New Trends in Addressing Environmental Problems in Small Mills

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ABSTRACT:-- With changing requirement for environmental conditions, the trends in environmental management have undergone significant changes. The combination of anaerobic treatment followed by conventional aerobic systems are becoming popular, by virtue of the selective biodegradability and possibility of bioenergy recovery. Pulp and paper mill effluent, particularly from those mills, which do not have chemical recovery unit discharge effluents with high concentrations of biorefractory materials and anaerobic treatment followed by aerobic treatment has definite advantages. This paper highlights some of the approaches made in this direction, particularly the need for seggregation of biorefractory materials and behaviour of different biological systems towards effluents carrying different organic & inorganic substrates.

INTRODUCTION

The pulp and paper Industry as such is essentially a chemical process industry with a distinctive impact on environment. Pollution associated with the pulp industry is dependent on the process applied & end products. Small size agro based mills; which have come up in early 70's did not have any legislation for discharge characteristics of waste water. These mills due to their size constraint are unable to instal an economically viable chemical recovery system, thereby loosing large quantities of organic biomass through spent pulping liquor and at the same time creating severe pollution problems. This resource drainage on National level have been estimated to be approx. 1.0 million tonnes equivalent of coal per annum. Apart from resource drainage it be comes a formidable task for these mills to comply with environmental regulations.

Anaerobic treatment of industrial waste water has, of late received a lot of attention. Many full scale treatment plants have been installed. Lower energy requirement, relatively low operating costs and the production of useful energy as by product in the form of methane gas offer additional advantages. Additionally, anaerobic treatment systems reduce considerably the volume of excess sludge produced due to low cell yields of anaerobic bacteria. The low excess sludge production makes anaerobic treatment methods particularly attractive since waste sludge disposal is becoming major problem for aerobic treatment systems. The low nutrient requirement of anaerobic bacteria is also an advantage in the treatment of nutrient deficient waste water from pulp & paper mills.

Despite all above advantages, the most significant drawback, which have hampered the wide spread application of anaerobic system for treatment of pulp mill effluents to desired efficiency levels particularly in agrobased mills has been the quality of the substrate i.e. spent pulping liquor which has not been properly understood by the equipment manufactures, technologists & scientists. As these liquors essentially contain large quantities of biorefractory organics like lignin and its derivatives

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which restrict to achieve the desired treatment efficiency of the biological system. Central Pulp & Paper Research Institute, in last 10 years of research has concentrated its efforts to study the nature of black liquors generatd in these pulp mills and the efficient ways of handling these liquors from view point of efficient resource recovery & environment. The present paper highlights new trends in tackling the environmental problems for small agro based mills by way of lignin removal from spent liquors and its impact on biomethanation process in terms of pollution loads.

DISCUSSIONS

Table-1 shows typical pollution loads in terms of COD & suspended solids in different processes of pulp & paper mill effluents. From the above data, it is clearly evident that the major pollution is contributed by agrobased mill. The agro based paper mills accounts for about 40% of the total paper production in this country.

Table-1

Typical pollution loads in different process water in Pulp & Paper Industry

Process	Water consumption (m^3/adt. pulp or paper)	COD (kg/adt. pulp)	SS (kg/adt. Paper)
Wet debarking	5-25	5-20	NR
Groundwood-pulping	10-15	15-32	NR
TMP			
Unbleached	10-30	40-60	10-40
Bleached	10-30	50-120	10-40
CTMP			
Unbleached	10-15	70-120	20-50
Bleached	10-15	100-180	20-50
NSSC Kraft			
Unbleached	40-60	40-60	10-20
Bleached	60-90	100-140	10-40
Ca-sulfite			
Unbleached	80-100	NR	20-50
Bleached	150-180	120-180	20-60
Mg sulfite			
Unbleached	40-60	60-120	10-40
Papermaking	10-50	NR	NR
Agrobased small paper mill soda	200-250	1000-1100	50-100
Kraft paper mill	150-200	250-300	--

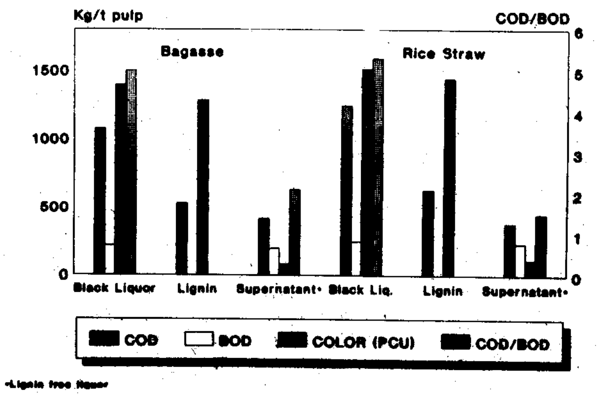
NR.Not reported in refrences.adt. air dry tonns

ANAEROBIC DEGRADIBILITY OF ORGANIC MATTER & POLLUTION LOADS IN SMALL MILLS

Thus, magnitude of pollution largely depends upon the raw material used, pulping process employed & extent of recyling of black liquors. The spent pulping liquor in an agrobased mills typically constitutes over 70% of organic matter in the form of carbohydrates, degraded orgnic acids & lignin

Fig.-1 shows the pollution loads in agrobased

FIG.1 POLLUTION LOADS OF BLACK LIQUOR AND ORGANICS



mills employing bagasse & rice straw as raw materials. It is clearly seen from the Fig. that around 50% of the COD is only biodegradable which mainly is derived from carbohydrates & degraded organic acids. The remaining COD contributed by lignin is apparently non biodegradable, thus limiting the treatment efficiency in any biological system.

LIGNIN AS BIOREFRACTORY MATERIAL

Lignin & its derivates contribute to nearly 50% of the total organic matter. Due to its highly complex structure, it has become a major component of concern. Over 85% of lignin due to its large polymeric structure, so called high molecular weight (HMW) fraction, is not only biorefractory but some times also acts as recalcitrants/ bioinhibitory subbiological treatment systems. Considering that the majority of the lignins belonged to high MW fraction, poor COD elimination & little or no color removal are observed during anaerobic treatment of complex pulp & paper mill effluents.

SEPARATION TECHNIQUES FOR LIGNIN REMOVAL & ITS STATUS

The many techniques for lignin removal from black liquor are reported. The common ones cited in the literature are :

Ultrafiltration

Ultrafiltration has been reported as one of the techniques for lignin separation. However, studies conduted at CPPRI in the last couple of years has proved that lignin removal from black liquor by ultrafiltration is not a techno-economically viable process due to its high energy requirement and non availability of indigenous membranes resulting in high capital and operating cost.

2. Activated Carbon

Like ultrafiltration, activated carbon does not selectively remove just the specific compounds of interest, which means that the carbon is quickly exhausted. Thereby making it a cost prohibitive technique for lignin removal.

3. Chemical Precipitation

There are various methods to bring about lignin precipitation in black liquor which are CO_2 precipitation, precipitation with inorganic/organic coaugulant and acid precipitation. Among various chemicals used during chemical precipitation, lowering of pH with mineral acid or in combination of organic acid has been found to be effective due to technoeconomic reasons. Although precipitation of lignin in wood based liquor has been practiced in various parts of the world, but its separation specifically from agro based liquors has always been a problem when we think of its further treatment by anaerobic means. Considering number of limitations of anaerobic bacteria in biomethanation process like inhibitory and toxicity effects of ionic concentration, all measure have been taken to optimise the conditions in respect of inorganic/organic ionic concentrations not to exceed the limits to avoid any toxicity effect and on the other hand, the portion of lignin macromolecules which are recalcitrant & responsible for high COD & colour are removed without affecting further processing of the liquor for biomethanation.

EFFECT OF LIGNIN REMOVAL & ITS OVERALL IMPACT ON BIOMETHANATION PROCESS

Attempts for pretreatment of effluent from agro

Table-2

Lignin precipitation studies on mills spent pulping liquor in an agrobased mill

Particulars	Sample No. 1	2	3	4
Initial pH at 25°C	9.0	9.0	9.0	9.0
Final pH at 25°C	4.5	4.1	3.9	3.95
Mineral acid requ. kg/m³	6.0	7.5	8.9	6.5
Organic acid requ. kg/m³	--	--	--	2.6
% Lignin removal	15.1	36.6	40.7	58.0
% COD removal	21.0	28.0	38.9	29.0
Sludge volume, %	15.0	20.0	28.0	30.0

Table-3

Impact of lignin removal on high rate biomethanation

	Original spent liquor	Original spent liquor after anaerobic digestion	Spent liquor after lignin removal	Liquor after lignin removal subject to biodegradati
pH	8.5	6.9	4.1-6.8	6.8
T.D.S, g/l	49	--	39	--
Lignin, g/l	15.9	13.9	7.9	7.1
% Lignin removal	--	--	50.0	--
COD, g/l	45	24	30	13
% COD removal	--	48	--	73
BOD, g/l	11.8	--	10.9	--
% BOD removal	--	70	--	83
Biogas prodn. m3/kg COD ruduced	--	0.32	--	0.35
Energy requirement during secondary aerobic treatment, kWh/tp to achieve desired BOD level	--	160	--	90

based mills by precipitation of lignin and its separation (partial) have been made so as to make the resulting effluent amenable for anaerobic treatment. Table-2 shows the results of lignin precipitations studies and its effect on COD removal efficiencies conducted with one of the spent liquor from agro based mills employing alkaline sulphite pulping.

From the data shown in Table-2 it is evident that lowering of spent liquor pH by mineral acids and its combination with organic acids could result in 40-50% of lignin removal with simultaneous reduction in COD of supernatant liquor at optimized conditions of pH and temperature.

The resultant supernatant liquor after partial removal of (HMW) lignin was subjected to bioassy test to predict the biodegradation efficiencies in anaerobic systems. The results are shown in Table-3.

The data shown in Table-3 indicated that partial removal of lignin at optimized pH level could help in partial removal of COD to extent of nearly 40%.

This is the portion of lignin removed which is all HMW lignin and is biofractory and recalcitrant. COD reduction efficiencies of the liquor when subjected to biomethanation process is also improved from 48% to 73%. In this way the overall loading on secondary treatment by ASP is liable to be reduced in terms of input chemicals and energy. It will further be possible to achieve values of pollution parameters like BOD and COD nearer to that specified by concerned authorities.

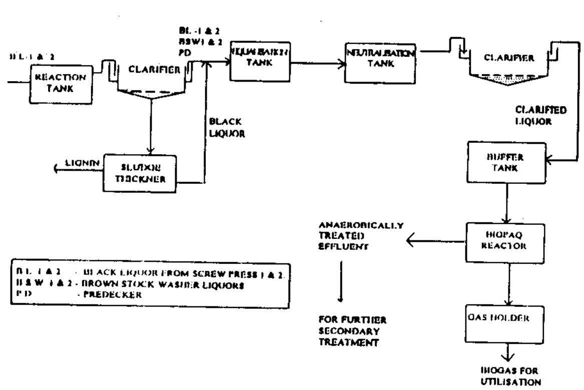


FIG. 2 PROPOSED PROCESS FLOW DIAGRAM OF BIOPAQ SYSTEM WITH MODIFICATIONS

Configuration of treatment in future installations is shown in Fig.-2.

EXPERIENCE OF SOME INHIBITORS LIKE SILICA & SULPHUR COMPONENTS DURING COMMISSIONING OF PILOT/DEMO BIOMETHANATION PLANT

During commissioning of trials in pilot plant & commercial demo biomethanation plant, inhibition due to presence of silica & sulphur components (In case of mill employing sulphite process) has been experienced.

During few months of operational experience, the activity of the sludge has been found to be adversely affected where concentration of SO_3^{2-} exceeds the limit i.e. 100 mg/l. 50% inhibition has been reported at 125 mg/l of SO_3^{2-} concentration. Silica has also been found to have an adverse effect on activity of sludge which when entered into reactor, may go on building in the sludge, sometimes may form coating on the methanegens. Experiments are in progress in order to get a better understanding of the inhibiting factors.

CONCLUSIONS

1. Looking into the various advantages, biomethanation process appears to be a promising route for treatment of pulp mill effluents from agrobased mills.

2. For mills which can not afford to go for chemical recovery the bioenergy recovery through above route will supplement partial energy requirement while taking care of 50% of pollution loads in terms of COD.

3. Partial separation of HMW lignin from spent liquors which otherwise behaves as biorefractory and recalcitrant material could further improve efficiency of biomethanation process in respect of COD and color to a greater extent. The partial separation of lignin may have to be an integral part of biomethanation process in future installations.

4. With the setting-up of demo biomethanation plant under UNDP/GEF assisted MNES programme agro based paper mills may have an alternative to treat black liquor laden waste water.

REFERENCES :

1. Lettinga, G., Field, J.A., Sierra-Alvarez, R. Van Lier J.B. and Rintala, J (1990). Future perspectives for the anaerobic treatment of forest industry wastewaters. Proc.3rd. IAWPRC Symposium on Forest Industry wastewaters, Tampere Univ. Technology, Tampere, Finland, June 5-8.

2. Rinzema, A and Lettinga' G. (1988). Anaerobic treatment of sulfate-containing waste water. Biotreatment syst. 3:65.

3. Ferguson, A.M.D. Conrod, K.G. and Frenette, J.R. (1988). On site anaerobic treatment proves higher design loading rate at Lake Utopia Paper Limited. Proc. 43rd. Purdue Industrial Conference, Lewis Publishers Inc., Chelsea, Michigan. pp. 689-697.

4. Habets, I.H.A. & de Vegt. A.I. (1990). Anaerobic treatment of Bleaching TMP and CTMP effluent in the BIOPAQ UASB system. Proc.3rd. IAWPRC Symposium on Forest Industry Wastewaters, Tampere University of Technology, Tampere, Finland, June- 5-8.

5. Collberg, P.J. (1988). Anaerobic microbial degradation of cellulose, lignin oligolingnols, and monoaromatic lignin derivatives. In: Biology of Anaerobic Microorganisms. A.J.B. Zehnder (Ed)., John Wiley and Sons, Inc., N.Y. USA. pp. 333-372.

6. Schink, B. (1988). Principles and limits of anaerobic degradation: Environmental and technological aspects. In: Biology of Anaerobic Microorganisms, J.B.Zehnder (Ed)., John Wiley and Sons, Inc., N.Y. pp. 771-846.

7. Holliger, C. Stams, A.J.M. and Zehnder, A.J.B. (1988). Anaerobic degradation of recalcitrant compounds. In: Anaerobic Digestion 1988, E. R.Hall and P.N. Hobson (Eds)., Pergamon Press, N-Y. PP. 211-223.

8. Kulkarni, A.G; "Biomethanation Technology as practices in Development Countries", Course Manual of Training Programme on Development of Biomethanation Process for Pulp & Paper Mill Wastes" March 18-29, 1996.

9. Abha Gupta, "Lignin Removal Process" An Integral Part of High Rate Biomethanation Process, Course manual of Training Programme on Development of Biomethanation Process for Pulp & Paper Mill Wastes" March 18-29, 1996.