STUDIES ON THE DEVELOPMENT OF RO/UF MEMBERANES IN THE TREATMENT OF PULP AND PAPER MILL EFFLUENTS FOR POLLUTION ABATEMENT WITH RECYCLING

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INTRODUCTION

Biggest deficiency in the conventional waste treatment processes based on biochemical reactions, is their inability to remove pollutants on molecular level, and consequently, treated effluents are normally not suited for recycling. Apart from its inherent defects, non-biodegradable pollutants, along with toxins, are normally present in good many industrial effluents like Pulp and Paper Mill discharges and removal of such pollutants by the tertiary conventional systems, are generally exorbitantly costly, and inapplicable for the removal of dissolved salts like chlorides, sulfates, Nitrates, and other inorganic salts.

With the emergence of Membrane techniques (MT) in industrial processing during the late sixties, extensive basic research, and engineering studies, have been carried out in the field of Reverse Osmosis (RO), ultrafiltration (UF), and Electrodialysis(ED) membrane development, for applications in concentration/separation operations, and in the field of industrial effluent treatment for pollution control, along with recycling of water/chemicals for re-utilization in process operations[1-3].

In our earlier communications, MT performance in the treatment of Paper Mill and Rayon Plant effluents by ED/RO/UF, based on cellulosic RO/UF membranes, and ion-exchange ED membranes, have been evaluated with encouraging results.[4-8]

While earlier results were encouraging, it was felt desirable to develop high performance cellulosic and non-cellulosic membranes, having high thermal and pH stability, which could eliminate considerably fouling and compaction problems, during treatment of Pulp & Paper Mill effluents at higher temperatures (45-70°C), and pH range of below 4, and above 8, by RO/UF process.

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Recently, high performance thin film composite (TFC), based on non-cellulosic membranes, has been developed in western countries, which is now in commercial operations in Japan in two pulp and paper Mills having capacity ranging from 1100 to 3000 TPD Pulp production[9-10]

In the present Work, an attempt has been made, to optimize casting parameters, for the development of high performance cellulosic, and non cellulosic membranes, for applications in the treatment of pulping effluents from sulfate, and sulfite Mills, major objectives being to control pollution, along with recovery, and recycling of water, and chemicals like useable pulping chemicals, and Lignosulfonates for utilization in industrial operations as adhesives, and as a aid in oil drilling operations.

PLAN OF WORK

Sulfate and sulfite spent liquors at about 50-60 % TDS concentrations have been obtained in sealed drums of 300 litres capacity, from Paper Mills manufacturing Pulp & Paper by sulfate and sulfite process respectively. BL analyses have been carried out by TAPPI standard procedures, with respect to TDS, Organic and Inorganic constituents like total soda free soda compounds. Colour rejection studies by UF have been monitored spectro-photometrically in the visible range, while Lignin content in BL has been estimated by UV Spectrophotometer.

Cellulosic and non-cellulosic membrane casting parameters have been optimized, and membrane performance evaluated in Test-Cell,based on membrane development in TLC applicator, according to the procedures outlinned in our earlier communications.

For Cellulosic membranes, Cellulose-Di-Acetate(CDA), Acetone(A), and DMF tertiary system has been used, and for non-cellulosic membrane, styrene acrylonitrile (SAN, obtained from GSFC, Baroda) in DMF solvent has been used, and all the influencial casting variables like percent polymer, solvent and modification agent, composition, evaporation time and temperature, membrane thickness, gelling temperature, and annealing time with temperature, have/evaluated, and optimized, based on membrane performance estimation in Test-cell, in terms of permeate flux, and colour rejection in feed, at different feed flow rate and feed pressures.

Based on RO/UF membrane development, under optimal conditions, further studies have been carried out in spiral wound RO/UF modules of 2.80m^2 membrane modules as per the experimental set-up depicted in fig.2.

RESULTS AND DISCUSSIONS

Membrane casting parameters, with reference to % composition of polymer and the solvent constituents, for applications in RO/UF processing under optimal conditions, could be evaluated with the help of the triangular phase diagram of the tertiary system of CDA-A-DMF, as presented in Fig.I. Within the tertiary phase diagram, drawn based on extensive experimental work with indigenous CDA, under different formulations with DMF and Acetone, (Fig.I)., line AF represents lower selectivity of salt, and high permeate flux (around 700 LMD), while the line CD depicts membranes with high flux (around 700 LMD), while the line CD depicts membranes with high salt rejection, and low flux,which may be used as a tight RO membrane for the removal of low molecular weight solutes like dissolved inorganic salts.

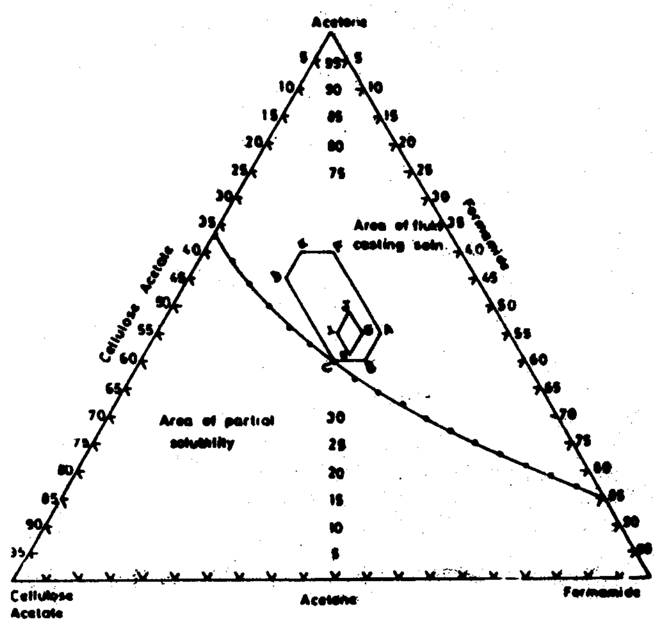

FIG.1 TERTIARY PHASE DIAGRAM FOR OPTIMISING MEMBRANE CASTING SOLUTION COMPOSITION.

Therefore, the area formed by AFDC in Fig.I, represents the limiting composition of the three components i.e., CDA. A, and DMF,which could be utilized for the development of membranes for useful applications. Any casting composition outside the area of AFDC, membranes will give poor performance, in terms of solute rejection, and permeate flux, which may not be economically attractive.

From the triangular phase diagram, it is seen, that UF type of membranes could be made from CDA, when it is around 20-23 %(keeping content of DMF to 28-32%, giving salt rejection of 70-80 %, and 640 lit/m^2/hr(LMH) permeate flux). Similarly, RO membrane may be made if the CDA content is reduced from 30 % to 25 %(along the line IH),whereby membranes of high solute rejection (90-95 %), and moderate permeate flux of 520 LMH is produced.

Therefore, optimal composition may be presented as follows:

UF membrane: CDA-22.50, DMF-40, Acetone-47.50, all figures in weight %,
RO membrane: CDA-25.00, DMF-30, Acetone-45.00, all figures in weight %.

CDA based membranes, evaluated and made under optimal casting conditions (as per the triangular phase diagram, presented in Fig.I),have been used in the treatment of kraft and sulfite spent liquor, and the results in terms of permeate flux, and % rejection of Lignin, under varying feed pressures, are depicted in Fig.3.

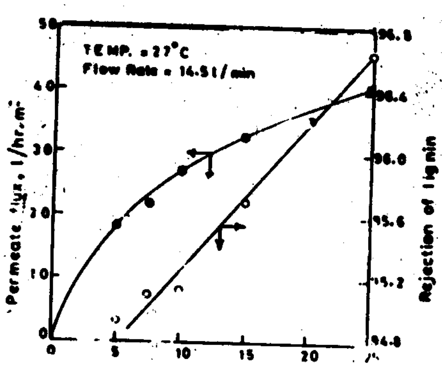

FIG.3 VARIATION OF PERMEATE FLUX, l/hr. m^2, AND REJECTION OF LIGNIN WITH PRESSURE ACROSS THE MEMBRANE (CDA BASE)
System = Pulp and Paper mill effluent 821 ppm ligni
UF membrane cut-off = 500
Spiral-wound membrane area = 2.8 m^2

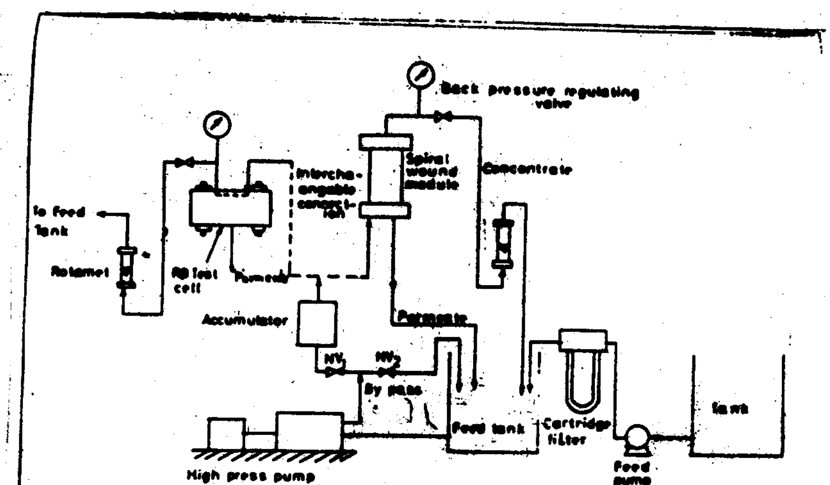

FIG2... TESTING LOOP FLOW SHEET

Results indicate, that, Lignin rejection(which is associated in the removal of colour in BL) could be maintained to the level of 95 % to 97%, with fairly good permeate flux of 28-30 LMH at 10 Kg/cm^2 feed pressure with UF membrane having molecular weight (MW) cut-off of 500. Small amount of lignin permeation through the membrane is associated with low MW fractions of Lignin, which is normally present in BL in polydisperse conditions having wide MW range of the Lignin fractions.

Experimental results on flux declining of diluted BL(equivalent to the Decker effluent of Pulp Mill) at different TDS concentration(Ranging from 0.1-0.70 % TDS), at different feed pressures (Fig. 4), indicate insignificant amount of flux drop, when the feed pressure is maintained to 15 Kg/cm^2. Higher permeate flux drop at higher feed pressure may be attributed to compression effect to the gel polarized macromolecular solution at the membrane interface, whereby impact of higher driving force (in terms of higher feed pressure) is counterbalanced by increased resistance to the mass transportation across the membrane.

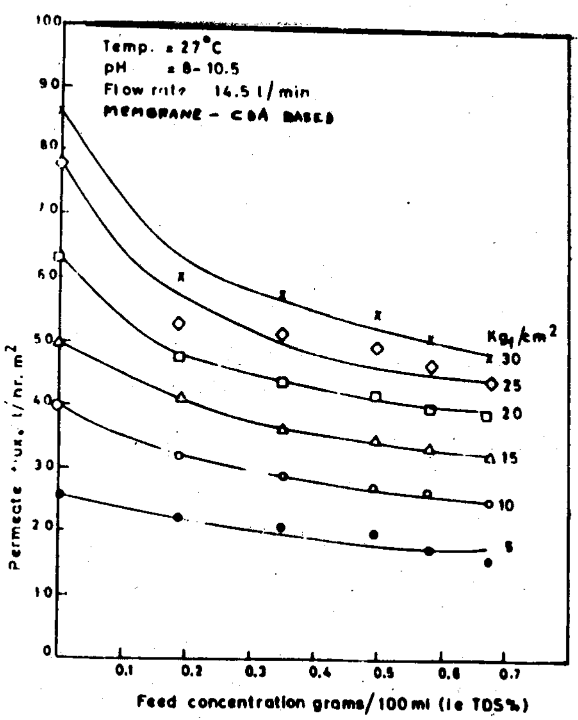

FIG.4 VARIATION OF PERMEATE FLUX WITH FEED TDS CONCENTRATION

System = Pulp and Paper Mill effluent
UF membrane cut-off = 500
Spiral - wound membrane area = 2.8 m^2

Further studies, carried out on the recycling characteristics of Decker effluent treatment by UF process (measured in terms of % colour rejection and % soda recovery from Decker effluent feed), are presented in Fig. 5. It indicates the possibilities of recycling of the Docker effluent (in the form of permeate flux at the level of 85-90 % of Decker effluent feed), to Pulp washing, whereby 35-45 % of the total Soda present in the effluent, could be recovered, along with controlling of the pollution load from the Decker effluent stream. Concentrate stream from the UF treatment of Decker effluent (around 10-15 % of the feed) may be recycled to the multi-effect evaporation unit (at about 8-10 % TDS concentration), thus giving rise to zero effluent discharge from the Pulp washing operation, which is normally associated with 25-30 % of the total pollution load from an integrated Pulp and Paper Mill.

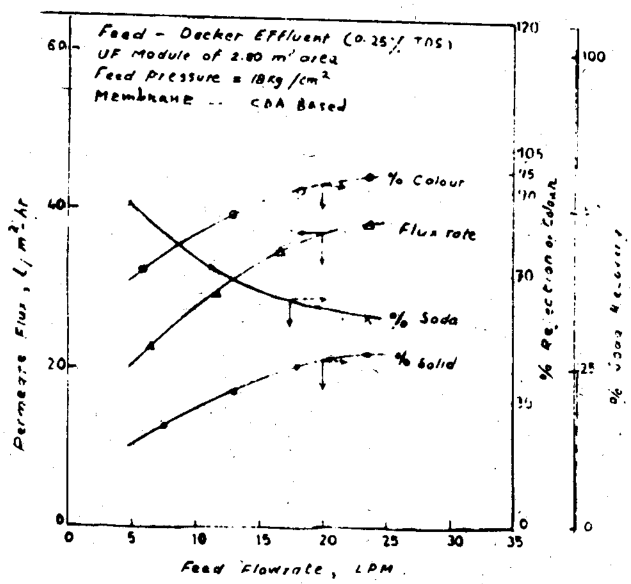

FIG 5 IMPACT OF FEED FLOWRATE ON PERMEATE FLUX AND % REJECTION AND % RECOVERY OF SODA.

Further experimental investigations have been carried out on the development of non-cellulosic UF membrane, based on indigenously available SAN from the GSFG, Baroda, and results in terms of membrane performance, under different casting conditions, are presented in figures 6,7 and 8.

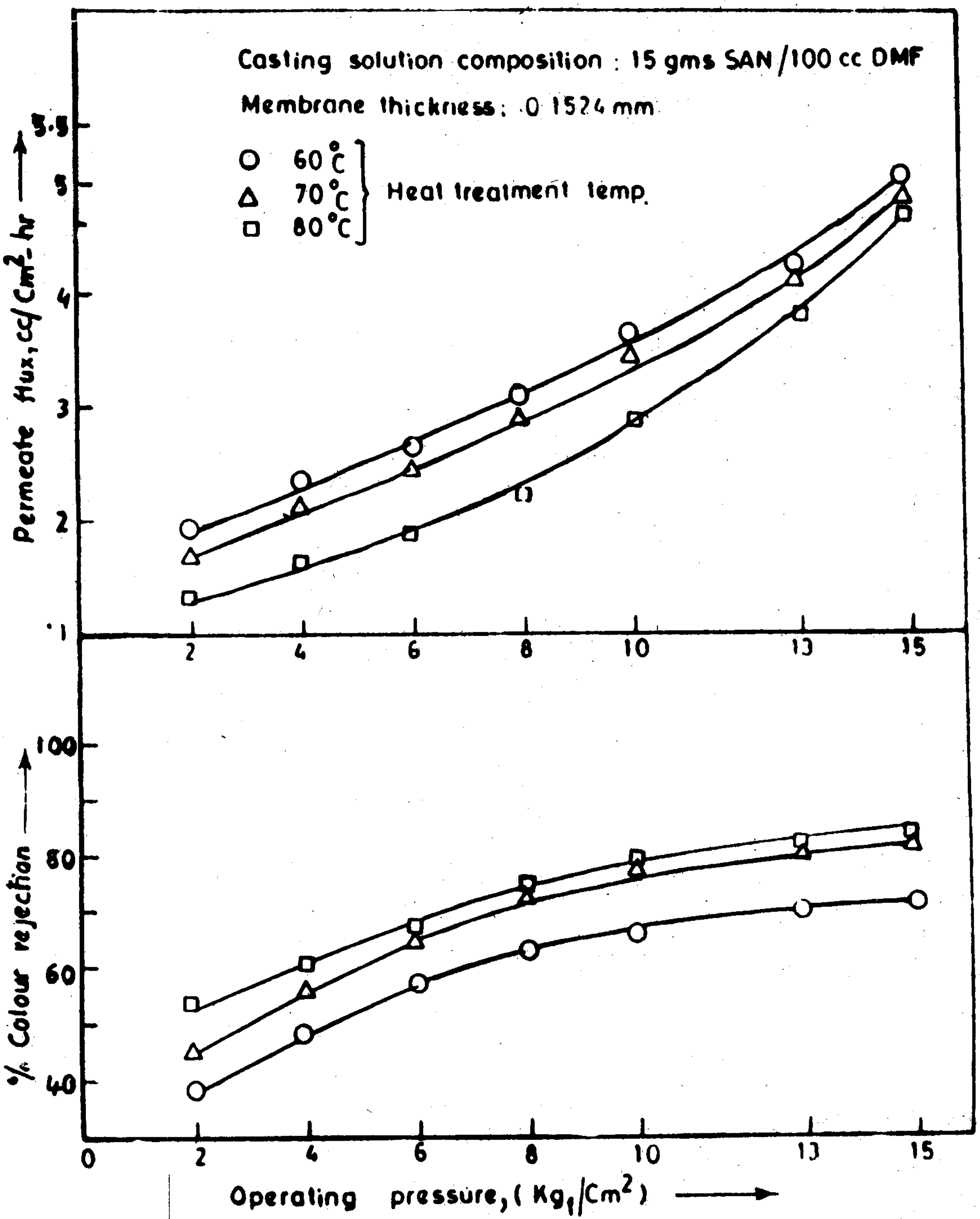

FIG. 6. VARIATION OF PERCENTAGE COLOUR REJECTION AND PERMEATE FLUX WITH HEAT TREATMENT TEMPERATURE (SAN Membrane)

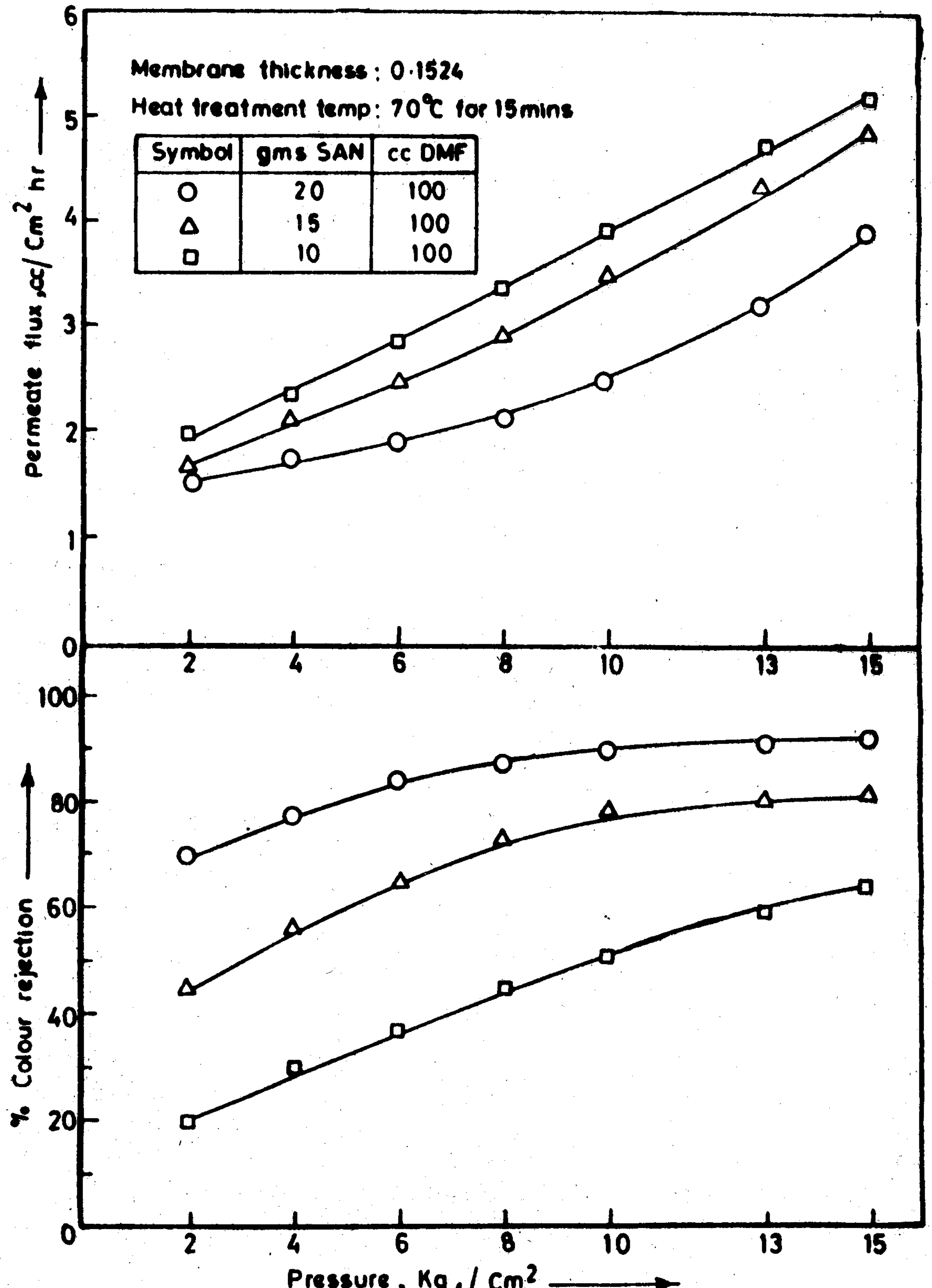

FIG. 7. VARIATION OF PERCENTAGE COLOUR REJECTION AND PERMEATE FLUX WITH CASTING SOLUTION COMPOSITION (SAN membrane)

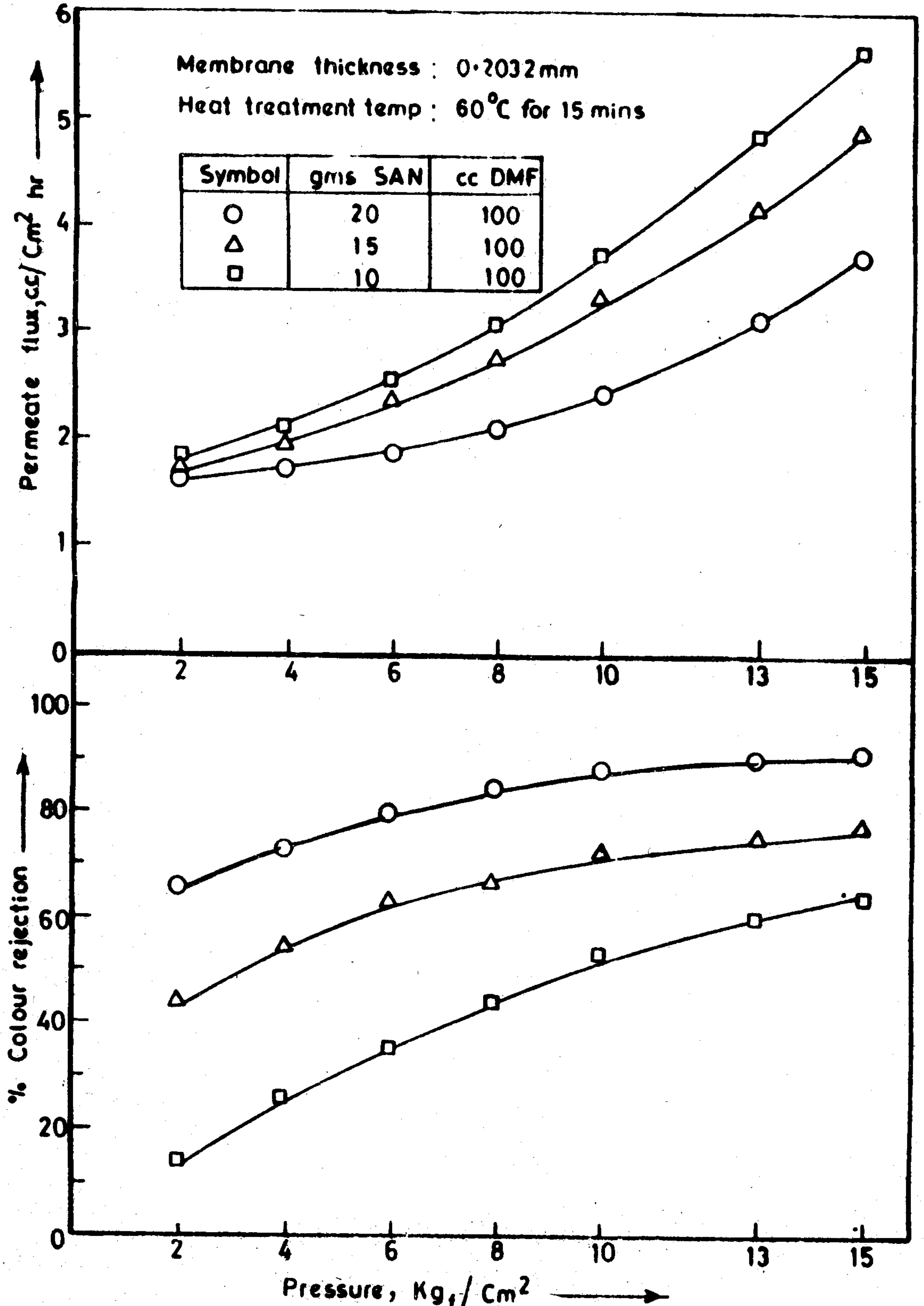

FIG. 8. VARIATION OF PERCENTAGE COLOUR REJECTION AND PERMEATE FLUX WITH CASTING SOLUTION COMPOSITION (SAN membrane)

Results, carried out with spent sulfite liquor at about 2.5 % TDS concentration, indicate, that, high permeate flux (around 3.50 cc/cm^2-hr i.e., around 35 LMH) and % colour rejection of 88-92, may be obtained with SAN based membranes, when % polymer content is taken to the level of 20 g per 100 cc of DMF solvent (Fig.7).

There is a significant impact of annealing temperature during casting of membrane, on permeate flux, and colour rejection (Fig. 6), and depending upon requirement, it could be optimized to the level of 70°-80°C For the enhancement of membrane performance at higher temperature at pH levels of 2-4, and 8-11, thermal stability and pH resistance of the SAN based membranes have been evaluated, by membrane performance estimation, after keeping the membranes in highly acidic, and highly alkaline solutions, at different temperatures (ranging from 50-60°C), for one month. Preliminary investigations indicate, that, SAN membrane stability could be maintained with the pH range of 2-4, and 8-11, at elivated temperatures of 50°C, without significant dropping of pure water permeability (PWP), and % colour rejection.

Further work is in progress on membrane performance evaluation on long-range basis on the feed pretreatment requirement based on MFI (developed at the IIT-Bombay), and on the separation, purification, and recovery of Lignosulfonates from spent sulfite liquor, with the help of UF-coupled Diafiltration process.

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