Membrance Separation Processes In Pulp And Paper Industry

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ABSTRACT

Membrane separation techniques have been found to be highly useful for the removal of colour and organic rafractories which are not removed through conventional treatment processes and for the recovery of chemicals from spent liquor of small paper mills and sulfite mills. This paper presents a brief account of the basic principles of membrane separation processes and discusses their applications in pulp and paper industry for effluent treatment, recovery of chemicals from small paper mills and sulfite mills and in concentration of black liquor with reference to Indian paper industry.

INTRODUCTION

Pulp and paper industry is a major consumer of water at various stages of operation and about 200-250 m^3 of waste water per tonne of paper is generated. It is one of the twenty highly polluting industries notified by the Central Government. By conventional waste-water treatment processes removal of colour, refractory and toxic pollulants is not possible. All of these are present in appreciable quantity in the effluent. Economic recovery of chemicals from small paper mills also has been a challenge to engineers and technologists. Due to presence of high silica, conventional recovery processes cannot be used. The problem of colour removal from pulp and paper industry has also been a serious concern.

There are about 288 pulp and paper units with an installed capacity of 27.5 lakh tonnes, the total production during 1987 was only 16.8 lakh tonnes[1]. The profile of Indian paper industry is given in Fig. 1. Large integrated pulp and paper mills use bamboo and hardwood as main raw materials and are based on kraft pulping process. Small paper mills use straw, bagasse, jute sticks, grass, etc., and employ soda pulping. These are not having chemical recovery system due to high silica content. Sulphite process is being used by one mill only. Newsprint mills which utilise 70-75% mechanical pulp and 25-30% kraft pulp are employing stone ground pulping, thermo - mechanical pulping, chemical-mechanical pulping and use bamboo, hardwood, bagasse, etc.

With the development in the feasibility and practical application of membrane separation technology in various processes, use of membrane technology for treatment of effluent and recovery of chemicals in paper industry has been extensively investigated and practiced during last decades in developed countries. Reverse osmosis and ultrafiltration have been found to be highly cost effective and suitable for colour removal, recovery of chemicals from small paper mills and sulfite mills, in preconcentration stage for evaporation of black liquor, and separation of lignin and lignosulphonates from spent liquors.

The present paper reviews the basic principles of membrane separation processes and their applications in pulp and paper industry for recovery of chemicals in small paper mills and sulfite mills, for removal of colour and in preconcentration stage. A case is also built-up for the use of these proeesses in Indian paper industry.

WATER POLLUTION CONTROL MEASURES

Tne various primary and secondary treatment methods and colour removal methods used In paper indus-

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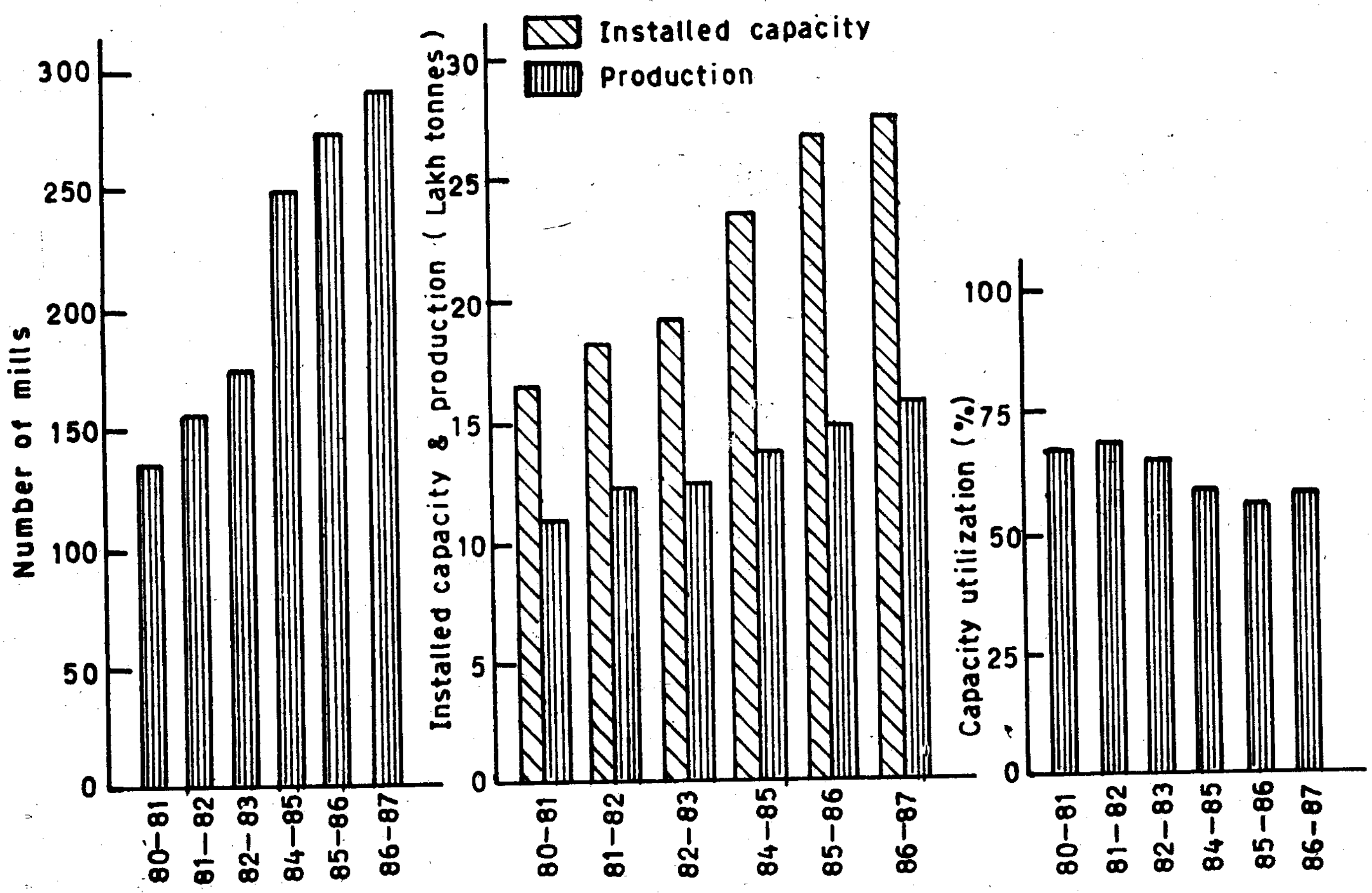


FIG. 1 - PROFILE OF INDIAN PAPER INDUSTRY

try are given in Fig. 2. Although a substantial amount of money is being invested on control measures for air, water and noise pollution control by developed countries, the situation in developing countries is entirely different. Due to poor financial conditions, investment on pollution control measures is generally considered nonproductive and the measures being adopted are still inadequate.

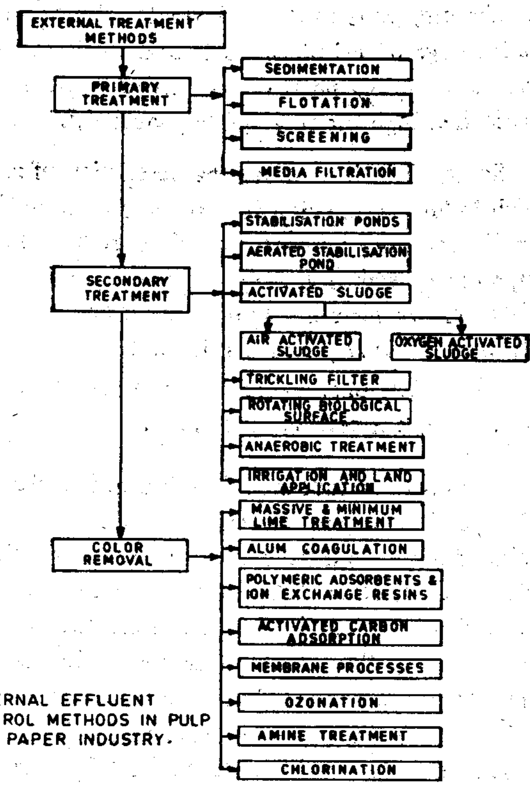
The pollution control measures in Indian paper industry especially in case of small paper mills have suffered a set back due to raw materials shortage; rising cost of cellulosic raw materials, coal, power and chemicals; low retention prices and decline in consumption. Large integrated mills are usually having primary treatment and secondary treatment systems-lagoon, aerated lagoons, activated sludge and anaerobic lagoons.

MEMBRANE SEPARATION PROCESS

The principle of separation used in the membrane separation technology is selective permeation of one or more components of the fluid mixture through a semipermeable membrane barrier so that a permeate stream enriched in more permeable components of the feed mixture and a residue stream enriched in the less permeable components is obtained. Basic principle of membrane separation processes are shown in Fig. 3 and 4.

Reverse osmosis and ultrafiltration are similar processes since both use a semipermeable membrane as separating agent and pressure gradient as driving force to achieve separation. However, there are some important differences between reverse osmosis and ultrafiltration (Table 1). Electrodialysis is another variation of membrane process in which the transport of ions through membrane is a result of electrical driving force. Sometimes combined ultrafiltration and reverse osmosis are also used for high removal efficiency.

Factors affecting performance of membrane processes[6] are (i) type of influent-higher the percentage of



2- EXTERNAL EFFLUENT CONTROL METHODS IN PULP AND PAPER INDUSTRY.

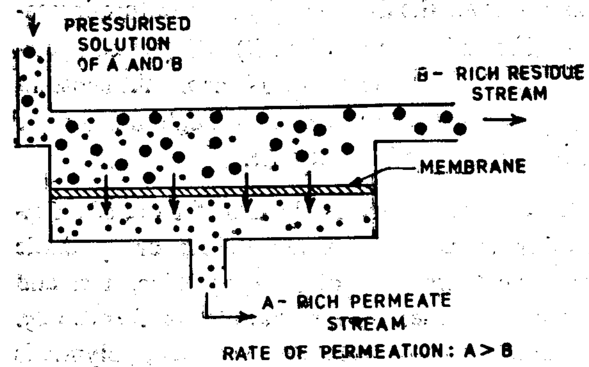


FIG-3- MEMBRANE SEPARATION PRINCIPLE.

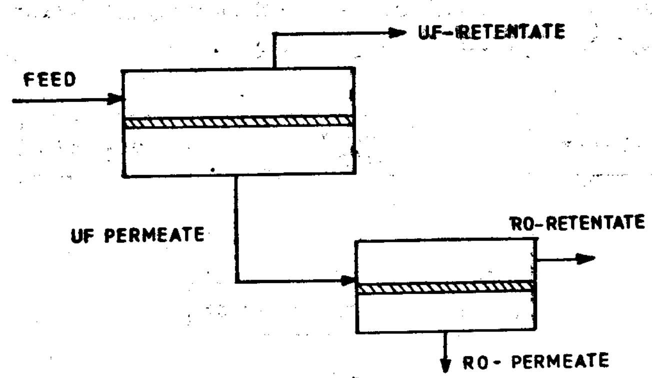


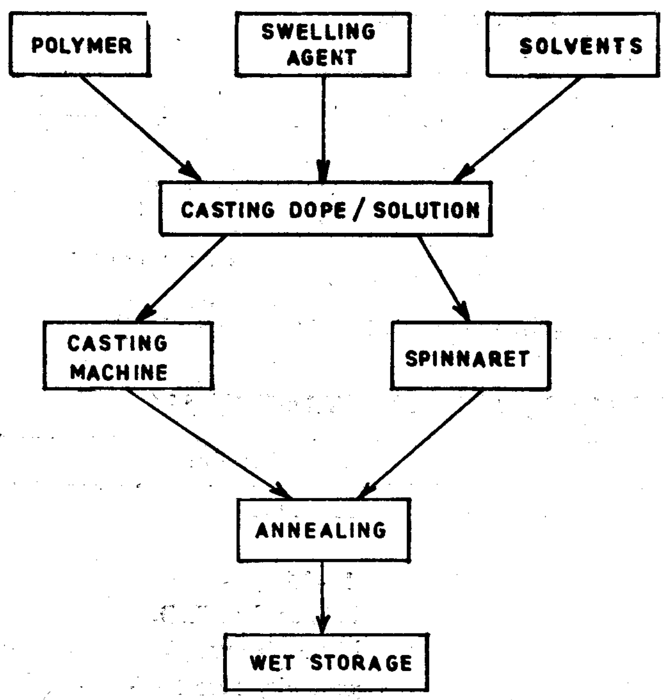
FIG-4- TWO STAGE MEMBRANE SEPARATION

TABLE—1. COMPARISON OF REVERSE OSMOSIS AND ULTRAFILTRATION[3,4,5]

Parameters	Reverse Osmosis	Ultrafiltration
1. Pore size of membrane,°A	5—15	15—1300
2. Pressure, kg/cm^2	28—60	1—15
3. Permeate flux	Lower than U.F.	Higher than R.O.
4. Size of solute retained	Molecular weights generally less than 500—1000	Molecular weight generally over 1000
5. Osmotic pressure of feed solution	Important, can range over 68 kg/cm^2	Generally negligible
6. Nature of membrane retention	Diffusion transport barrier ; possible molecular screening	Molecular screening
7. Chemical nature of membrane	Important in affecting transport properties	Unimportant in affecting transport properties so long as pore size & pore size distribution are obtained

solids in feed lower the flux rate (ii) temperature-increases rate of flux and permeability (iii) pH (iv) compaction (v) velocity of feed across membrane. At constant operating pressure the waterflux through anisotropic membranes decreases with flux time.

The raw materials used in the manufacture of industrial membranes are polymers-cellulose or synthetic polymer; solvent acetone, dioxane, pyridine, etc. and swelling agents-magnesium perchlorate or formamide. In the process of manufacture of membrane, polymer is dissolved in a suitable solvent and a swelling agent is added. The solution is cast and solvent is allowed to evaporate. Skin layer of polymer is formed having assymetric structure. The flow sheet showing membrane preparation process is shown in Fig. 5.



FIG·5 - GENERAL PROCEDURE FOR MANUFACTURE OF MEMBRANE.

Some of the commercially available membranes are-cellulose acetate, cellulose di-and tri-acetate, cellulose acetate and cellulose triacetate blast cellulose ester, cellulose nitrate gelatin, polyacrolonitrile (PAN), polyvinyl chloride polyvinyl copolymer, polyamide (aromatic), polysulfone, polybenzimidazole, polybenzimidiazolone, polycarbonate, polyester, polymide, polypropylene, polytetrafluoroethylene, polyvidnyliene fluoride[7,8] etc. Commonly used cellulose acetate membranes have some advantages-high flux, high rejection, easy to manufacture, renewable raw material etc. The main disadvantage of cellulose acetate membrane is narrow temperature range. narrow pH range 3-6, poor resistance to chlorine, high biodegradable meterial[6,7].

Some of the important characteristics of membrane which influence its efficiency are surface pore size, pore size distribution, percent porosity, rejection rate, flux temperature, stability, solvent resistance and pressure resistance. In membrane separation processes no auxiliary chemical is required as in casc of other treatment processes. The only operating cost is power for pumping and replacement of membrane.

Fouling of membrane arises due to the precipitation of iron and mangese oxides or calcium carbonate and calcium sulfate and from attachment of organic macromolecules. Further the membrane life can be shortened by chemical attack and solvation of the membrane skin, enzymatic digestion of cellulose acetate by microorganism, etc. Some of the basic steps taken to minimise the fouling are-filtering the feed, maintaining iron and manganese oxides in the reduced form by excluding air or adding reducing agents, adding precipitation inhibitors such as sodium hexametaphosphate, controlling the pH to prevent precipitaion and passing the feed through an activated carbon column to remove organics.

Reverse osmosis units are available in four common designs-spiral wound hollow fiber, tubular, plate-and-frame. Commonly ultrafiltration membranes modules includes-tubular, plate and frame, spiral wound, hollow fiber, thin channel and parallel-leaf-type modules.

MEMBRANE SEPARATION PROCESS IN PAPER INDUSTRY

The various laboratory and pilot plant studies on membrane separation processes have shown capability of reverse osmosis and ultrafiltration as promising tools for treatmcnt of effluent-removal of colour and non biodegradable pollutants, recovery of chemicals, lignin and lignosulphates from the effluents of small paper mills and sulfite mills, for concentration of black liquor in preconcentration stage for better steam economy. High level of rcjection and concentration of dissolved material is possible consistently.

Prior to treatment in the membrane unit some pretreatment on the feed is needed. The common pretreatment of effluent or black liquor prior to processing through membrane includes filtration, pH and temperature adjustment to avoid the damage of membrane. The filtration involves two stage filtration for removing suspended solids and other impurities. Filtration helps to minimise any possible fouling of the membranes. Adjustment of pH in membrane processes is essential in case of cellulose acetate to avoid deteriotation of the membrane. Rate of hydrolysis of cellulose acetate membrane is minimum at pH 5 and optimum pH is 3-7.5[4]. However, nylon membrane has advantage as it needs no pH adjustment and at the same time it also prevents the fouling of membrane that can result from precipitation of organics as result of pH adjustment. Optimum temperature to be maintained is 40-50°C. Higher temperatures damage the membrane. Fouling of organic matter also becomes increasingly critical at lower temperature[4].

TREATMENT OF BLACK LIQUOR FROM STRAW BASED PAPER MILLS

The black liquor from straw based pulping are different in physical and chemical characteristics and lack the provision of chemical recovery system. They are usually charasterised by their high ash content which comes from the cellulosic raw materials used (Table 2). The black liquor from straw based units is of low concentration due to slow drainage characteristic and have high silica content resulting in highly viscous black liquor and leads to scaling in evaporator. The various available technologies for the recovery of chemicals from straw based mills are-Direct Alkali Recovery System Ferrite. Recovery process (DARS Ferrite Process), Membrane Processes-Reverse Osmosis Ultrafiltration, Broby Recovery System, Copeland Process, BKMI Process, Smelter Cyclone Evaporator System, Destromax Recovery System[9,10,11].

Among these processes DARS Ferrite Process and Membrane Separation Processes are very promising and cost effective. In the process of membrane separation free soda as permeate through membrane is more than 60% of total soda content of black liquor. Lignin fractions are rejected at membrane interface. Comparison of reverse osmosis and ultrafiltration used for straw black liquor for a 30 TPD plant with initial conentration of 4% total solid is given in Table 3. It is clear that higher colour removal efficiency is obtained from reverse osmosis as compared to ultrafiltration.

TABLE-2

ASH CONTENT OF VARIOUS FIBROUS RAW MATERIAL

Raw Material	% Ash
Rice straw	15.0—17.0
Wheat straw	4.0—8.0
Sabi Grass	6.0
Bagasse	1.2—3.0
Bamboo	2.0—3.0
Soft wood	0.1
Hard wood	0 1
Kenaf	0.44
Jute Stick	0.6—1.2

MEMBRANE SEPARATION PROCESS IN EFFLUENT TREATMENT

Due to higher rejection and removal efficiency of colour, dissolved and suspended solids the membrane separation processes, both ultrafiltration and reverse osmosis, have received much attention during the last few years. During various stages of pulp and paper manufacture, coloured effluent is discharged. Characteristics of effluent from integrated pulp and paper mills, newsprint mill, and small paper mills based on agricultural residues and waste paper are given in Table 4. Amount of colour discharged from various pulping processes are given in Table 5. The problem of colour removal has been a subject of serious concern in the last two decades as the colouring materials from pulp and paper mills are difficult to remove by conventional sedimentation and biological treatment methods From caustic extraction stage of bleach plant highly coloured effluent is discharged. The effect of various colour removal methods on bleach plant effluent colour and COD removal efficiency is shown in Table 6. The waste-water streams where membrane process can be used effectively and economically are-Washing stage effluent, Evaporator condensate, Deinking plant effluent, Dye waste from coloured paper manufacture. For colour bodies found in kraft mills effluent, a membrane

TABLE—3. CHARACTERISTICS OF EFFLUENT FROM PULP AND PAPER MILLS[13,14]

Raw Materials	Integrated Pulp and Paper Mills	News Print Mills	Agrobased Small Paper Mills	Waste Paper based Mills
Raw Material	Bamboo Hard wood	Salai, Bamboo Hardwood	Rice straw Wheat steaw Bagasse etc.	Waste Paper
Wastewater m³/Tonne	250—350	200	200—380	70 – 150
pH	6.0—9.0	7.2—7.3	6.0—8.5	6.0—8.5
Suspended Solid mg/l	300—450	375	400—1100	300—900
Total Solids mg/l	1200–1600	1500	3000-3500	3000
BOD5 mg/l	100—160	105	220—1100	100—270
COD mg/l	500—700	500	2000—4800	470—900
Pollution Load kg/Toone Paper				
Suspended Solids	100—150	100	90—240	50—80
BOD	35—50	45	85—270	13—40
COD	150—200	135	500-1100	50 -90

TABLE-4.

TREATMENT OF BLACK LIQUOR FROM SMALL PAPER MILLS BY MEMBRANE PROCESS[12]

Parameters	Reverse Osmosis	Ultrafiltration
Rejection of Colour %	95	80
Rejection of Soda Compounds %	85-90	50
Optimum feed pressure kg/cm²	40	10
Permeate Recovery	35	38

TABLE—5

COLOUR DISCHARGED FROM VARIOUS PULPING PROCESSES[15]

Effluent	Kg of Colour Unit per Ton of Product
Kraft Pulping	25—150
Kraft Bleaching	100—150
Kraft Paper Making	1.5—4
NSSC Pulping (Recovery)	100—125
Sulfite Pulping (Recovery)	15—100
Sulfite Bleaching	25—150

TABLE—6.

THE EFFECT OF COLOUR REMOVAL METHODS ON BLEACH PLANT EFFLUENT COLOUR AND COD[16]

Method	% Reduction Colour	COD
Massive and minimum Lime	85—95	—
Ion Exchange	65—90	50—70
Absorption with Alumina	95	70
Ultrafiltration	90	70
Anaerobic/Aerobic Treatment	Good removal of acute toxicity and chlorinated phenols 60–70%	

with a pore size of about 0.01 to 0.05 micron is used. The pore size can be varied depending upon the colour bodies[17].

The various steps involved in reverse osmosis and ultrafiltration process in effluent treatment is given in Fig. 6. Results of the ultrafiltration and reverse osmosis treatment of bleach plant caustic extraction stage effluent has been given in Table 7, By combined reverse osmosis and freeze concentration process high quality product water and a concentrated stream (approximately 2% of original feed) containing 90% of original colour was obtained from pilot plant scale trial of three mills by Wiley, et ai[20,21]. In treatment of caustic extraction stage effluent by ultrafiltration process about 84-90% colour removal was obtained with three types of membranes used[15]. Ten different types of wastewater streams coming from barking, pulping, bleaching and evaporation were treated by reverse osmosis and have been found very effective[22]. About 90-97% colour removal from caustic extraction stage effluent was observed by Fremont et al[23] by ultrafiltration, whereas 90% colour rejection from NSSC mill effluent was reported by Doshi et al[22].

In-plant treatment of effluent by membrane processes will be more economical than external treatment to avoid treatment of large amount of effluent discharged through various streams.

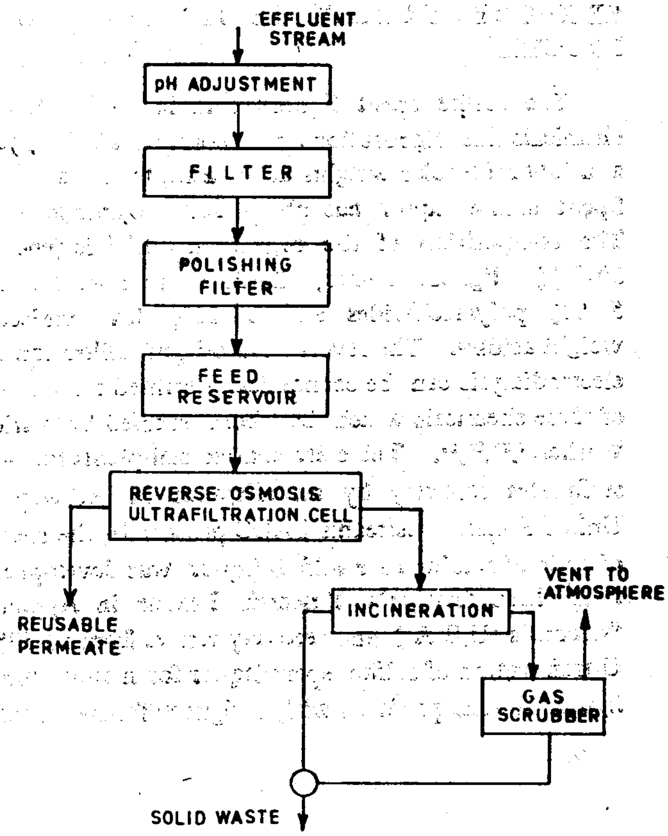


FIG-6- REMOVAL OF COLOR FROM KRAFT MILL EFFLUENT BY MEMBRANE FILTRATION.

TABLE—7.

TREATMBNT OF KRAFT BLEACHING PLANT EFFLUENT BY REVERSE OSMOSIS AND ULTRAFILTRATION[19]

Parameters	% Removal Reverse Osmosis	Ultrafiltration
Colour	95	80
Chloride	85–95	30–40
TDS	85–95	30–40

Operating Conditions

Flow Rate 12 LPM

Feed Pressure

Reverss Osmosis 30 kg/cm²

Ultrafiltration 15 kg/cm²

TREATMENT OE SULPHITE SPENT LIQUOR FOR RECOVERY OF CHENICALS BY MEMBRANE PROCESS

The sulfite spent liquors contain useful organic chemicals like lignosulfonates, vanillin, alcohol, yeast and low molecular weights-acetic acid, formic acid, etc. Spent sulfite liquor has about 90% organic material. The composition of the organic material is generally 50-60% lignosulfonates, 20-25% monosaccharides, 5-10% polysaccharides and 10-15% low molecular weight acids[23]. The reverse osmosis, ultrafiltration and electrodialysis can be economically utilised for recovery of these chemicals which has been studied by various workers[4,25,26,27]. There are commercial plants for ligno sulfonates recovery by ultrafiltration in Norway and United States. 4.streams BALC process for the electrodialysis of soluble base sulfite liquor was developed by Pulp Manufacturer's Research League in Appleton, Wisconsis (U.S A.) and recovery ranges from 60-80%[4]. Ultrafiltration of sulfitc spent liquor for manufacture of lignosulfonate products with a lignosulfonates content in the range 90% + range has been going on regular commercial basis[28].

REVERSE OSMOSIS AND ULTRAFILTRATION FOR EVAPORATION OF BLACK LIQUOR AT LOW CONCENTRATION

Reverse osmosis and ultrafiltration has been found useful and more attractive in preconcentration of black liquor in low concentration range for energy conservation and better economy due to increasing fuel prices. It has been reported that combined ultrafiltration and reverse osmosis could reduce the thermal energy requirement to one third of that required for conventional evaporation system. Cost of removing huge quantity of water from thin black liquor by evaporation can be reduced to the extent of 25-30% through reverse osmosis at preconcentration stage[29]. From Table 8 it can be seen that cost of water removal by reverse osmosis is substantially less in comparison to normal multiple effect evapoiation system for weak black liquor.

TABLE—8. ENERGY REQUIREMENT BY EVPORATION AND REVERSE OSMOSIS FOR WATER REMOVAL[28,29]

System	KCal/m³ of water removal	Steam Required T/m³	Cost of Steam Rs/m³
6— Stage Multiple Effect Evaporator	118250	0.219	37 23
5— Stage Multiple Effect Evaporator	148500	0.275	46.75
4— Stage Multiple Effect Evaporator	189750	0.351	59.47
3— Stage Multiple Effect Evaporator	236500	0.538	74.46
Reverse Osmosis	8250	0.015	9.59*

*Cost of electricity/m³ of water removal
Cost of steam Rs. 170.00/Tonne
Cost of Electricity Rs. 1.00/kwh.

CONCLUSIONS

The membrane separation processes have high potential for the recovery of chemicals and removal of pollutants from wastewaters. These are being used on large scale by the developed countries for the removal of colour and recovery of important chemicals like lignin lignosulphate, etc., for concentration of black liquor in preconcentration stage for better steam economy. In India some work is undergoing at IIT, Bombay on laboratory and pilot plant scale units for effluent treatment of bleaching plant effluent and recovery of chemicals from small paper mills. There is an urgent need to try the viability and feasibility of these processes in Indian paper Mills also. Adoption of this technology will not only help in reducing the pollution load from these industries but will also provide valuable raw material in the form of recovered chemicals.

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