Anaerobic Treatability of Straw Spent Liquors-A Potential Alternative For Environmental Management

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ABSTRACT

The majority of small paper mills based on agricultural residues are operating without chemical recovery system and they discharge Black liquor as effluent which is the major source of pollution in these mills and complience with environmental norms is a challenge before these mills.

The anaerobic treatability of black liquor from wheat & rice straw was evaluated by UASB process. The maximum COD reduction in wheat straw was 55-60% at VLR 6.0 kg. COD/m³.d. and at VLR 10.0 kg. COD/m³.d, the reduction in COD was 42%. While in rice straw the maximum COD reduction was 45-50% at VLR 6.0 kg. COD/m³.d., but the reduction in COD reduced to 34-35% at VLR 10 kg. COD/m³.d. The wheat straw black liquor is easier to treat compared to rice straw black liquor. The sludge/ active biomass washout was observed in rice straw beyond VLR 10 kg. COD/m³.d. This paper highlights the study carried out on adaption of UASB technology for anaerobic treatment.

INTRODUCTION

India has a large number of agro based pulp & paper mills below the production capacity of 60 t/day and they contribute about 36% of total production of paper & boards. The generation of pollution loads from these mills is much higher than the big mills mainly due to absence of chemical recovery system and a large amount of organic & inorganic mass is discharged into the waste water. On the basis of raw materials used, it is estimated that in integrated mill, roughly 46% is burnt in recovery furnace, 4.5% ends up as solid waste, 4.5% goes into waste water as dissolved solids and 3% goes as suspended solids into waste water. While in small mills without recovery system, around 9% goes as solid waste and about 55% contains organic substances which discharges as effluent (Kulkarni, A.G.). In big integrated mills, the major source of pollution is bleach plant effluent which contributes about two third of BOD and 80-90% of coloured substances. However in small pulp mills, the major pollution is from pulping spent liquor which shows about 90% of colour and 50% of COD is due to lignin & lignin derivative compounds.

In addition to pulping spent liquor, these mills in absence of chemical recovery and high cost of alkali, use less chemical at cooking stage, consequently higher residual lignin in pulp and subsequently higher chlorine consumption (10-25%) in bleaching of pulp which ultimately lead to the formation of more toxic chloro-compounds in bleach plant effluent.

Due to increased pressure from environmental regulating authorities, there is a tremendous pressure on these mills to reduce the pollution loads in order to achieve the stipulated discharge standards. These mills are facing the environmental problems and are forced to modify or to put the adequate facilities for effluent treatment. In this context, the mills specially new installation are switching over/looking to the use of secondary fibre. The fresh water consumption and pollution load from waste paper based mills are

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Table-1

Characteristics & Pollution loads of Effluents from pulp & paper mills (Kulkarni, A.G.)

Particulars	Integrated pulp & paper mills	Newsprint mills	Agorbased small paper mills	Waste paper based mills
- Raw material	Bamboo Hardwood	Bamboo Hardwood	Rice straw wheat straw Bagasse	Waste paper
- Waste water m^3/t	230-250	200	200-380	70-150
- pH Pollution load kg/t paper	6.0-9.0	7.2-7.3	6.0-8.5	6.0-8.5
- Suspended solids	100-150	100	90-240	50-80
- BOD_5	35-50	45	85-270	10-40
- COD	150-200	135	500-1100	50-90

comparatively lower. **Table-2** shows the water consumption & pollution loads in waste paper based mills. (Kulkarni, A.G.).

Present Practices of Waste Water Treatment in small paper mills & alternative:

In agro based mills without chemical recovery system, the pulping spent liquor is the major contributor to the pollution load due to the presence of lignin which is almost a biorefrectory compound in nature. The present practice of aerobic treatment of effluent suffers from major disadvantage of high operational cost and requirement of higher energy for aeration and chemicals (nutrients). The another disadvantage is the high production of biosolids (0.5 kg/kg.BOD removed) resulting the solid waste disposal problems. Due to these problems, especially the small mills are forced to look into alternate economically viable treatment technologies in order to achieve the discharge standards.

Anaerobic treatment may be an alternative approach to treat the effluents. Due to development of high rate Biomethanation and good understanding of microbiology and process insight, anaerobic process has been recognised as a proven technology to treat the complex industrial effluents including pulp & paper mill effluents. Since it has several advantages over aerobic process like generation of methane rich biogas, less requirement of energy, nutrients and also less biosolids generation. A comparative account of anaerobic & aerobic system is shown in **Table-3.** The number of full scale anaerobic treatment plant are already in operation in recycled fibre, paper & boards etc. But the use of this process to treat the chemical pulping spent liquor is still limited due to the presence of lignin compounds.

The present paper highlights the possibility of anaerobic treatability of soda pulping spent liquors from wheat & rice straw which are the main fibrous raw materials used by small paper mills.

Process selection

Different anaerobic treatment systems are available for the treatment of industrial effluents. The

Table-2

Water Consumption & Pollution Load in Waste Paper based Mills

Process	Fresh watr m^3/t	BOD kg/t	COD kg/t	Suspended solids kg/t
I. Waste Paper based mills *				
- Mechanical treatment	1	15	40	50
- Deinking by flotation	10	25	55	150
- Deinking by washing	90	30	65	150
II. Agro based Mill	300	250	1090	200

* The suspended solids in category I includes rejects & ink-sludges.

Table-3		
Anaerobic-Vs-Aerobic Digestion		
Particulars	**Anaerobic**	**Aerobic**
Bacterial growth	Slow	Fast
Carbon balance	95% - CH_4+CO_2	50% - CO_2
	5% - Biomass	50% - Biomass
Energy balance	90% - Retained in CH_4	60% - Biomass
	5% - Biomass	40% - Heat prodn.
Energy input for aeration	No	Yes
KWH/ tonne COD reduction	(15)	(1100)

main anaerobic technologies are contact or Anamet system, anaerobic filter, anaerobic fluidised bed system & UASB system. Out of different system, mainly contact & UASB process are in commercial operation to treat industrial effluents, including pulp & paper mills. The UASB process is becoming more attractive due to some advantages over contact process. In UASB process, retention of high active biomass results in to achieve high organic loading and more resistance to shock loads due to variation in process. In present study, UASB system was selected to evaluate the anerobic treatability of pulping spent liquor from rice & wheat straws.

MATERIALS & METHODS

Pulping spent liquors were generated in laboratory by cooking of wheat & rice straws with soda employing the conditions followed in the mills.

Cooking Conditions:	Wheat Straw	Rice Straw
NaOH, applied %	16	10
Bath ratio	1:5	1:5
Temperature, ^0C	165	140
Time at Max. Temp, mins	120	60
Screened pulp yield, %	41.3	--
Pulp Kappa No.	21	18

The soda pulping spent liquors were analysed for various pollution parameters. The results are given in **Table-4.**

Anaerobic Biodegradability

The pulping spent liquors from wheat and rice straws were evaluated for their anaerobic biodegradability by using standard batch fed bioassays. The bioassays were carried out at 30^0C using unadapted anaerobic sludge. The results are as follows:

Particulars	Biodegradability, %
Wheat Straw -	60.3
Rice Straw -	53.8

RESULTS & DISCUSSION

Anaerobic treatment by UASB process:

(i) Wheat straw pulping spent liquor:-

The upflow anaerobic sludge blanket (UASB) pilot reactor (30 lit. capacity) was seeded with flocculant anaerobic sludge collected from a full scale UASB sewage treatment plant. The characteristics of sludge are given below:

Table-4		
Characteristics of Pulping Spent Liquors		
Parameters	**Wheat Straw Black Liquor**	**Rice Straw Black Liquor**
pH	11.04	10.40
Suspended solids, mg/1	900	675
Total solids, g/1	102	83.00
COD, mg/1	93258	71600
BOD_5 mg/1	28750	17710

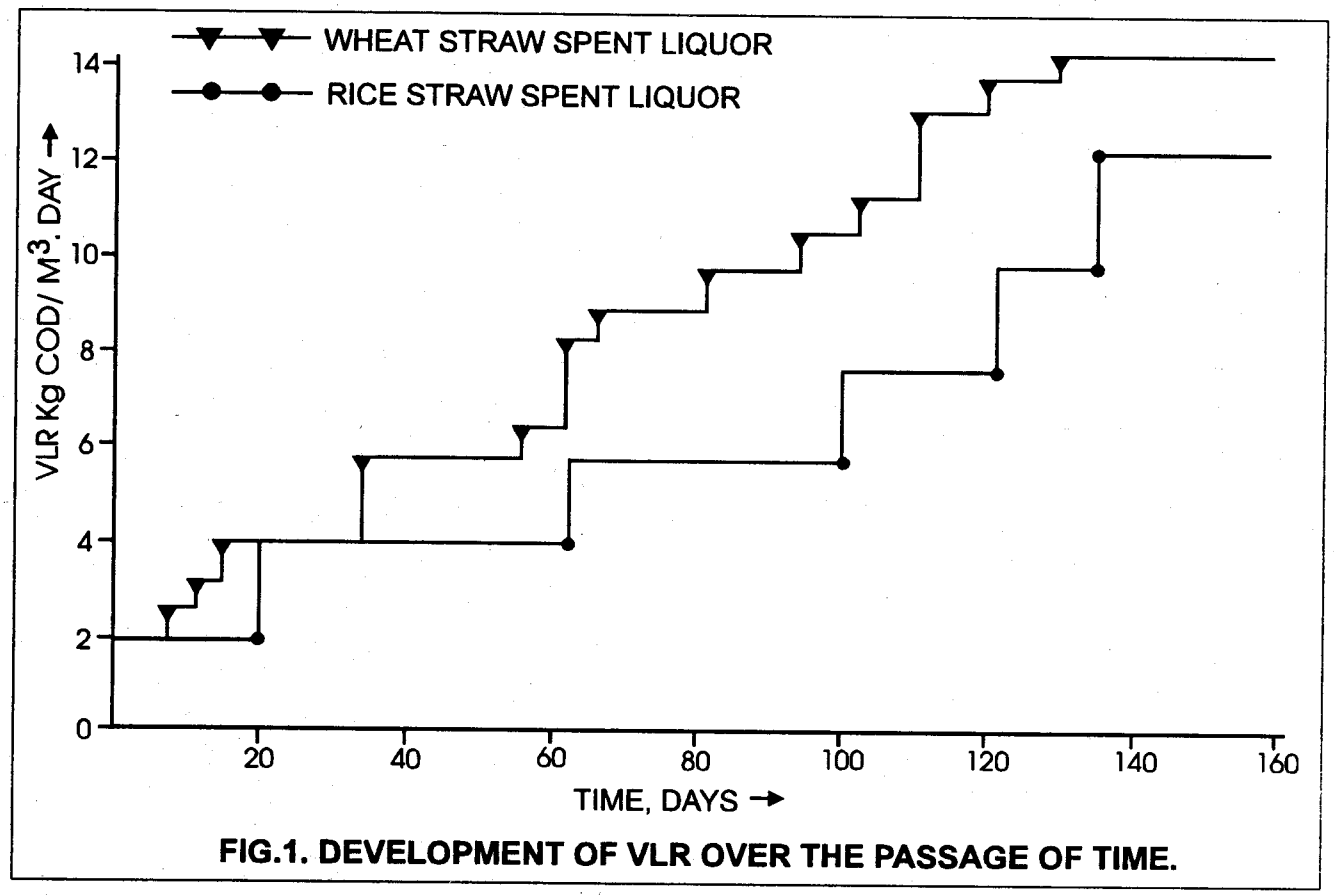

FIG.1. DEVELOPMENT OF VLR OVER THE PASSAGE OF TIME.

T.S.S., g/l	104.05
V.S.S., g/l	62.43
Ratio of VSS on TSS basis, %	60.00

The following treatment conditions were maintained through out the treatment period.

pH	-	7.0 ± 0.5
Temp., ^{0}C	-	37 ± 2
Hydraulic Retention Time (HRT), hr	-	24

The essential macro nutrients (nitrogen & phosphorous) & micro nutrients were supplied for proper growth of bacterial biomass. Alkalinity was maintained by adding sodium bicarbonate to buffer the eventual accumulation of volatile fatty acids in the system. The hydrochloric acid was used to adjust the pH of raw influent.

The UASB reactor was operated by continuous feeding of diluted black liquor and volumetric loading rate (VLR) was kept at 2.0 kg. COD/m^3.d. The VLR was increased gradually in small fraction from 2.0 to 14 kg.. COD/m^3.d. Over the period of five months. The development of VLR is shown in **Fig. 1.**

The performance of reactor was monitored regularly by analysing influent and effluent for pH, VFA, alkalinity, TSS., COD and BOD_5. The performance of reactor at different VLR is shown in **Table-5 & Fig. 2.**

The results (Table-5) indicate that the maximum COD removal achieved was 50-62%, upto VLR 6.0 kg. COD/m^3.d. with corresponding BOD_5 removal of 81%. When VLR was increased, the COD removal efficiency dropped and performance was more or less stabilised with COD removal of 42-45% at VLR 10.0 kg. COD/m^3.d. After stabilising the performance, the VLR was again increased up to 14 kg. COD/m^3.d. The reduction in COD & BOD dropped to 22-25% & 29% respectively at VLR 14 kg. COD/m^3.d. and no further improvement in COD reduction was observed even after two weeks of continuous operation.

Table-5			
COD & BOD removal for Wheat Straw Spent Liquor at different VLR			
Sl. No.	VLR kg COD/m^3/day	COD reduction %	BOD_5 reduction %
1.	2.0	50	--
2.	3.0	55	--
3.	4.0	51	--
4.	6.0	62	81
5.	8.5	37	--
6.	10.0	42	--
7.	12.0	21	49
8.	14.0	25	29

Influent and effluent were also analysed for total suspended solids and about 41.5% reduction in TSS was observed at VLR 8.0 kg. COD/m^3.d. while the reduction in TSS was dropped to 19% at VLR 14 kg COD/m^3.day.

(ii) Rice straw pulping spent liquor

The anaerobic treatability of rice straw pulping spent liquor was evaluated by maintaining similar treatment conditions as in wheat straw. The efficiency of the process was evaluated upto VLR 12.0 kg. COD/m^3.d. The results of COD & BOD_5 removal are given in **Table-6** and **Figure-2.**

The results given in Table-6 show that the maximum reduction in COD & BOD achieved was 45-50% and 80% respectively at VLR 6.0 kg. COD/m^3.d. while at VLR 10 kg. COD/m^3.d., the reduction in COD dropped to 34-35%. The VLR was further increased to 12 kg. COD/m^3.d. and experiment was continued to observe any improvement in COD removal, but no improvement in COD reduction was observed. The influent and effluent were analysed for total suspended solids. The results of T.S.S. at different VLR are given in **Table-7.**

The results indicate that the concentration of T.S.S. in effluent was higher than influent, which shows the sludge washout at higher VLR i.e. 12 kg. COD/m^3.d. The washout of sludge and low COD reduction in rice straw pulping spent liquor may be due to presence of fines, colloidal nature of lignin and may be due to high amount of silica, which may have the adverse effect on sludge quality.

Biogas generated was analysed for methane content by using orset apparatus. The methane content analysed was 80-84% and CO_2 was 16-20%. The biogas production was in the range of 0.30-0.35m^3./kg. COD removed.

CONCLUSIONS

- The laboratory studies carried out reveal that pulping spent liquors diluted to 8-10g COD/1 can be treated anaerobically to an appreciable extent but treatment efficiency decreases at higher concentrations.
- The maximum COD reduction in wheat straw black liquor achieved was 55-62% at VLR 6.0 kg. COD/m^3. while at VLR 10.0 kg COD/m^3.d. the reduction in COD was 42%.

Table-6			
COD & BOD removal for Rice Straw Spent Liquor at different VLR			
Sl. No.	VLR kg COD/m^3/day	COD reduction %	BOD_5 reduction %
1.	2.0	50	80
2.	4.0	45	80
3.	6.0	45	--
4.	8.0	41	--
5.	10.0	34	83
6.	12.0	20	50

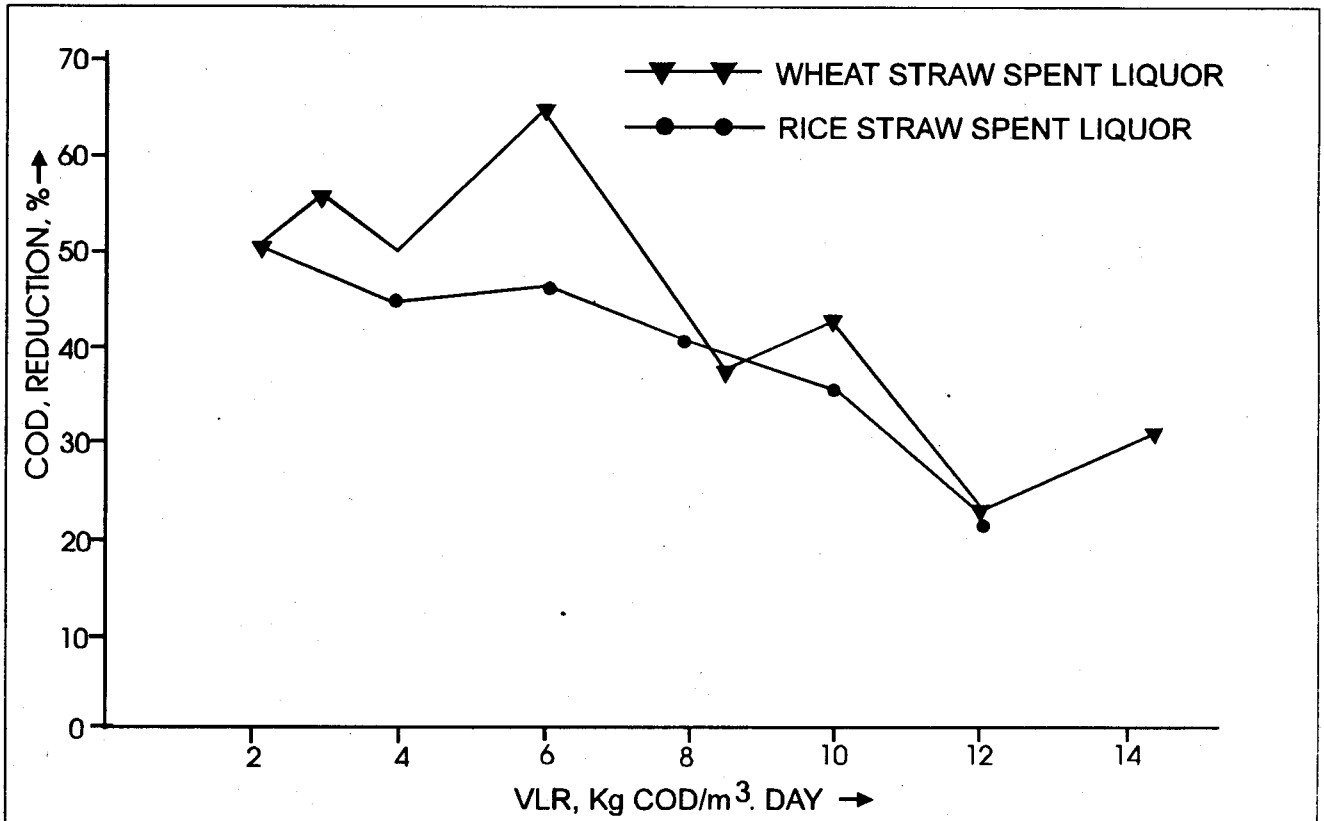

FIG.2. COD Removal Efficiency For Wheat & Rice Straw Soda Pulping Spent Liquor at Different VLR.

- The maximum COD reduction in rice straw black liquor achieved was 45-50% at VLR 6.0 kg/m³.d. while at VLR 10kg. COD/m³.d., the reduction in COD was reduced to 34%.

- Wheat straw pulping spent liquor is easier to treat anaerobically even at higher COD concentration compared to rice straw.

- In rice straw, the sludge washout was observed beyond VLR 10kg. COD/m³.d., the sludge washout may be due to presence of silica & fines in rice straw pulping spent liquor.

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Table-7

Results of suspended solids at different VLR in Rice straw spent liquor

VLR kg COD/m³. d.	Influent mg/1	Effluent mg/1	Reduction, %
2.0	500	160	60
4.0	800	300	63
8.0	500	400	20
12.0	600	1300	--

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ABBREVIATION

BOD - Biochemical Oxygen Demand

COD - Chemical Oxygen Demand

HRT - Hydraulic Retention Time

TSS - Total Suspended Solids

UASB - Upflow Anaerobic Sludge Blanket

VFA - Volatile Fatty Acids

VLR - Volumetric Loading Rate

VSS - Volatile Suspended Solids