White Water System Closure by Ultrafiltration Membrane

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ABSTRACT:-- Membrane filtration is one of the separation processes currently used in the pulp and paper industry. The rising demand of environmental protection, energy saving and recovery of valuable products has accelerated the application of membrane filtration in many industries. Membranes are already successfully employed on a commercial scale for treating E-stage effluent from a bleaching plant of pulp and paper mill. Treatment of paper machine white water and concentrating spent liquor from chemi-mechanical pulping are the new promising applications for membrane usages. In this research, an attempt was made to develop ultrafiltration membrane for treatment of excess white water to close the system in order to reduce the effluent. Membranes having different pore sizes were made from polyethersulfone by phase inversion technique. These membranes were tested for laboratory made feed solutions of various concentrations of clay and SBR. A very sharp flux reduction was observed immediately after the start of the experiment for all the membranes studied. The higher the feed concentration, the higher was the flux reduction. For 0.1% feed concentration, flux reduction in first 15 minutes of run was in the range of 25-50% while it was 95-97% for 30% feed concentration. Flux was substantially higher when SBR was not present in the feed. Flux reduction was attributed to pore clogging and cake layer formation over the membrane. In a Scanning Electron Microscope (SEM) picture of the cross-section of a used membrane, a distinct layer of foulants over the membrane could be seen. X-ray dispersive image of this layer revealed that it was mainly made of clay. Resistances contributed by this layer and by the blocked pore were very high and controlling the permeate flux. Final permeate fluxes were very similar for all the four membranes used irrespective of the initial permeate fluxes. Separations of both clay and SBR were very high. Permeate obtained from the membrane was very clean and can be used for most of the applications on the paper machine where fresh water is currently used.

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Pulping and papermaking operations use large amounts of fresh water which becomes contaminated during the use and is discharged as effluent. The discharge of the harmful materials needs to be limited in order to protect the environment and to comply with the government regulations. Continuous progress has been made by the pulp and paper industry in reducing the water use. In a survey, it was found that in 1988, compared to 1959, 70% less water was required to produce one ton of paper (Miner and Unwin, 1991). Water use reduction has been done, primarily, by closing up the water system. System closure, however, results in an increased concentration of suspended, dissolved and colloidal materials in the white water of a paper machine resulting in poor quality and operational problems.

Since the introduction of the membrane filtration about thirty-five years ago, the possibilities of using this process in various industries including the pulp and paper industry have been strongly investigated. The discovery of the asymmetric cellulose acetate membrane by Leob and Sourirajan at the beginning of the 1960'ies is regarded by everyone as the first and decisive milestone concerning the development of the ultrafiltration and reverse osmosis membrane processes. With the development of new pH and temperature resistant membranes, the uses of membranes are ever increasing.

PRINCIPLE OF REVERSE OSMOSIS AND ULTRAFILTRATION

A membrane acts as a barrier to flow, allowing selective passage of a particular species (solvent) while other species (solutes) are retained partially or completely. Solute separation and permeate flux (solvent) characteristics of membranes depend on the membrane material selection, the preparation procedures and the operating condition. The driving force for transport across the membrane in both the reverse osmosis and the ultrafiltration processes is a pressure differential.

MEMBRANE APPLICATIONS IN PULP AND PAPER INDUSTRY

Membrane filtration is one of the separation processes used in the pulp and paper industry. The rising demand of environmental protection, energy saving and recovery of valuable products has accelerated the application of membrane filtration in many industries. Paleologou et al. (1994) discussed the membrane applications in the pulp and paper industry with respect to technical feasibility, process integration, and the economics of the mill system. Since Bansal had presented in 1977 ultrafiltration and reverse osmosis as efficient methods of treating process water form pulp and paper and food industries, technology of the field has steadily progressed. Followings are some of the applications of membrane separation processes in the pulp and paper industry.

BLEACH PLANT EFFLUENT

The two most harmful bleach plant effluents are acidic chlorination filtrate from chlorination stage (C-stage) washer and the alkaline first extraction filtrate from E-stage washer, as most of the chlorinated substances originate from these two stages.

a. E-Stage Effluent

Most of the published work on membrane applications in the pulp and paper industry, have focused on E-stage effluent treatment. E-stage effluent is very well suited for ultrafiltration process because of its comparatively small volume and high-molecular-weight-substances in it. There are several ultrafiltration plants of commercial scale for this application Sanyo Kokusaku Pulp Mill and Taio Paper Co. Japan) (Jonsson, 1987). In a typical plant, E-stage effluent contributes 140-150 kg of color and 5-6 kg of BOD_7 per ton of pulp. Ultrafiltration of this effluent can reduce TOCl by 60-70% (Jonsson, 1987), COD by 50-80%, AOX by 90% (Jonsson, 1989), color by 90% and BOD_7 by 25-50% (Lundahl and Monsson, 1980). The overall effect of ultrafiltration of E-stage effluent on the total mill effluent will be 65-70% reduction in color, 40% reduction in COD and 10% reduction in BOD_7.

b. C-Stage Effluent

C-stage effluent contains mostly low-molecular-weight-substances. This makes C-stage effluent difficult to be treated with ultrafiltration. The large amount of effluent is a factor that makes the membrane treatment of C-stage even more difficult (Jonsson and Petersson, 1989). Most of the substances in the C-stage effluent are too small to be retained, even by a very dense ultrafiltration membrane. Considering experimental results of both laboratory and pilot scale, it seems impractical to apply ultrafiltration to chlorination stage effluent on a commercial scale. Jonsson and Petersson (1988) conducted experiments by mixing C-stage and E-stage effluents in their actual proportions, however results were not very encouraging.

PAPER MACHINE WHITE WATER

The constant search for more environmentally friendly paper mills coupled with the necessity to increase process efficiency and cost reduction has led to the closure of the white water circuits. Treatment of paper machine white water by membrane processes is very promising (Jonsson and Wimmerestedt, 1985). The white water system of an integrated pulp and paper mill accounts for between 15 to 25% of the water consumed. The first full-scale reverse osmosis installation in pulp and paper industry was put into operation in 1972 at Green Bay Packaging Inc., USA, (Nelson et al., 1973; McLeod, 1974) for white water treatment. This installation formed an integrated part of the closed white water system of the mill for couple of years before it was put off due to mill expansion and consequent changes in the white water requirements.

Jonsson and Wimmerestedt (1985) achieved a separation of 99% for suspended solids in paper machine white water with laboratory scale ultrafiltation process. Sierka et al. (1994) tried commercially available membranes (microfiltration, ultrafiltration, nanofiltration and low pressure reverse osmosis) for processing three white waters collected from three different kraft paper mills. It is to be noted that the three white water collected varied significantly in their molecular weight distribution of the organic compounds. Membranes used gave very varied performance because of the variations in white water. Nuortila-Jokinen et al. (1995) tested five ultrafiltration and three nanofiltration membranes on laboratory scale. The best ultrafiltration permeate flux was over 200 l/m^{2}h, however the separation was rather modest.

COATING PLANT EFFLUENT

Paper coatings are composed of pigments, binders and flow modifiers. Typically a mill wastes 3 to 5 of the daily coating. Ultrafiltration of coating plant effluent has three advantages. First, no coating effluent is released. Second, the concentrated effluent can be recycled. Third, the permeate can be used as a wash water. Pichon et at. (1992) had demonstrated that the ultrafiltration system was technically and economically feasible for coating plant effluent. Quite high fluxes were obtained with no loss of pigment and negligible loss of binder while concentrating coating waste from 10% to 60% by ultrafiltration membrane (Woerner and Short, 1991). The coating raw materials recovered in the concentrate retained their original properties. Stridsberg et al. (1992) had achieved a flux of 200 l/m^{2}h at a working pressure of 20 to 28 psi while concentrating coating plant effluent from 0.5% to 46% in a CR-filter system. However, a flux reduction was observed because of severe fouling due to clogging of membrane pores.

OTHER USAGES OF THE MEMBRANE IN THE PULP AND PAPER INDUSTRY

- Water removal by reverse osmosis (RO) from black liquor prior to evaporation, in order to reduce steam cost or to expand evaporation capacity (Pepper and Tingle, 1983).
- Recovery and purification of valuable by-products by fractionation with ultrafiltration (Anon., 1982).
- Zero effluent mechanical pulp mills using ultrafiltration and reverse osmosis technology (Jantunen et al., 1992; Paleologou et al., 1994).
- Incremental kraft recovery capacity and caustic soda production through the electrolysis of a fraction of black liquor.
- Production of bleaching chemicals using bipolar membrane electrolysis (Paleologou et at., 1992).

BENEFIT OF CLOSING WHITE WATER SYSTEM

Closing of the white water system is cost saving (Springer et al., 1985). When the quantity of solids containing effluent leaving the white water system is reduced, the need of fibrous material reduces and, hence, the cost of raw materials also falls. A reduction in the use of fresh water lowers the cost of fresh water treatment. In closed white water system, temperature of white water rises and its viscosity decreases. With reduced viscosity, drainage of water from web sheet is easily facilitated. Paper web enters the drying part of the paper machine hotter than before and hence requires less drying energy (Norman, 1975). Most important indirect benefit of white water closure, is the reduced pollution load on recipient lake or river. Closed cycle mill design can offer numerous other advantages, including freedom to the site in areas with inadequate water resources and the protection from future cost to meet tightening efflent regulations.

In most of the studies commercially available membranes have been tested to whether or not they suit for a specific application in the pulp and paper industry. Not much efforts have been made to develop a membrane for waste water treatment from a pulp and paper mills. The basic objective of this research was to develop a synthetic polymeric ultrafiltration membrane to treat excess white water from paper machine and effluent from coating plant section of a pulp and paper mill and also to study the mechanism of the fouling, which is one of the main constraint for this application.

EXPERIMENTAL

Materials and Membrane Making

Polyethersulfone (PES, Victrex 4100P) supplied by Imperial Chemical Industries was used for the preparation of ultrafiltration (UF) membranes. Asymmetric Membranes were made by phase inversion technique using polymer casting solutions of different concentrations (10,12, 15 and 20 wt.%) of PES in N-methylpyrrolidone (NMP) solvent. Polyvinlypyrrolidone (PVP), an additive, was added to increase the membrane flux and at the same time to enable the membrane casting with lower PES concentrations in the casting solution. The ratio of PES and PVP in casting solution was kept one by weight (Lafreniere et al., 1987). Membranes were cast at room temperature and gelled in ice cold water of about 4°C. They were immersed in cold water for 40 minutes before storage in distilled water till the use. These laboratory made ultrafiltration membranes were designated as 10U, 12U, 15U and 20U. The first two digits in the above nomenclature indicate the PES concentration in the casting solution.

Preparation of Feed Solution

Synthetic feed solutions were made in the laboratory to represent the white water and the coating plant effluent. The feed spolutions contained clay (Ultra Cote, Engelhard, particle size ~80-82% <2 μm) and Styrene Butadiene Rubber (SBR, CP620NA, Dow Chemicals, particle size ~1750 A, 50% w/w emulsion). The ratio of clay and SBR was kept at 100/15 by weight. Different feed concentrations were studied for permeate flux and solute separation for the membranes made in the laboratory.

UTRAFILTRATION EXPERIMENT

Ultrafiltration experiments were conducted by using laboratory test cells with an effective area of 13.2 cm^2, details of which were described elsewhere (Sourirajan and Matsuura, 1985). All the experiments were conducted at the operating pressure of 50 psig at room temperature. The feed solution was circulated through the feed chamber of permeation cell at a flow rate of 0.7 US gal/min. (2650) ml/min.). Ultrafiltration experiments were conducted with a constant feed concentration and also with an increasing feed concentration. In the experiment with constant feed concentration, both permeate and retentate were recycled to the feed tank. While in the other experiment, feed concentration was gradually increased by collecting the permeate in a separate tank. For each experiment pure water permeation (PWP) and the permeate flux (PF) in the presence of solute, both in l/m^{2}h, were measured. The permeate flux was also measured on intervals over the operational period. Both PWP and PF were converted to the value at 25°C by using density and viscosity data of water. Solute separations for both clay and SBR were calculated by using the equation

$$F = \frac{Cf - Cp}{Cf} \times 100 \qquad (1)$$

where f is the solute separation and Cf and Cp are the feed and the permeate concentrations of the solute. Sample of feed solution was placed in a crucible in a oven at 105°C for 8 hours to find out the total weight percent of clay and SBR. Crucible with dried clay and SBR was further placed in muffle furnace at 925°C for 8 hours. SBR was oxidized at 925°C and only clay was left in the crucible. SBR contents in the permeate were measured in terms of total organic carbon (TOC) by total organic carbon analyzed (DC-190, Folio Instruments).

RESULTS AND DISCUSSIONS

All the flux and solute separation data are the average of three data points from three coupons of a same membrane in three permeation cells. Pure water permeation data are the average of 10 data points.

PURE WATER PERMEATION OF THE UF MEMBRANES

Each membrane was compacted at 80 psig for 5 hours before starting pure water permeation (PWP) measurement at 50 psig. Pure water permeation means the water flux through the membrane when the feed is pure water. As expected, PWP was higher for the membrane made from a casting solution having lower PES concentration. For example, PWP was the highest for a 10U membrane (1025.34 l/m²h) while it was the lowest for a 20U membrane (530.91 l/m²h). It is to note that the pore size of the 10U membrane was the largest while that of the 20U membrane was the smallest. PWP data for all the four membranes (10U, 12U, 15U and 20U) are shown in Figure-1.

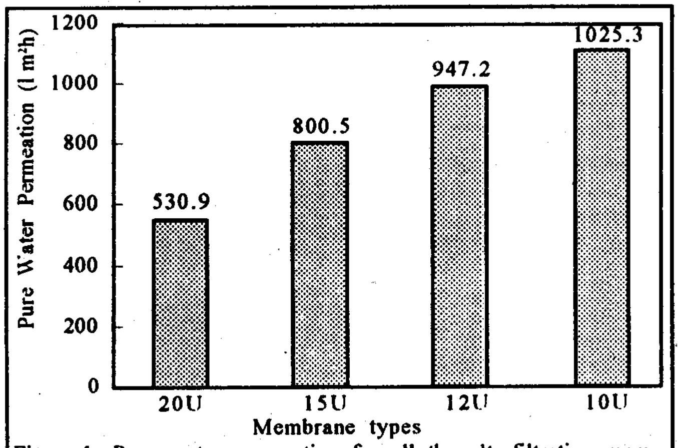
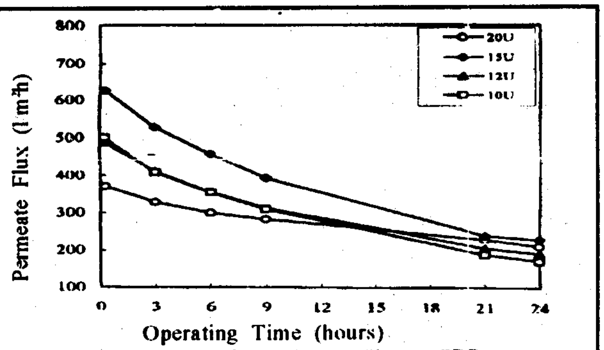


Figure-1. Pure water permeation for all the ultrafiltration membranes used

PERMEATE FLUX OF THE UF MEMBRANES

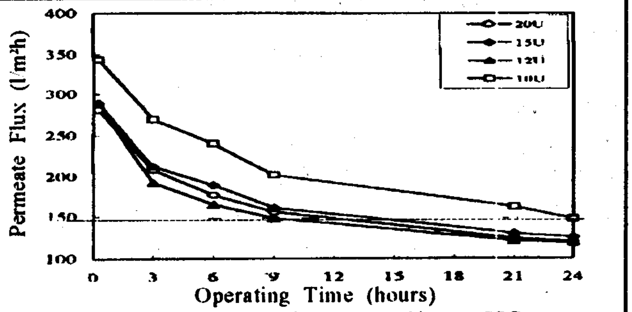
a. With the Constant Feed Concentration

Feed solutions with different concentrations (0.1, 1, 10, 20 and 30 wt.%) of clay and SBR (clay/SBR = 100/15) were used to test the performance of the membranes in terms of the permeate flux and solute separation. All the experiments were conducted for 24 hours. Tremendous flux reduction was observed in first 15 minutes of the experiments for the all the membranes tested and also for all the feed concentrations. Permeate fluxes for the membranes over a period of 24 hours are shown in Figure 2 for different feed concentrations. Flux

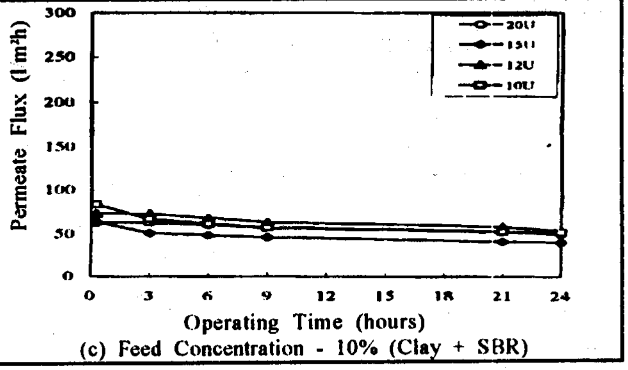


(a) Feed Concentration - 0.1% (Clay + SBR)

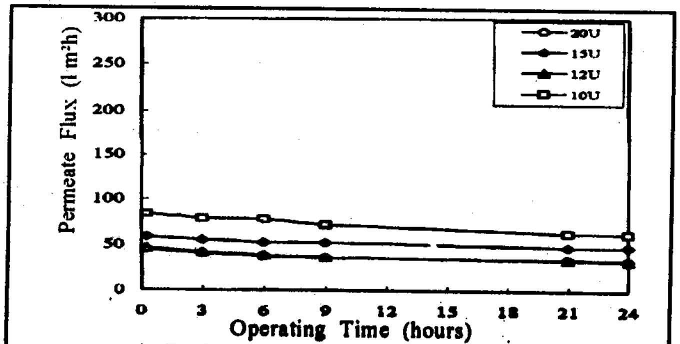
Figure-2. Permeate flux over a period of 24 hours of operation for all the four membranes with feed concentration of (a) 0.1%, (b) 1%, (c) 10%, (d) 20% and (e) 30% of clay and SBR (Clay/SBR = 100/15)



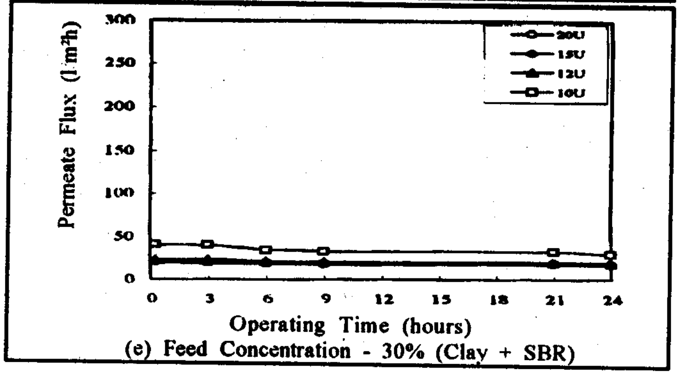
(a) Feed Concentration - 1% (Clay + SBR)



(c) Feed Concentration - 10% (Clay + SBR)



(d) Feed Concentration - 20% (Clay + SBR)



(e) Feed Concentration - 30% (Clay + SBR)

reduction was more severe for more porous membranes such as 10U and 12U for all the feed solutions. Flux reduction is defined as

$$FR = \frac{PWP-PH}{PWP} \times 100 \qquad (2)$$

where FR is the flux reduction. Although pure water permeations and initial fluxes in the first 15 minutes were very different, the final fluxes after 24 hours of operation were similar for all the membranes studied at a given feed concentration. This was especially true for lower feed solution concentration like 0.1% and 1%. Table 1 shows flux reductions with time at a feed concentration of 1% for all the four membranes. Flux reductions with time for all the five feed solutions are shown in Figure-3 for 20U membrane. It can be seen from Figure-3 that the flux reduction was the highest for 30% feed concentration while it was the lowest for 0.1% feed concentration. With the feed concentrations of 10%, 20% and 30%, the initial flux reduction was 85-95% and there was not much change in the fluxes after 15 minutes. Final permeate flux for 15U membrane at the end of 24 hours operation was 225 l/m²h for 0.1% feed concentration and was only 30 l/m²h for 30% feed concentration. It is important to mention that no attempt was made to clean the membranes during the operation.

Table-1

Flux reduction with time for all the four membranes with 1% feed concentration of clay and SBR (clay/SBR = 100/15)

	Flux Reduction %			
Time (hrs)	20U	15U	12U	10U
0.25	52.6	63.0	68.1	68.0
3	64.8	72.8	78.7	74.9
6	70.2	75.8	81.7	77.6
9	73.7	79.4	83.8	81.2
21	79.1	83.4	86.6	84.9
24	79.8	84.0	86.8	86.3

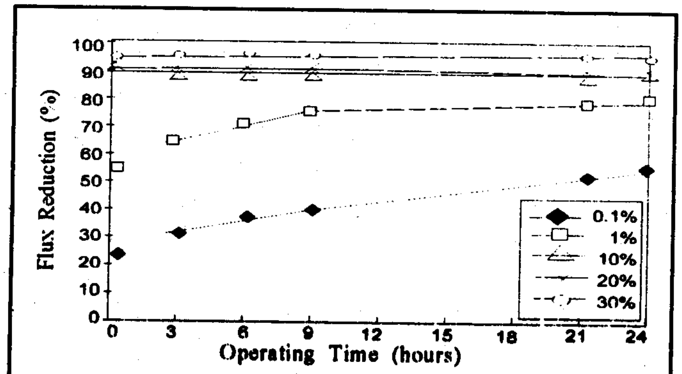


Figure-3. Flux reduction with time for all the feed soluions (0.1%, 1%, 10%, 20% and 30%) with 20U membrane

b. While Concentrating the Feed Solution

Feed solution of 1% clay and SBR was concentrated by collecting permeate in a separate tank until the feed concentration became 30%. The permeate fluxes with time are presented in Figure-4. Flux decline was very steep in the beginning and leveled

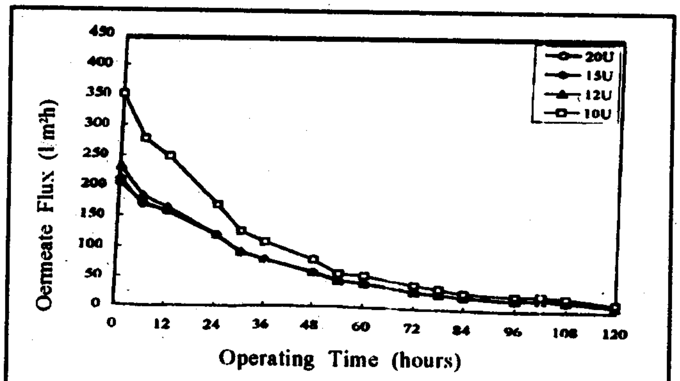


Figure-4. Permeate fluxes with time while concentrating the feed solution (clay + SBR) from 1% to 30% for all the four membranes used

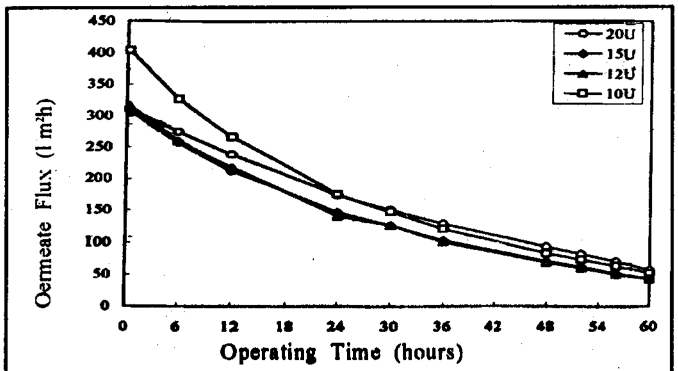


Figure-5. Permeate fluxes with time while concentrating the feed solution (only clay) from 1% to 30% for all the four membranes used

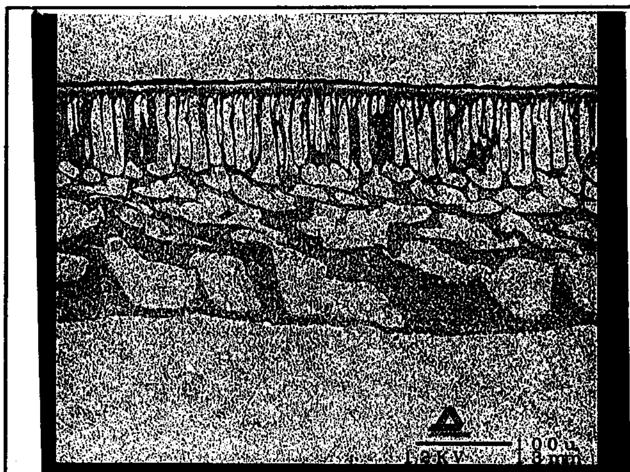
off later. Final permeate fluxes were similar for all the four membranes used. Similar experiment was also performed with a feed solution containing 1% clay (without SBR). The changes in the permeate fluxes with time during this experiment are shown in Figure-5. In the latter experiment, it took only 60 hours to reach 30% concentration form the initial 1%, while in the experiment with clay and SBR it too 120 hours. Final permeate fluxes were only in the range of 10-12 l/m^{2}h when SBR was present in the feed while they were 44-55 l/m^{2}h in the absence of SBR. This could be understood by considering SBR as a binding material which enhances the clay deposition on the membrane surface. The presence of SBR also makes the clay layer more dense and thus increasing the resistance to the flow of the permeate.

MEMBRANE FOULING

Initial flux reduction was very steep for all the membranes studied. As mentioned earlier, higher was the flux reduction for higher feed concentration. Flux reduction could be attributed to the following two effects.

1. Partial or complete pore clogging
2. Cake layer formation over the membrane

As soon as an experiment was started, pore blocking and cake layer formation over the membrane started to occur. It was speculated that it was pore blocking which took place in the very initial stage of the experiment followed by a clay layer formation. It was observed that the final flux for all the four membranes used were very similar for a given feed concentration. This indicates that the total resistances (combined resistances of the blocked pore, the cake layer and the membrane matrix) were very similar for all the membranes used. The resistances due to the polymeric membrane matrix were quite different for different membranes as indicated by different PWP values. Resistances due to the blocked pore and the cake layer were very high compared to that of membrane matrix and controlling the permeate flux. Nuortila-Jokinen et al. (1995) also found that permeate flux was independent of memberane types (molecular weight cut-off point and pore size). They attributed the flux reduction to the adsorption of the foulants on the membrane surface and to the plugging of membrane pores. A scanning electron micrograph of the cross-section was taken for a 20U membrane which was used for a ultrafiltration experiment for 24 hours. The micrograph clearly indicates a distinct layer of the foulants over membrane surface (Figure-6). X-ray dispersive images of this layer (Figure-7) showed that it



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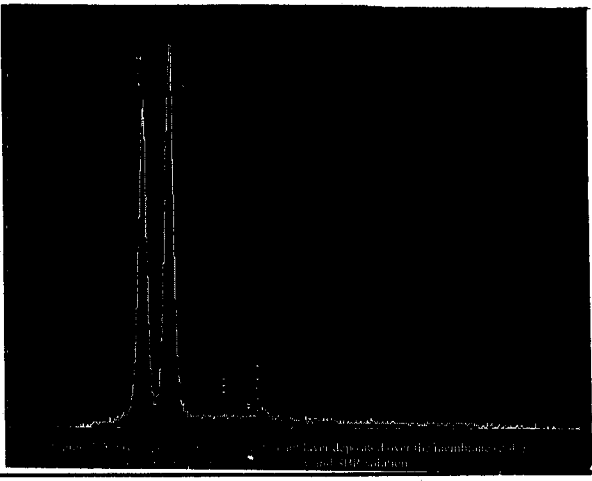

[illegible] layer deposited over the membrane [illegible] and SBR solution was primarily made of aluminum and silica. This indicates that the foulants layer was mainly made of clay thickness of which was around 5 μm.

SOLUTE SEPARATION

Solute separation for clay particles was nearly equal to 100%. There was no trace of clay particles in the permeate as permeate was clear. SBR concentration in the permeate was dependent on the feed concentration, although its separation was always very high (more than 97%) for all the membranes studied and for all the feed solutions tested. Figure-8 shows the separation of SBR which was nearly 100%. These results are in agreement with that of Woerner and Short (1991). High separation could be expected because of large particle sizes of both clay and SBR compared to the size of the pores of the membranes used in this study. It is evident from these results that the separation of both clay and SBR are more than desired. For recycling of permeate even lower separation could be accepted.

CONCLUSIONS

Ultrafiltration is a very promising method to treat white water in order to close the water circuit. Water recovered from ultrafiltration is very clean and can be used in most of the applications in paper machine section where fresh water is currently used. The major drawback of the process for this particular application is the flux decline over the time due to fouling. A very sharp flux reduction was observed immediately after the start of the experiment for all the membranes studied. Flux reduction was attributed to the resistances of blocked pore and cake layer formed over the membrane. Flux reduction was considerably higher when SBR was present in the feed solution. Final permeate flux was dependent on the feed concentration but was independent of the characteristics of the membrane used in this study. Foulants layer was mainly made of clay.

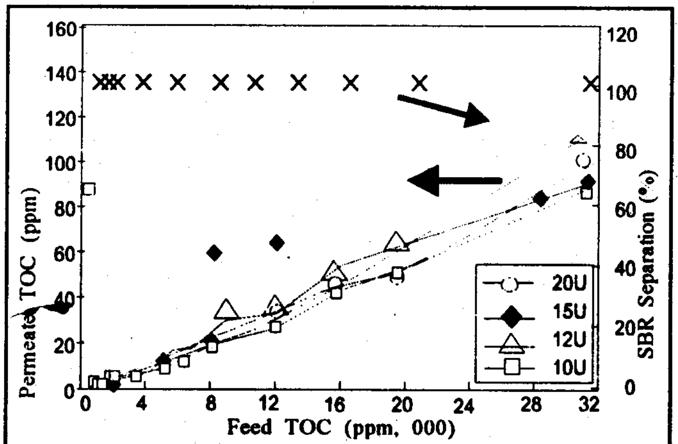

Figure-8. SBR contents in feed and permeate (in term of TOC) and also solute (SBR) separation for all the four membranes while concentrating the feed solution of clay and SBR from 1% to 30%.

REFERENCES

Anon, "How to filter out a better lye", Pulp Paper Int., 24 : 40(1982)

Bansal, I.K., "Progress in developing membrane systems for treatment of forest products and food processing effluents", AICHE Sym. Series, 73(166): 144(1977).

Jantunen, E., G. Lindholm, L.M. Lindroos, A. Paavola, U. Parkkonen, R. Pusa, and M. Soderstrom, "The effluent free newsprint mill", Paper and Timber, 74 : 41(1992)

Jonsson, A.S. and E. Petersson, "Treatment of C-stage and E-stage bleaching plant effluent by ultrafiltration", Nordic Pulp Paper Res. J., 4(3):184(1989).

Jonsson, A.S. and E. Petersson, "Treatment of C-stage and E-stage effluents from a bleach plant using a ceramic membrane", Nordic Pulp Paper Res. J., 3(1) : 4(1988).

Jonsson, A.S. and R. Wimmerstedt, "The application of membrane technology in the pulp and paper industry", Desalination, 53: 181(1985).

Jonsson, A.S., "Treatment of effluent from alkali extraction with ultrafiltration and reverse osmosis", Nordic Pulp Paper Res. J., 4(1) : 33(1989)

Jonsson, A.S., "Ultrafiltration of bleach plant effluent", Nordic Pulp Paper Res. J., 2(1): 23(1987).

Lafreniere, L. Y., F. D. F. Talbot, T. Matsuura and S. Sourirajan, "Effect of polyvinylpyrrolidone additive on the performance of polyethersulfone ultrafiltration membranes", Ind. Eng. Chem. Res., 26: 2385 (1987)

Lundahl, H. and I. Mansson, "Ultrafiltration for removing color form bleach plant effluent", Tappi, 63(4) : 97(1980).

McLeod, M., "Mill achieves maximum reuse of water with reverse osmosis", Pulp & Paper, 48(11):62(1974).

Miner, R. and J. Unwin, "Progress in reducing water use and waste water loads in U.S. paper industry", Tappi, 74(8):127 (1991).

Nelson, W.R., G.O. Walraven and D.C. Morris, "Process water reuse and upset control modification at an integrated NSSC mill", Tappi, 56(7):54(1973).

Norman, N.E., "Reuse of water in the pulp and paper industry", Appita, 29 : 36(1975).

Nurotila-Jokinen, J.,P. Martin and M. Nystrom, "UF and NF as internal methods for the make-up waters of a neutral MFC machine", Proceedings of Euromembrane, 1995, I-521(1995).

Paleologou, M., J.N. Cloutier, P. Ramamurthy, R.M. Berry, M.K. Azarniouch and J. Dorica, "Membrane technologies for pulp and paper applications", Pulp Paper Can., 95(10):T386 (1994).

Paleologou, M., P-Y. Wong and R.M. Berry, "A solution to caustic/ chlorine imbalance: Bipolar membrane electrolysis", j. Pulp Paper Sci., 18(4): J138(1992).

Pepper, D. and J. Tingle, "Reverse osmosis and ultrafiltration for energy conservation and pollution control", Pulp Paper Can., 84(10): T219(1983).

Pichon, M., R. Camatta, G. Tardy and D. Woerner, "Ultrafiltration applied to the treatment of effluents to the paper and paper board coating plants", 1992 Environmental conference, Tappi proceeding, 731(1992).

Sierka, R. A., H.G. Folster and J.J. Avenell, "The treatment of whitewaters by adsorption and membrane techniques", 1994 International Environmental Conference, TAPPI Proceedings, 249(1994).

Sourirajan, S. and T. Matsuura, "Reverse osmosis/ultrafiltration process principles", National Research Council of Canada, 1985.

Springer, A.M., J.P. Dullforce and T.H. Wegner, "The effect of closed white water system contaminants in strength properties produced from secondary fibre, 1985 Tappi Papermaking Conference Proceedings, 1 (1985).

Stridsberg, S., T. Nyberg and L. Robinson, "Recovery of waste coating by ultrafiltration", 1992 Environmental conference, Tappi proceedings, 737(1992)

Woerner, D.L. and J.L. Short, "Recovery of coating losses", 1991 coating conference, Tappi proceedings, 19(1991).