 11.2 and 10.8 for samples I, II and III respectively. At the end of solubilization period of 14 days, pH was found to be 9.5, 7.9 and 7.5 (Fig. 4). Similar pH
reduction due to hydrolysis and acidogenesis of LF is reported\(^\text{10}\).

**Acidification Efficiency**

Acidification efficiency is a ratio between VFA present in reactor to theoretical VFA of substrate\(^\text{11}\). Theoretical VFA was calculated from empirical formula\(^\text{12}\) of LFs as \(\text{C}_4\text{H}_{11}\text{NO}_2\) and theoretical COD is 1.49 time of VS\(^\text{13}\).

\[
\text{Acidification (\%)} = \frac{\text{VFA}_{\text{produced}}}{\text{VFA}_{\text{theoretical}}} \times 100 \quad \text{(1)}
\]

where, 
- \(\text{VFA}_{\text{theoretical}}\) = theoretical VFA of substrate added,
- \(\text{VFA}_{\text{produced}}\) = total VFA produced from solubilization process (VFA conc x volume of reactor)

Acidified COD is equal to 100% and the maximum methane COD, which is generally 97% biodegradable COD. Acidified COD is nearly equal to maximum “methane COD” in most cases. It is assumed that potential methanization of a wastewater COD is approximately equal to acidification as reported\(^\text{14}\). Acidification efficiencies on solubilization for different mixing ratios were estimated (Fig. 5). Maximum acidification efficiency of 52% and 38% were obtained on 8th and 7th day for samples II and III respectively. After obtaining maximum acidification efficiency, VFA concentration dropped due to initiation of methanogenic activity. In sample II, VS (1.2 g) was added as inoculum per 1 kg of LFs (moisture 90% and VS 80%), which was found to be more suitable ratio for solubilization of LF.

**Kinetics of Solubilization Rate**

Solubilization rate of organic residues follows first order kinetics relationship\(^\text{15,16}\) as

\[
-dC/dt = kC \quad \text{(2)}
\]

\[t = -\frac{1}{k} \ln \left( \frac{C}{C_0} \right) \]

where, 
- \(k\) = first order specific rate constant (day\(^{-1}\)),
- \(C\) = concentration of biodegradable particles at time \(t\) (g VS/l), and 
- \(C_0\) = initial concentration of particles at time zero (g VS/l).

Based on Eq. 2, solubilization rate data has been plotted (Fig. 6) and value of specific rate constant during solubilization of LF is obtained as 0.55 day\(^{-1}\).

Similar results are reported\(^\text{13}\) for food waste (0.24-0.47 day\(^{-1}\)).

**Effect of Thermo-Chemical Pretreatment (PT-TC) on Solubilization of Lime Fleshings (LF)**

PT-TC studies showed that solubilizations of LFs were 68.2, 73.8, 85.4, 88.5, 90.1 and 48% for samples pretreated with NaOH solution concentrations of 1, 2, 3, 4 and 5% and control respectively (Table 2). Similarly, COD\(_{\text{soluble}}\) of LFs were 69.1, 74.4, 86.3, 89.7 and 91.4 % for samples pretreated with KOH concentrations of 1, 2, 3, 4 and 5 % respectively. PT-TC of waste activated sludge\(^\text{9}\) also resulted in solubilization at 88% in the form of COD.

Before pretreatment, COD\(_{\text{soluble}}\) concentration in sample was 2500-2600 mg/l, probably due to dissolution of proteins in LFs under alkaline conditions. After pretreatment, COD\(_{\text{soluble}}\) concentration increased to 48546 mg/l and 49246 mg/l for samples treated with 5% of NaOH and KOH solutions respectively, indicating
Table 2—Effect of NaOH and KOH in thermo chemical pretreatment of limed fleshings

<table>
<thead>
<tr>
<th>Description</th>
<th>Control</th>
<th>NaOH, %</th>
<th>KOH, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before treatment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (T), mg/l</td>
<td>53880</td>
<td>53880</td>
<td>53880</td>
</tr>
<tr>
<td>COD (s), mg/l</td>
<td>2510</td>
<td>2574</td>
<td>2584</td>
</tr>
<tr>
<td>After treatment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (s), mg/l</td>
<td>25874</td>
<td>36746</td>
<td>39763</td>
</tr>
<tr>
<td>Solubilization of LF, %</td>
<td>48</td>
<td>68.2</td>
<td>73.8</td>
</tr>
<tr>
<td>VFA, mg/l</td>
<td>720</td>
<td>780</td>
<td>800</td>
</tr>
</tbody>
</table>

Weight of LFs, 1 kg; moisture, 83%; pH, 12.8; VS, 134.7 g/kg wet LFs

Table 3—Characteristics of solubilized limed fleshings (LFs) after PT-TC and PT-AI

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solubilized limed fleshings (LFs)</th>
<th>PT-TC</th>
<th>PT-AI</th>
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<tbody>
<tr>
<td>pH</td>
<td>11.2-12.1</td>
<td>7.5-8.8</td>
<td></td>
</tr>
<tr>
<td>COD\textsubscript{soluble}, g/l</td>
<td>38-50</td>
<td>37-50</td>
<td></td>
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<tr>
<td>VFA, meq/l</td>
<td>20-30</td>
<td>200-300</td>
<td></td>
</tr>
<tr>
<td>TKN, g/l</td>
<td>10-12</td>
<td>8-12</td>
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</tr>
</tbody>
</table>

Characteristics of Solubilized Lime Fleshings (LFs)

Solubilized LFs after pretreatment with alkali (PT-TC) and anaerobic inoculum (PT-AI) indicated (Table 3) that pH of LFs were: PT-TC, 11.2-12.1; and PT-AI, 8. Thus LFs are more suitable for further anaerobic treatment without any pH correction. VFA (12000-18000 mg/l) was higher in LFs with inoculum addition due to hydrolysis and acidogenic activities. No such activity was observed in thermo-chemical process.

BMP studies (Fig. 7), carried out on LFs after PT-TC (5% KOH and NaOH) and PT-AI treatment (sample II), indicated that cumulative volume of methane generated in initial 10 days was 85 ml for both fleshings pretreated with alkali, whereas in case of LFs pretreated with inoculums, methane (300 ml) showed three times increase. After 10 days, amount of methane generated was less in LFs pretreated with alkali. At the end of 20th day, volume of methane generated was only 180 ml and 380 ml for LFs pretreated with NaOH and KOH respectively. In inoculum treated LFs, amount of methane generated was 650 ml at the end of 20th day, which is a 3 fold increase when compared with LF pretreated with alkali. Thus methane generation with NaOH and KOH were 0.06 and 0.104 m\textsuperscript{3}/kg COD\textsubscript{total} respectively. Methane generation increased with PT-AI to a maximum methane production of 0.16 m\textsuperscript{3}/kg COD\textsubscript{total} added, which is 2.7 and 1.5 times higher than NaOH and KOH, respectively.

Conclusions

After PT-TC, solubilization of LFs was 90.1 and 91.4% with 5% NaOH and KOH respectively, whereas
LFs treated with PT-AI showed higher solubilization (93.3%) and higher VFA concentration (15600 mg/l) during same period for sample II. Corresponding VFA concentration for PT-TC showed only 1572 and 1807 mg/l with 5% NaOH and KOH respectively. Thus sample II (VS conc., 1.2 g) was effective in solubilization of LFs within 8 days and corresponding solubilization rate was found to be 0.55 day\(^{-1}\). LFs with PT-AI generated 0.16 m\(^3\)/kg COD total added, which was 2.7 and 1.5 times more than LFs pretreated with NaOH and KOH respectively. Thus maximum solubilization of LF can be obtained within 8 days. No pH correction is done before anaerobic digestion, and no energy or chemical is required for PT-AI and enhanced methane production.

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References