Anaerobic treatment of agricultural residue based pulp and paper mill effluents for AOX and COD reduction

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Received 20 December 1999; received in revised form 7 February 2000; accepted 19 March 2000

Abstract

Black liquor and bleach effluent from an agroresidue based pulp and paper mill were treated anaerobically to reduce their high chemical oxygen demand (COD) and adsorbable organic halide (AOX) contents. Addition of 1% w/v glucose yielded 80% methane from black liquor with concomitant reduction of COD by 71%, while bleach effluent generated 76% methane and produced 73 and 66% reductions in AOX and COD, respectively. In the absence of glucose, black liquor and bleach effluent produced only 33 and 27% methane with COD reductions of 43 and 31%, respectively.

Keywords: Anaerobic treatment; Methane generation; Adsorbable organic halides (AOX); Chemical oxygen demand (COD)

1. Introduction

India is a fibre deficient country and no single fibre is able to meet the growing demands of the paper industry [1]. The Indian paper industry therefore uses a variety of raw materials including wood, bamboo, agricultural residues and recycled secondary fibres (Table 1) [2]. The limited availability of forest based raw materials coupled with a consistently increasing demand for pulp and paper products has placed a great pressure upon forest resources. As a result, many paper mills are forced to use alternate non-wood raw materials such as agroresidues including bagasse, cotton stalks and linters, jute, kenaf, etc., which are abundant in an agricultural country.

The majority of the Indian agroresidue based mills are small, with an installed capacity of less than 30–40 tons per day (tpd). While larger paper mills (installed capacity > 50 tpd) have an infrastructure for recovery of chemicals from the spent liquor (sulphate pulping), it is economically non-viable for the smaller mills to operate such chemical recovery systems. As a result, all the small and several medium sized mills discharge their effluents, namely, black liquor and bleach effluent, containing high levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids, chlorinated compounds (measured as adsorbable organic halides, AOX), etc., directly into the receiving water bodies [3]. Considering that each ton of paper produced consumes nearly 200–350 m³ of water [4], it is not difficult to perceive the magnitude of pollution being caused to the receiving water bodies by discharge of these effluents. Various aerobic and anaerobic processes have been employed for the treatment of pulp and paper mill effluents [5–7], with anaerobic treatment being preferred over aerobic means. It has been realized lately that not only is anaerobic treatment a very cost-effective alternative, but it can also offer a payback on investment through generation of biogas, thus reducing electrical power consumption [8]. In this context, anaerobic treatment of black liquor and bleach effluent becomes significant for two primary reasons:

1. To reduce aquatic pollution produced by these effluents and

2. To co-generate energy from the organics (mainly lignin and lignin-derived compounds) inherently present in these effluents.
Table 1
Installed capacity, effective capacity, production and capacity utilization of different types of mills

<table>
<thead>
<tr>
<th>Mill category</th>
<th>Installed capacity (million tons)</th>
<th>Effective capacity (million tons)</th>
<th>Production (million tons)</th>
<th>Effective capacity utilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood based</td>
<td>1.44</td>
<td>1.11</td>
<td>0.95</td>
<td>83</td>
</tr>
<tr>
<td>Agro based</td>
<td>1.24</td>
<td>0.94</td>
<td>0.01</td>
<td>96</td>
</tr>
<tr>
<td>Wastepaper based</td>
<td>3.94</td>
<td>2.93</td>
<td>2.51</td>
<td>78</td>
</tr>
</tbody>
</table>

This study was undertaken to evaluate the response of black liquor and bleach effluent to anaerobic treatment. The effect of addition of an external carbon source on methane generation was also studied.

2. Materials and methods

2.1. Effluents

Black liquor and bleach effluent were obtained from a pulp and paper mill utilizing a mixture of bagasse, rice and wheat straw as raw material (courtesy of Indian Agro Paper Mills Association (IAPMA), New Delhi). Samples were collected in plastic cans and stored at 4°C.

2.2. Inoculum

The inoculum used was procured from a batch anaerobic reactor in operation in our laboratory at 37°C over the past 3 years. Prior to using the inoculum, its methanogenic activity was determined by chromatographic analysis. Only when the methane composition of reactor gas was 60% or more (indicating an active methanogenic consortium), was the inoculum used for seeding experiments using the effluents.

2.3. Anaerobic reactor

The experimental set-up is shown in Fig. 1. The reactor was carried out in 1-l aspirator bottles fitted with corks. A glass tube was fixed in the centre of the cork to which was fitted one end of a silicon tube. The other end of the tube was connected to the graduated limb of a manometric device. The gas produced in the system was collected by a water displacement method.

Two groups of reactors (control and experimental) were set up. Each contained black liquor or bleach effluent inoculated with active anaerobic inoculum (10% v/v). No glucose was added in the control group whereas in the experimental group glucose (1%, w/v) was used as a supplementary carbon source. All set-ups were maintained at a pH of 7.0 and a temperature of 37°C. Biogas was collected by puncturing the silicon tubing with a gas tight syringe and its composition determined by injection into a gas-liquid chromatograph.

2.4. Analyses

All analyses of untreated and anaerobically treated effluents were carried out according to standard methods [9]. Biogas composition was estimated using a gas chromatograph (AIMIL-NUCON Series 5700, New Delhi, India) fitted with a thermal conductivity detector (TCD). A 6-ft long Porapak Q stainless steel column was used with oven, injector, and detector temperatures set at 40, 60 and 60°C, respectively, and hydrogen was used as the carrier gas. The instrument was calibrated using a mixture of 50% methane and 50% carbon dioxide (Spancan, Spantech Products, UK). Samples (0.5 ml) were withdrawn from all the reactors at 24-h intervals using a 1-ml gas tight syringe (Hamilton, USA) and injected into the gas chromatograph for determination of biogas composition.

COD was measured in accordance with the dichromate open reflux protocol suggested in standard methods. Chlorinated organic compounds were measured as adsorbable organic halides (AOX) using an AOX analyzer (Metrohm, Germany).

![Fig. 1. Schematic representation of aspirator bottle and biogas collection device.](image)
Table 2
Characterization of black liquor and bleach effluent from agroresidue based pulp and paper mill

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Black liquor</th>
<th>Bleach effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.8</td>
<td>8.0</td>
</tr>
<tr>
<td>Colour (platinum-cobalt units)</td>
<td>10 841</td>
<td>1473</td>
</tr>
<tr>
<td>Total solids (g/l)</td>
<td>31.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Total volatile solids (g/l)</td>
<td>17.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Total fixed solids (g/l)</td>
<td>14.1</td>
<td>2.0</td>
</tr>
<tr>
<td>Total suspended solids (g/l)</td>
<td>7.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Total dissolved solids (g/l)</td>
<td>24.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Dissolved volatile solids (g/l)</td>
<td>10.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Dissolved fixed solids (g/l)</td>
<td>14.0</td>
<td>1.2</td>
</tr>
<tr>
<td>COD (mg/l)</td>
<td>24 500</td>
<td>2500</td>
</tr>
<tr>
<td>AOX content (mg/l)</td>
<td>Not</td>
<td>32.2</td>
</tr>
<tr>
<td>Phosphorus (mg/l)</td>
<td>16</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 3
Effect of anaerobic treatment

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Final</th>
<th>% Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Untreated (effluent + inoculum)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black liquor</td>
<td>30 000</td>
<td>17 000</td>
<td>43</td>
</tr>
<tr>
<td>Bleach effluent</td>
<td>7400</td>
<td>5106</td>
<td>31</td>
</tr>
<tr>
<td>Treated (effluent + glucose + inoculum)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black liquor</td>
<td>38 400</td>
<td>11 000</td>
<td>71</td>
</tr>
<tr>
<td>Bleach effluent</td>
<td>4400</td>
<td>1400</td>
<td>66</td>
</tr>
<tr>
<td>AOX (Cl− mg/l)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleach effluent</td>
<td>32.2</td>
<td>8.6</td>
<td>73</td>
</tr>
</tbody>
</table>

3.2. Effect of anaerobic treatment

Methane production in both black liquor and bleach effluent of the control group was initiated only after 51 days (Table 3). However, once the methanogens had acclimated, they exhibited good growth. This indicates that although the nature of inhibition in the two effluents is different, lignin and ligninated compounds in black liquor and chlorinated compounds in mixed liquor, the degree of inhibition was similar. Moreover, the fact that the methanogens grew in the effluents once the acclimation period was attained, indicates that the inhibition afforded by these effluents can be overcome by the methanogens given sufficient time for acclimation. The reactors with glucose as carbon source took less time (38 days) to exhibit methanogenic activity since the partially acclimated inoculum of the control group was used as inoculum.

3.3. Effect of glucose on methane generation

Methane generation in the control group was quite small (Fig. 2), even insignificant, being 33 and 27% for black liquor and bleach effluent, respectively. On the other hand, in the experimental group, methane activity peaked at 80% after 50 days in black liquor supplemented with glucose while bleach effluent showed a maximum of 76% after 58 days. This signifies the need for supplementing the effluents with a readily assimilable carbon source rather than using highly recalcitrant lignin as the sole carbon source.

3. Results and discussion

3.1. Effluent characterization

Black liquor and bleach effluent were first completely characterized with respect to their various physicochemical constituents such as solids, phosphorus and AOX contents, COD, etc. (Table 2). The AOX content and COD values were much higher (in addition to other parameters) compared to their recommended discharge levels as listed in Minimum National Standards (MINAS), prescribed by the Central Pollution Control Board (CPCB), India [1]. It was not possible to determine the BOD since at the time of writing this paper there was no acclimated, aerobic seed available to perform the test.

![Methane generation with and without glucose](image-url)
3.4. Reduction in AOX and COD

COD was considerably reduced in both effluents, there being 71 and 66% reduction in COD of black liquor and bleach effluent, respectively, in the experimental group. Interestingly, AOX exhibited a very sharp decline of 73% from 32 to 8.6 g/l after 70 days. There have been few reports concerning the removal of AOX in bleach effluent from pulp and paper mills via anaerobic means [10–17]. For instance, Ferguson et al. reported AOX removal of 40–65% from kraft bleaching wastewaters [16] and Hagglund used a combination of aerobic and anaerobic treatments to achieve >65% AOX removal [17]. More attention has been paid to aerobic cultures, particularly white rot fungi [18–27]. For instance, 40–60% AOX was removed by Phanerochaete chrysosporium from bleach pulp effluents [23,24]. Similarly, Palleria and Chambers reported 52–59% AOX removal with Trametes versicolor [25], while Bergbaeber et al. [26] demonstrated 45% AOX reduction with the same fungus. More recently, Coriopriopsis subvermispora has been shown to remove 32% AOX and 45% COD from bleach kraft effluents [27], whereas Ali et al. using Saccharomyces cerevisiae in bleach effluent of agroresidue based paper mill could reduce the AOX and COD by 64 and 75%, respectively [28]. Ferguson attempted AOX removal by combining anaerobic and aerobic treatments [29]. There was 30–35 and 40–45% AOX reduction by aerobic and anaerobic methods, respectively, while a combination of the two was found to remove 50–55% AOX. Similarly, Rintala et al. experimented with a mixture of thermophilic aerobic and anaerobic microbes to treat kraft bleach effluents [30] and obtained 36–56% reduction in AOX levels. However, it is important to note that the majority of these studies involve utilization of highly specialized dechlorinating microbes, grown in optimum sterilized conditions in the presence of enriched medium. The economic viability of adopting such a strategy for treatment of a waste stream is highly questionable. Moreover, despite employing such sophisticated 'ideal conditions' approaches, AOX removal rates have not been shown to be significantly high, peaking at 60% on average. To the best of our knowledge, the reduction in AOX obtained in this very simple, unsterilized anaerobic system is the highest reported so far.

4. Conclusions

Both black liquor and bleach effluent from an agroresidue based pulp and paper mill responded well to anaerobic treatment. The time taken for both these effluents to commence methane production was the same indicating that through the nature of toxicity in the two effluents was different, both exerted a similar degree of inhibition to methanogenic bacteria. In the absence of glucose, which was used as a supplementary source of carbon, methane production was small whereas that produced with glucose as additional carbon source was significant. Moreover, methane production in black liquor and bleach effluent led to a considerable reduction in AOX and COD as well. This observation indicates that given suitable exposure time, methanogens are eminently capable of not only withstanding biorecalcitrant and bioinhibitory environments but also of thriving in them. However, the removal mechanism of AOX and the role of acclimated anaerobic consortium needs to be elucidated since it is still not clearly understood. The results of this study thus reinforce the fact that anaerobic treatment of agroresidue based pulp and paper mill effluents can be considered as a serious option not only for energy cogeneration but also as a means of significantly reducing some of the more important, albeit recalcitrant, objectionable parameters.

Acknowledgements

The authors are grateful to P.G. Mukundan, Secretary-General, Indian Agro Paper Mills Association (IAPMA), New Delhi, India for the supply of agroresidue based pulp and paper mill effluents. The cooperation extended by Dr Makhijani and B.K. Jakhmola, of the Central Pollution Control Board (CPCB), New Delhi, India, for AOX analysis is also acknowledged.

References


