Membrane Filtration of Non-Wood Spent Liquors-An Emerging Tool For Environmental Management in Pulp & Paper Industry

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ABSTRACT

Membrane filtration (Ultrafiltration process) initially developed for the treatment of bleach plant effluents (1) is now finding its place in the treatment of spent pulping liquors. The process was conceived way back in early 80's but the initial studies did not give encouraging results. The improved understanding of the chemical nature of spent pulping liquors, particularly the molecular chemistry, has given increased hope for adoption of this technique by way of seperation of COD rich high molecular weight fraction of lignin.

Extensive studies have been carried out at CPPRI employing DDS-lab scale membrane filtration module. The studies have revealed that black liquor from non-woody raw materials like bagasse & straws containing complex organic substances, were effectively processed through membrane filtration. The studies included characterisation of spent pulping liquor for molecular properties, membrane filtration employing various molecular weight cut off membranes & detailed analysis of each fraction for chemical & pollutional parameters. Some studies were conducted at mill site and the results have indicated the COD reduction efficiencies to the extent of 45-50%. The resultant permeate, of low molecular weight fraction stream carry high proportion of carbohydrates i.e. 60% as against less than 40% in original spent pulping liquor and of these more than 90% were biodegradable in biological treatment systems both aerobically & anaerobically. The studies have given clear indication that by maintaining proper pH level the separation is highly effective, which leaves different options for the paper industry like removal of high molar mass lignin through ultrafiltration followed by biomethanation. The combination of ultrafiltration & biomethanation process followed by the secondary treatment by aerobic means should facilitate in achieving the tolerance limit specified by pollution Control authorities. However this technique needs to be tested on pilot scale & efforts are made to upscale the lab scale research to pilot scale research.

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INTRODUCTION

Current strategies to decrease environmental impact from industrial activities emphasize waste prevention & reutilization/recycling. The increased concern over the environmental impact of the discharges from Indian Pulp & Paper Industry, specifically from small agro based mills have led the environmentalists & technologists to give a serious thought to tackle the problems in a techno-economically viable & ecofriendly manner, since the small mills in absence of a viable chemical recovery system, are forced to discharge their black liquor in to recipient stream which not only creates severe problems of pollution but results in heavy resource drainage in the form of energy through organic biomass & inorganic chemicals.

Central Pulp & Paper Research Institute (CPPRI) has been actively engaged for last many years in identification, development and demonstration of effective & viable technologies to handle effluents from pulp and paper mills. Among the technologies identified & developed, anaerobic treatment of spent pulping liquor (Biomethanation process) has proved to be an upcomming technological option. before the industry, to treat their pulp mill effluent rich in black liquor with subsequent recovery of bioenergy (2). However, certain limitations are encountered with the biomethanation process in respect of lower pollution reduction efficiencies specially in terms of COD which is restricted to nearly 50%. (2,3) Which is mainly restricted due to the presence of high molar mass polyphenolic components like lignin & its degradation products behaving as an recalcitrant and bioinhibitry substances. Even following the secondary treatment of the effluent coming out of the biomethanation plant and employing activated sludge process, it becomes difficult to achieve desired discharge standards specified by Pollution Control Authorities.

Application of anaerobic systems in conjuction with pretreatment methods may offer a situation for eliminating these high molar mass lignin based recalcitrants organic compounds. These pretreatment methods can be either physical, chemical or biological. This calls for additional stages of pretreatment of black liquor and sincere efforts are being made at CPPRI on the application of membrane filtration process as pretreatment stage to biomethanation process. The present paper highlights efforts being made at the Institute on the possibility of application of membrane filtration/ultrafiltration (UF) as an adjunct technology to biomethanation process to treat black liquor laden effluents in small agro based mills to improve the overall performance of the biological treatment systems.

RESULTS & DISCUSSIONS

Nature of Spent Pulping Liquor from Small Agro-based Pulp mills

Majority of small agro-based mills employ soda or alkaline sulphite pulping process. In absence of a viable chemical recovery system these mills discharge their spent pulping liquor as effluent. Table-1 shows typical characteristics of spent liquor discharged from small agro based mill employing soda process & using wheat straw, sarkanda & bagasse as major raw materials.

From the data shown in Table-1, it is clear that nearly 70% of the total solids are composed of organics, of which nearly 50%, is lignin. As seen from the Gel chromatographic studies, it is evident that most of the lignin present in these black liquors are high molecular weight lignin and is responsible for higher COD/BOD ratio. Higher COD/BOD ratio is an indication of recalcitrant/poor degradable nature of black liquor.

Lignin-A Recalcitrant/Bioinhibitory Material in Black Liquor (3)

The effluents containing black liquor discharged in an agro based pulp & paper mill contain complex mixtures of aromatic phenolic compounds ranging from low mol. wt. monomeric to high molecular weight polymeric substances known as lignin and its derivatives. These lignin based compounds contribute to higher pollution loads in terms of COD and Colour. Based on studies carried out at CPPRI, it has been

Table-1

Chemical Composition of Spent Pulping Liquor

Particulars	Values
pH at 25°C	8.3-9.0
Total solids, mg/l	20000-35000
Suspended solids, mg/l	5000-6000
Total organics, % w/w	70
Total Inorganic, % w/w (Sulphated Ash as NaOH),	30
Total sodium, mg/l	3500-5500
Silica, mg/l	500-1250
Lignin, mg/l	10,000-15,000
COD, mg/l	22,000-38,000
BOD, mg/l	6,000-9,000
COD/BOD Ratio	3.7-4.2

observed that molecular size/weight of the lignin has great influence on the COD values. Due to the complex nature, the major portion of lignin which has high molecular weight and contributes to more than 80% of the total lignin remain practically a recalcitrant material & some times bioinhibitory too during biological treatment of these black liquor laden effluents. This causes severe problems of pollution & therefore have become a component of major concern to environmentalists & technologists. In order to achieve the stringent discharge standards laid down by pollution control authorities, it is imperative that the portion of lignin in the black liquor which remain recalcitrant should either be degraded to low molar mass components or be separated from the black liquor before being treated in biological treatment system & finally discharged into the reciepient stream.

Biomethanation Technology in Pulp & Paper Industries & Need for Lignin Removal

Although anaerobic treatment technology has been adopted to treat industrial effluents including some specific streams from pulp & paper industries throughout the world empolying various biomethanation technologies, but Upflow Anaerobic Sludge Blanket (UASB) technology has been recognised as one of the ideal anaerobic system due to number of advantages.

- Flexibility in operation.
- Higher organic loading rates etc.

The technology is more or less established to treat various industrial effluents but the performance of the installations, to treat black liquor laden effluent in Indian Paper Industry has been a matter of concern, since pollution reduction efficiencies in terms of COD, are restricted to 50% or below.

In depth studies carried out at CPPRI on the basic nature of black liquor, coupled with laboratory & semi pilot scale studies on anaerobic biodegradation of black liquor laden effluents has indicated certain limitations, observed in respect of COD reduction & biogas production rates. Based on successful pilot scale studies, a demonstration biomethanation plant based on UASB Technology has been commissioned under UNDP/GEF project on High Rate Biomethana-tion being executed by Ministry of Non-Conventional Energy Sources (MNES), where CPPRI has been engaged as Technology Institution assisting MNES in execution of the project. The plant has been running continuously for last six months & is being operated at more than 100% organic loading rate. During six months of its operation, although the performance has been quite satisfactory with respect to biogas production, but poor COD elimination (below 50%) has been observed. After extensive examination and analysis of the data, the main reason for poor COD elemination has been found to be the presence of high molar mass lignin, which due to its highly complex structure & recalcitrant nature remain non-biodegradable & is passed on to the recipient stream even after secondary treatment.

In view of above, the need for lignin removal has been felt seriously and sincere efforts are being made in the direction to remove only that portion of lignin i.e. HMW fraction which is found to be non-biodegradable without affecting the other parameters considered important for biomethanation.

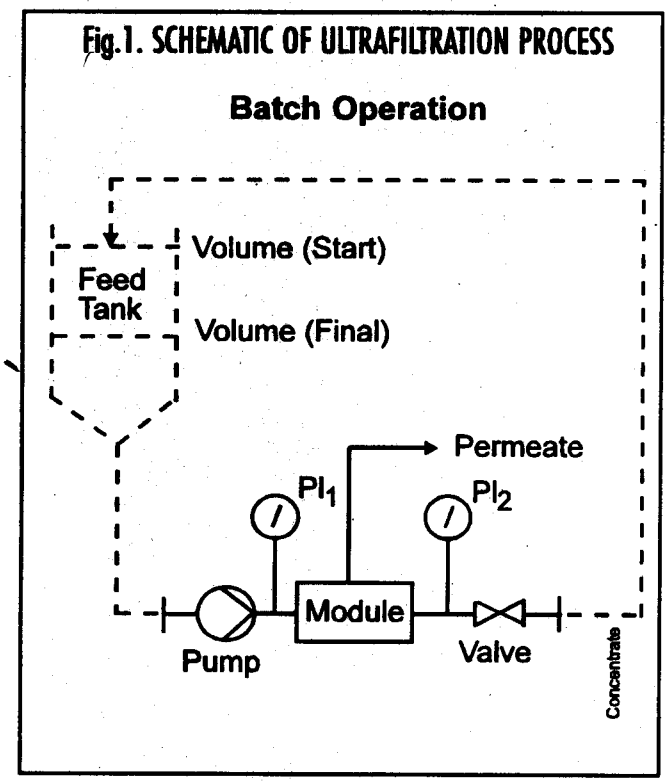
Membrane Filtration-An Option as Adjunct Technology to Biometnanation to Treat Pulp Mill Effluent (5)

Membrane filtration encompasses several separation processes, which use a membrane to affect desired separation of certain components from a liquid or gaseous stream. In context to removal of recalcitrant portion of HMW lignin from black liquor, the process has been proved to be a potential option and may have great relevance in Indian Paper Industry.

Central Pulp & Paper Research Institute has been engaged in ultrafiltration studies for the past several years and did extensive studies for exploring the possibilities of its application for selective removal of HMW fraction of lignin & its derivatives (6), which are biorefractory & bioinhibitory during biological treatment of black liquor. In the present studies, work has been carried out employing DDS Lab-10 model of plate & frame type UF module with GR 81 PP polysulphone membranes having molecular weight cut off value of 6000 dalton and using black liquor generated in an agro based mill (Bagasse and Wheat Straw)..

Fig.1 Shows schematic of Ultrafiltration process employing DDS-Lab 10 UF module.

The results of ultrafiltration studies of black liquor are shown in **Table-2** which clearly show that most of the high molar mass lignin, a biorefractory and/or recalcitrant material is retained in the concentrate fraction and constitutes less than 20% of the



total black liquor mass. Studies have further shown that this high molar mass fraction of lignin in the concentrate fraction leads to higher COD values i.e. as high as 2.10 g. COD/g of lignin, whereas COD values contributed by low molar mass lignin present in the permeate fraction contributes to comparatively lower COD values i.e. 1.2 g COD/g of lignin.(4) Now, the permeate rich in high proportions of carbohydrates coupled with lower molar mass fraction of lignin becomes amenable to biodegradation, which is reflected from the results of bioassay determination shown in **Table-3.** From the results of bioassay, it is clearly seen that the anaerobic biodegradability of the permeate fraction which is to be treated in biomethanation plant, has increased to 72.9% after separation of high molar mass fraction of lignin through concentrate stream, as against 40.5% of original black liquor. This is because of the removal of recalcitrant/bioinhibitory fraction of HMW lignin through concentrate fraction showing the anaerobic biodegradation efficiency 28.5% only.

Fig.2 shows fate of major pollution parameters like COD, lignin and sodium during various unit operations of biomethanation plant with & without use of ultrafiltration process. The data shown in Fig-2, clearly show that during biomethanation of the black liquor it is possible to achieve nearly 50% of the COD reduction efficiency and there is negligible reduction in lignin which is passed on to the secondary treatment. Therefore it becomes difficult to achieve standard limits in terms of COD.

Table-2

Ultrafiltration of Black Liquor (Physico-Chemical Analysis Data)

Particulars	Original B.L.	Ultrafiltration/Fractionated Liquor	
		Permeate	Concentrate
Qty of black liquor, gms	5150	4255	890
Total dissolved solids, % w/w	5.81	4.11	14.34
Total alkali, % w/w as NaOH	23.06	28.8	13.18
Sulphated ash as NaOH, % w/w	26.87	33.8	14.13
Organics, % w/w	73.13	66.2	85.87
Lignin, % w/w	32.06	8.71	60.11
COD contribution due to lignin (g COD/gm lignin)	1.68	1.4	2.1
Carbohydrate, % w/w (by difference)	41.07	57.49	25.76
Total sodium, % w/w	13.27	16.8	7.58
Silica, % w/w	0.43	0.54	0.39
COD, g/l	61.516	23.55	220.22
BOD, g/l	17.90	14.81	34.08
Bioassay, COD degradation, %	40.5	72.9	28.0

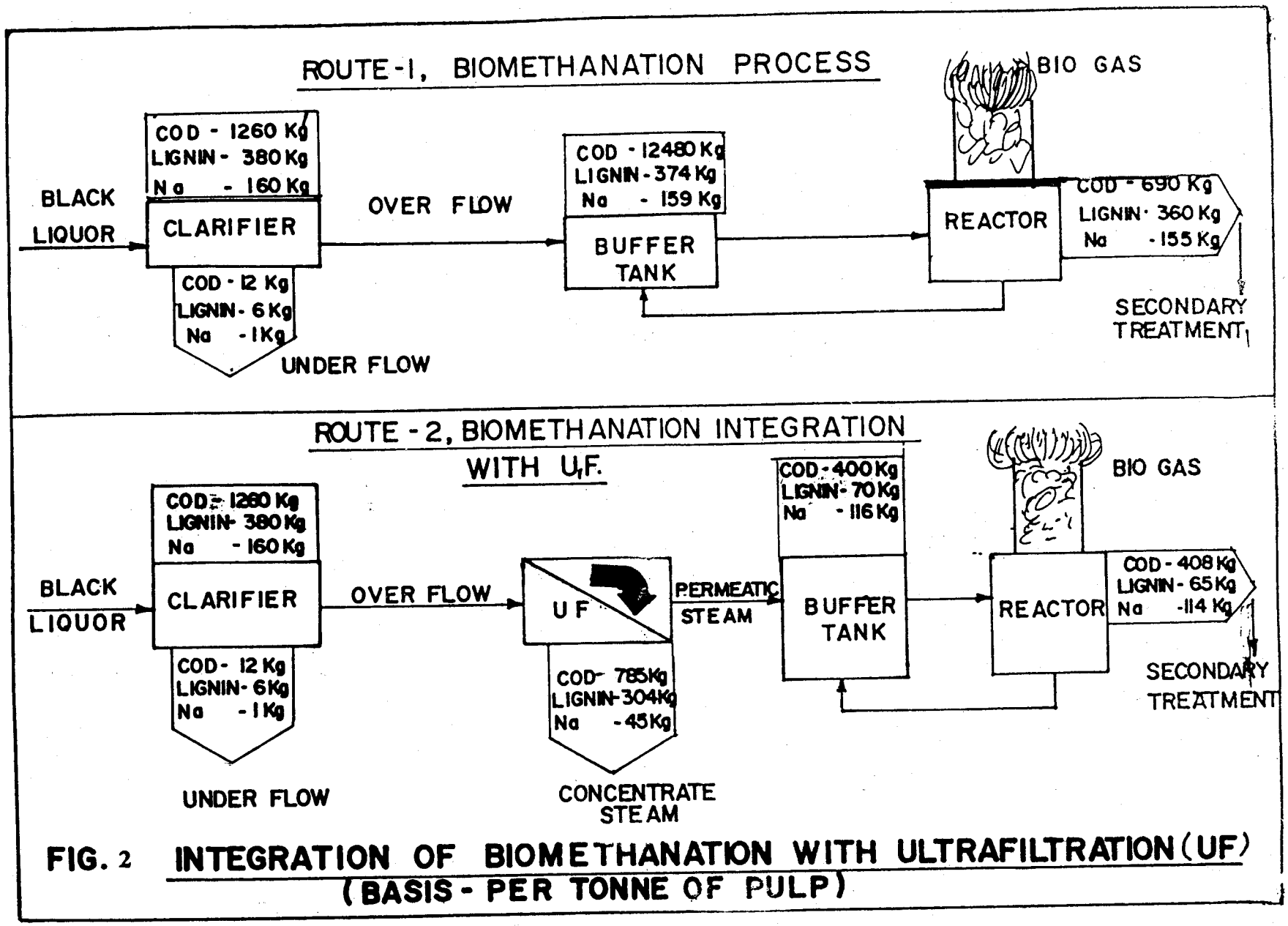


FIG. 2 INTEGRATION OF BIOMETHANATION WITH ULTRAFILTRATION (UF) (BASIS - PER TONNE OF PULP)

Table-3

Pollution Loads & Anaerobic Biodegradation Efficiency of Different Fractions of Black Liquor Before and After Ultrafiltration

Particulars	Original B.L.	Ultrafiltration of Black Liquor MW cutoff-6000	
		Permeate fraction	Concentrate fraction
COD, g/l	61.52	23.55	220.22
BOD, g/l	17.90	14.81	34.080
COD:BOD ratio	3.34	1.6	6.5
Bioassay determination			
a) COD degradation efficiency, %	40.5	70.9	28.5
b) Biogas production M^3/kg COD redn.	0.35	0.44	0.11

With the incorporation of ultrafiltration with biomethanation process, there is an overall improvement in the treatment efficiencies in terms of COD reduction which could be achieved as high as 90% with simultaneous reduction in HMW lignin to the tune of 80%.

Impact of Ultrafiltration on Pollution Loads & Performance of Biomethanation Process

Table-3 shows the impact of ultrafiltration process on the pollution loads in terms of COD, BOD and the anticipated performance of biomethanation plant. From the data, it is indicated that most of the COD which is imparted by the high molar mass fraction of lignin is retained in the concentrate stream. Mass balance calculation shows that out of 1260 kg COD/tp, 785 kg COD/tp is removed by way of concentrate fraction, thus resulting in reduction of 69% COD load. Due to improved nature of permeate, the anaerobic degradation efficiency is also improved to 70.9% as against 40.5%. This could further resulted in improvement of biogas production rate to the tune of 0.44 M^3/kg COD reduced as against - nearly 0.35 M^3/kg COD in the original black liquor. It might be possible that the pollution loads in terms of COD, fed to the secondary treatment is reduced to a great extent and with the incorporation of ultrafiltration, it might be further possible to achieve standards nearer to what are prescribed by the Pollution Control Authorities.

CONCLUSIONS

1. From the present study, it is concluded that during biological treatment of black liquor laden effluents, application of Membrane filtration coupled with biomethanation could be potential route for reduction of pollution load in terms of COD and it might be possible to achieve more than 90% COD reduction efficiency as against only 50% in biomethanation without using Ultrafiltration.
2. The Techno-economic viability of the ultrafiltration process needs to be ascertained on pilot scale in terms of operational cost, specifically the energy requirement, availability of the membrane and its shelf life etc.

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