Recovery of water and inorganic chemicals from kraft black liquor using membrane separation processes

Sirshendu De and Prashant K. Bhattacharya*

ABSTRACT: Recovery of water with inorganic compounds in kraft black liquor was studied by pressure carbonation followed by different combinations of membrane separation processes. Experiments were carried out to observe the effect of carbonation on black liquor, in terms of conversion of lignin-bound alkali compounds into carbonate salts. Further, the reaction rate during carbonation was studied and a correlation for decrease of active alkali with time is presented, which is equivalent to a first order rate equation. Different combinations of membrane processes used were (a) ultrafiltration of the carbonated liquor followed by nanofiltration, (b) nanofiltration of the carbonated liquor, and (c) direct nanofiltration of untreated black liquor. Comparisons were made in terms of recovery of the inorganics, quality of the permeate, and permeate flux. Of the three combinations, the first scheme yields higher rejection and better recovery as well as reasonable permeate flux. Recovery was higher for higher feed concentrations.

KEYWORDS: Bibliographies, black liquors, carbonation, filtration, kraft liquors, membranes, pressure, recovering, separation, water, ultrafiltration.

Recovery of valuable inorganic compounds from black liquor (BL) is an integral part of the kraft pulping process. In the conventional process, BL (with 150–160 kg/m^3 total dissolved solids) is concentrated to 600–650 kg/m^3 and then incinerated. The molten inorganic chemicals are then causticized to recover around 85% of sodium hydroxide. This process involves huge losses of water during the concentration step in multiple effect evaporators. Also, organics burnt during incineration cause environmental pollution. Apart from this, the equipment incurs high capital investment and energy cost. For small scale paper mills, black liquor concentration varies from 10 to 80 kg/m^3 total dissolved solids (tds). Sometimes, instead of processing, this BL is discarded as it is, therefore causing more pollution problems, lower efficiency of the adopted process and higher capital investment owing to the loss of valuable inorganics.

In kraft pulping, organics in BL are present mainly in the form of colloidal particles of alkali lignin *(1)*. Sodium compounds are present in free form to a lesser extent and most of them are bound with phenolic hydroxyl groups in the phenyl propane units which are a building block of lignin *(1)*. To achieve higher sodium recovery, sodium bound with alkali lignin should be separated. Pressure carbonation is one such process which lowers pH of the solution, frees the bound alkali and lignin is precipitated *(1, 2)*. Pressure carbonation, facilitated by absorption of carbon dioxide under stirring, was studied by Panda *(3)* to separate silica from green liquor. To control pH and reaction rate to a certain extent, dilute carbon dioxide mixed with air was employed. Basu *(4, 5)* studied carbonation of BL to produce modified green liquor; causticization of produced liquor was studied extensively.

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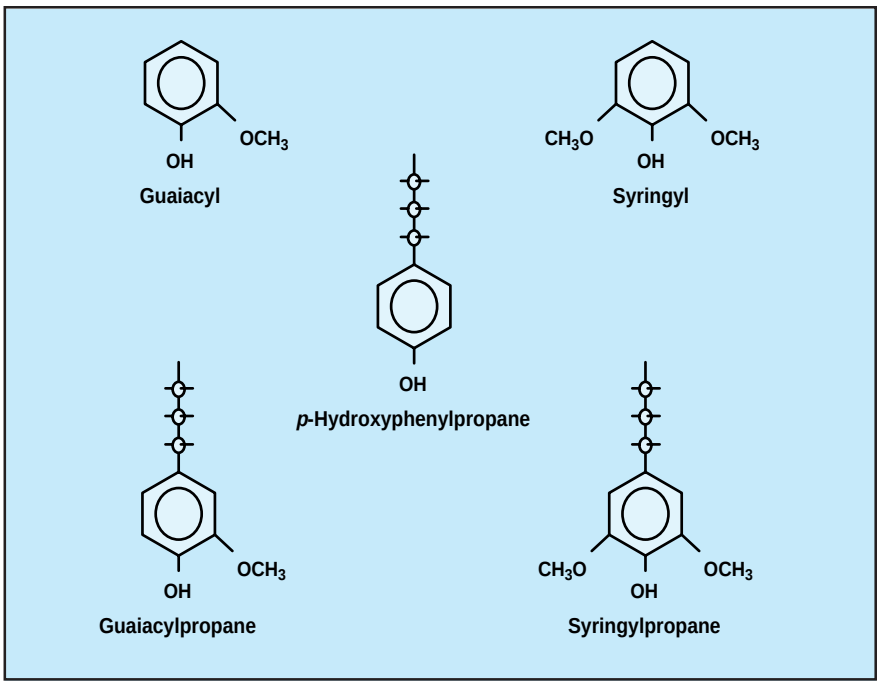
Membrane separation processes are used in the pulp and paper industry for different purposes. Most of the applications are still in the laboratory stage. Ultrafiltration (UF) has been applied to remove suspended solids in white liquor *(6)*. Concentration of spent liquors and bleach plant effluents by reverse osmosis (RO) were extensively studied by Wiley and co-workers *(7–9)*. Jonsson *(6)* reported concentration of spent sulfite liquor from around 150 to 250 kg/m^3 (tds) by RO. Separation of alkali lignin, i.e., fractionation of BL by UF, was also studied *(6, 10, 11)*. Bhattacharya and co-workers *(12-17)* carried out experimental studies and modeling of BL ultrafiltration in stirred and unstirred batch cells. Among the membrane separation processes, electrodialysis has been widely studied to recover sodium compounds from BL. BL in a batch electrodialyzer but at the expense of severe membrane fouling, low current efficiency and higher power consumption. Mishra *et al. (19, 20)* studied BL treatment by batch and continuous electrodialysis. They also observed high recovery but at the cost of higher energy consumption and lower current efficiency. Moreover, BL used was of very dilute concentration less tha 50 kg/m^3 (tds) feed Roychowdhury *(21)* observed only 30-35% solium recovery for a 50 kg/m^3 (tds) feed BL by continuous electrodialysis. He also observed severe fouling of the membrane at higher concentrations. Apart from this, electrodialysis. He also observed severe fouling of the membrane at higher concentrations. Apart from this, electrodialysis is a slow process and it may be difficult to operate in a continuous mode in a running plant.

Several extensive research activities were undertaken to recover inorganics and water or fractionate BL solutions. Every effort was associated with its own shortcomings. Hence, industries are reluctant to implement them. Attempts have also been made in our laboratory *(12-21)* to treat BL. This work is a continuation of the research efforts for a better treatment of BL.

1. Basic units of lignin



The present work has been undertaken in the direction of developing a technology for recovery of water with the inorganic chemicals from BL. The suggested three-steps process is of carbonation of BL followed by UF and nanofiltration (NF). The pressure carbonation was used to separate organics (lignin) from inorganics where inorganics become converted to carbonate salts. The resultant solution was treated by an open UF membrane in cross flow geometry at a low pressure to separate higher molecular weight fractions of lignin in BL. Hence, the premeate of UF may contain almost total sodium compounds and lower molecular weight fractions of lignin. The permeate of UF is then subjected to NF which rejects almost all of the organic molecules and passes water with inorganic salts which are mainly sodium carbonate salt. Further, cross flow UF (CFUF) improves the permeate flux and reduces concentration polarization *(22)*. The suggested three-step process study is an attempt for the eventual replacement of multiple effect evaporators and the incinerator in the conventional kraft recovery process. This study takes care of 50–90 kg/m^3 (tds) of feed BL solutions which is realistic for small scale paper mills. The kinetics for BL carbonation as a function of time was also studied.

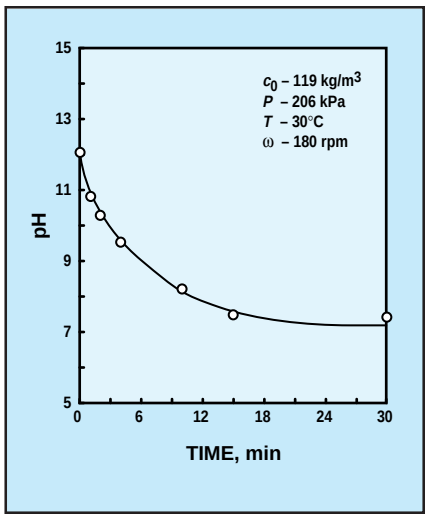
Results and discussions

Selection of feed solution concentration

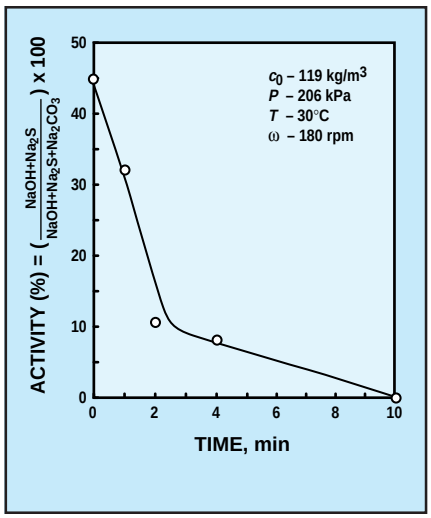
Depending on the type of alkaline pulping, capacity of the mill, and raw materials used, paper mills produce black liquors of different compositions and concentrations. The concentration of BL from brown-stock washers in bigger mills is around 150 kg/m^3 and that for smaller mills is 10–80 kg/m^3 (total dissolved solids content).

For the treatment of BL by asymmetric membranes, selection of feed concentration is very important. At higher concentrations, osmotic pressure of BL increases, therefore, permeate flux decreases to a large extent. Hence, at higher concentra-

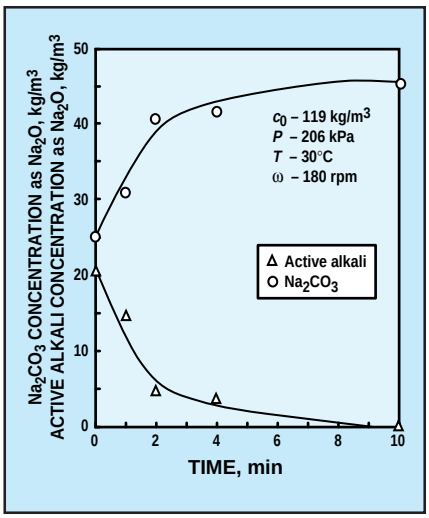
2. Variation of pH with time



3. Variation of activity with time



4. Change of concentration of active alkali and sodium carbonate with time



tions, low flux poses difficulties for comparative studies. Further, viscosity of BL also increases at higher concentrations and handling of the concentrated liquor by ordinary pumps becomes difficult.

BL is composed of a large number of macromolecular solutes of different molecular weights. During the ultrafiltration operation, solutes of lower molecular weight clog the pores, therefore reuse of the membrane becomes difficult. For all these reasons, an intermediate range of concentrations of BL in terms of total dissolved solids (tds) were chosen (~50, 70 and 90 kg/m^3) to study its effect on flux, rejection of the organics, and recovery of the inorganics. Hence, this study may be more relevant for small-scale paper mills. From here on, concentration mentioned in the text is tds.

Carbonation of BL

The inorganic constituents of BL are basically sodium compounds (NaOH, Na_2S, Na_2CO_3, Na_2SO_4, etc.). In the liquor, some of them are present in the free form, but most of the sodium is bound with the phenolic hydroxyl group of colloidal alkali lignin. The building block of lignin is the phenylpropane unit. Basic structural groups which are supposed to form lignin *(23)* are shown in **Fig. 1.** Lignin is formed as a three-dimensional polymeric structure with these basic units bound together by ether and carbon-carbon bonds.

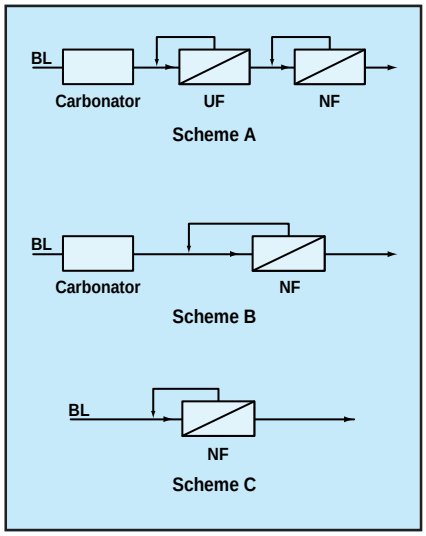
In BL solutions, phenolic hydroxyl groups of lignin are present in the form of -O-Na groups. These charged colloidal lignin particles are stable at pH greater than 7. As carbon dioxide is passed, the pH of the solution decreases and -O-Na bonds break; therefore, lignins precipitate and Na goes into the solution. After sufficient treatment with CO_2, almost all of the sodium compounds are converted to Na_2CO_3 and lignin settles in the fragmented form. In general, mass transfer in terms of absorption rate of CO_2 in the solution can be enhanced by applying higher pressure and stirring *(24)*. For a 119-kg/m^3 BL solution, the decrease of pH with time is shown in **Fig. 2.** As time proceeds, sodium hydroxide as well as sodium sulfide (after hydrolysis) is converted to Na_2CO_3. The drop of activity of BL solution, which is defined as the ratio of active alkali (Na_2S + NaOH) as Na_2O to the total titratable alkali (Na_2S + NaOH + Na_2CO_3) as Na_2O with time is shown in **Fig. 3.**

However, treatment of BL by CO_2 is advantageous for subsequent membrane separation processes. Cellulose acetate membranes used in the experiments were amenable to the degradation at high alkalinity (pH > 12) or high acidity (pH < 2). Consequently, direct treatment of BL which has a pH ~11.5 may shorten the membrane life. In this context, the present approach is more advantageous because after carbonation BL has a pH ~7.5, which causes less damage to the membranes during UF and nanofiltration (NF). As already mentioned, carbonation of BL results in the fragmentation of lignin molecules *(2)*. It was observed in the experiments that this fragmentation is associated with an increase in inhomogeneity of the solution. This experimental observation was more pronounced at higher concentrations *(5)*; however, this effect was not studied.

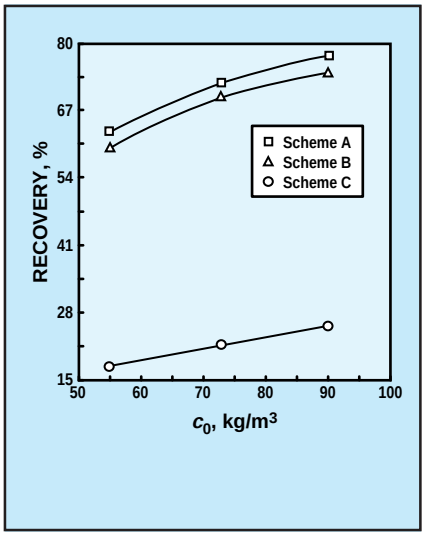
Kinetics of carbonation of BL

To study the kinetics of carbonation of BL, pH and composition of the carbonated liquor were analyzed for different contact times. Since almost complete carbonization could be achieved within a short period of time (within 2 min) for lower feed concentrations, a comparatively higher feed concentration of 119 kg/m^3 was chosen to study the kinetics. Figure 2 depicts the decrease of pH with time. A constant value of 7.5 was reached for a contact time of 15 min.

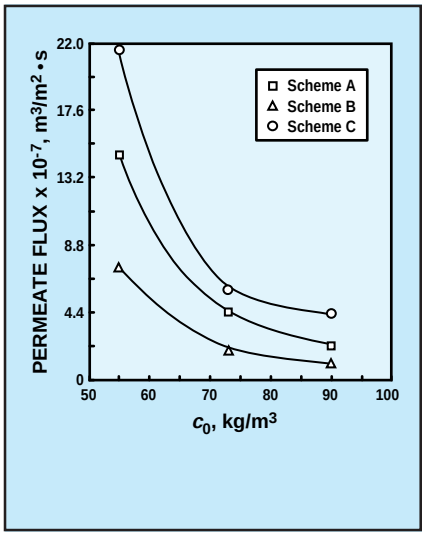
5. Different schemes which were studied



6 Variation of inorganics recovery with time



7. Steady state NF permeate flux for different schemes versus feed concentration



The uptake of CO_2 by the active alkali to form sodium carbonate was determined by titrametric analysis for different contact times, details of which are provided in the experimental section. The results have been plotted in **Fig. 4,** which shows rapid conversion of the active alkali into Na_2CO_3 initially followed by a more gradual conversion after about 3 min. A regression analysis of the experimental data was performed and the kinetics was described by the following correlation, with a correlation coefficient 0.99.

$$c/c_0 = \exp(-0.505t) \qquad (1)$$

Here, c is the concentration of the active alkali compounds present at any time t and c_o is that of the feed solution. The striking simplicity of the above correlation is remarkable because the first-order kinetics described by it actually represents a complex set of reactions. The alkali (Na^+) present in the BL exists in two forms, namely, free alkali (NaOH, Na_2S, etc.) and bound alkali in the form of alkali lignins. During carbonation, both free and bound sodium ions take part in the reactions. Therefore, the actual mechanism for the conversion of alkali compounds in the carbonate form is very complicated. However, the suggested correlation (Eq. 1) enables one to circumvent this difficulty and provides us the important data of the concentration of active alkali during carbonation.

Treatment of carbonated BL by membrane separations

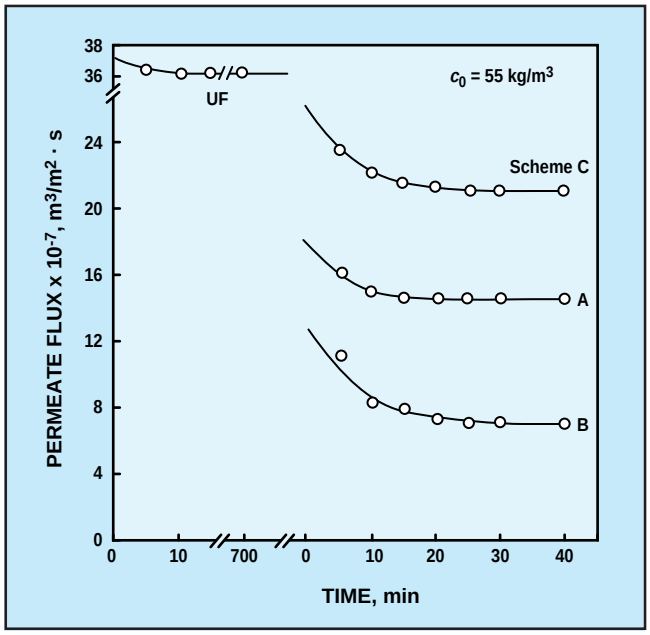
Selection of schemes. Three different schemes of membrane separation processes for BL treatment were considered. They are shown schematically in **Fig. 5.** First, carbonated BL was passed through a permeable UF membrane and the permeate of this was then subjected to NF process, as shown in scheme A. In scheme B, carbonated BL was treated by NF membrane to observe the effect of UF step in scheme A. In scheme C, BL was directly subjected to NF to demonstrate the significance of the carbonation step. The comparisons between these schemes were done in terms of inorganic recovery, permeate flux and quality of the product permeate.

Recovery of inorganics. The variation of recovery of the inorganics with feed concentrations for different schemes is shown in **Fig. 6.** Scheme A shows the maximum recovery followed by schemes B and C, in that order. The lowest recovery in scheme C may be explained due to the retainment of bound alkali whereas in schemes A and B the carbonation procedure converts the bound alkali into sodium carbonate, resulting in a higher recovery of the inorganics. When carbonated BL is treated by NF (scheme B), the membrane surface is polarized by low as well as high molecular weight fractions of lignin. Some of the pores on the membrane surface may also get clogged; even pore mouths, in some cases may get blocked. This phenomenon is considerably reduced by separation of higher molecular weight fractions of lignin fragments by UF as shown in scheme A. Therefore, during subsequent NF less hindrance is offered to the passage of the inorganic solutes and solvent through the membrane.

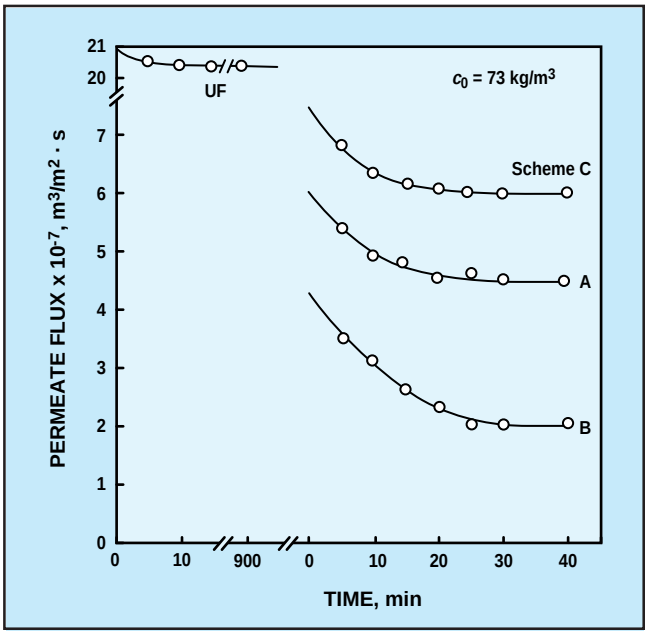
At feed concentration of 90 kg/m^3, recovery in scheme C is 25%; at the same concentration, recovery in scheme B is 74.4%, which is almost 200% more than scheme C. At these conditions, recovery in scheme A is 78%, which is 4.7% more than B and 214% more than C. Therefore, as far as recovery of the inorganics is concerned, scheme A is more promising. From Fig. 6, it is obvious that recovery increases as feed concentration increases.

At higher feed concentrations, more inorganic salts are present in

8. Flux decline with time for 55 kg/m^3 BL for different schemes



9. Flux decline with time for 73 kg/m^3 BL for different schemes



the solution, and hence recovery increases as more solutes pass through the membrane.

Permeate flux. In any membrane separation process, permeate flux is of utmost importance. It is one of the influencing parameters which determine the performance of the separation process. Steady-state NF permeate flux is plotted against the feed concentration in **Fig. 7.** Here, scheme C gives the highest flux compared to the other schemes but at the cost of the minimum recovery of inorganic salts. Obviously, this is not advantageous, as inorganic recovery is of prime importance to the pulp industry. Lower flux of the carbonated solution can be attributed to the presence of carbonate salts and fragmented lignins which increase the osmotic pressure of the feed considerably, thereby reducing the driving force.

This phenomenon can be explained by the phenomenological equation:

$$J = A(\Delta P - \Delta\Pi) \qquad (2)$$

where

$$A = 1/\mu R'_m \qquad (3)$$

$$\Delta\Pi = \Pi_m - \Pi_p \qquad (4)$$

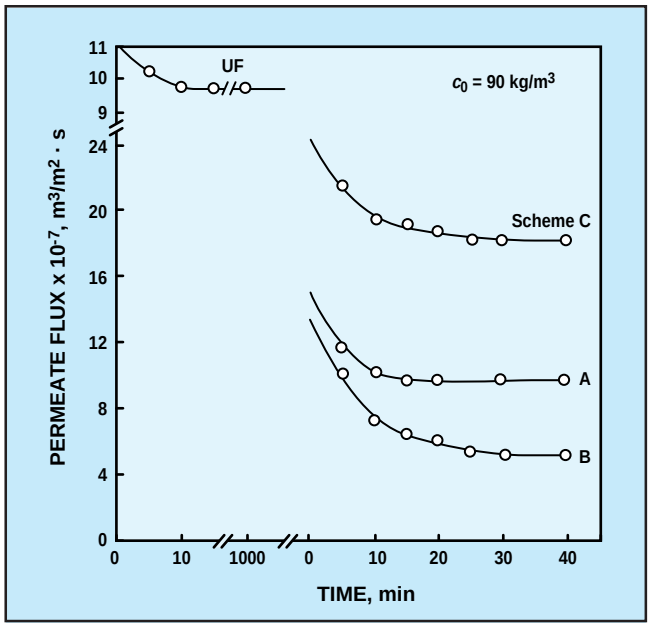
Π is an increasing function of concentration. Π can be expressed for dilute solution of salts as:

$$\Pi = RTc/M \qquad (5)$$

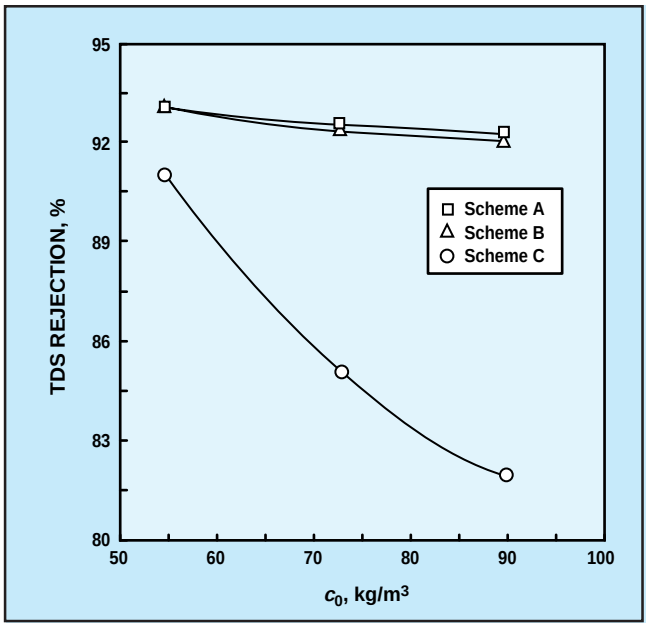
For salts, the molecular weight is generally very small compared to the macromolecular or colloidal particles. Hence, the osmotic pressure of the salt solution is very high. Osmotic pressure is further increased by increase of concentration. So, the available driving force is reduced and flux decreases. This also explains the reasons for the decrease of flux at higher feed concentrations. Thus, the osmotic pressure of the carbonated solution is higher with the release of the bound sodium salts in the solution. This results in reduced flux in schemes A and B. Also, smaller fragments of lignin may become adsorbed reversibly on the membrane surface and clog the pores to a larger extent than the solution without carbonation. In scheme A, the large molecular weight fractions of lignin are removed by preliminary UF. The permeate from UF is then subjected to NF, whereas in scheme B, the intermediate fractionations of higher molecular weight fractions of lignin is not performed. Therefore, the feed solution in the NF step is more concentrated in scheme B compared to scheme A. Consequently, the flux in scheme B is lower than that in scheme A. For example, at feed concentration 90 kg/m^3, the flux in scheme C is 4.53 x 10^{-7} m^3/m^2·s (1.63 L/m^2·h) and those in B and A are 1.28 x 10^{-7} m^3/m^2·s (0.46 L/m^2·h) and 2.43 x 10^{-7} m^3/m^2·s (0.88 L/m^2·h), respectively. Therefore, considering both flux and recovery, scheme A is the best among the three schemes. Further, after taking each run, membrane permeability was checked and that was found virtually constant. This proves there was no permanent adsorption on the membrane surface and the adsorption or polarization during operation was purely reversible in nature. Due to the high flow rate of the pump in the cross flow apparatus, the washings of the membranes were very efficient which restored the permeability to its original status.

Flux decline with time. In the pressure-driven membrane separation process, decline of flux is a major problem. As the separation process progresses, solutes start accumulating on the membrane surface, thus forming a boundary layer.

10. Flux decline with time for 90 kg/m^3 BL for different schemes



11. Variation of tds rejection with feed concentration for different schemes



This buildup of solutes offers an extra resistance to the flow through the membrane. This is termed as concentration polarization. Increase in concentration also increases osmotic pressure of the solution, thus lowering the effective driving force. There may be formation of a gel layer on the membrane surface, the thickness of which increases with time. This type of fouling is generally reversible in nature. Apart from this, there may be solute adsorption on the membrane surface (pore mouths are blocked), adsorption inside the pores (pores are blocked partially), or clogging of the pores. These types of hindrances may be either reversible (removable after washing of the membrane) or irreversible (not removable even after washing) in nature. All these resistances can simply be put in the form of a resistance in series model:

$$J = (\Delta P - \Delta\prod)/\mu(R'_m + R'_{bl} + R'_g + R'_{ad}) \quad (6)$$

where

R'_m = hydraulic resistance of the membrane

R'_{bl} = resistance in the boundary layer

R'_g = resistance in the gel layer

R'_{ad} = adsorptive resistance.

BL, a polydispersed liquid having solutes of a wide molecular weight range of 1000–100,000, is susceptible to severe polarization during the membrane operation. Several theories have been put forward to understand, quantify and control the concentration polarization *(22, 25-27).* One way to reduce concentration polarization is to allow feed solution to flow tangentially over the membrane surface, known as the cross flow ultrafiltration. This causes reduction in the growth of the boundary layer near the surface and increase in back diffusion from the surface to the bulk of the solution. Hence, permeate flux increases significantly. In the presence of the resistances mentioned above, the permeate flux declines with time and eventually reaches a steady-state value. The steady-state permeate flux during cross flow ultrafiltration can be expressed using film theory as,

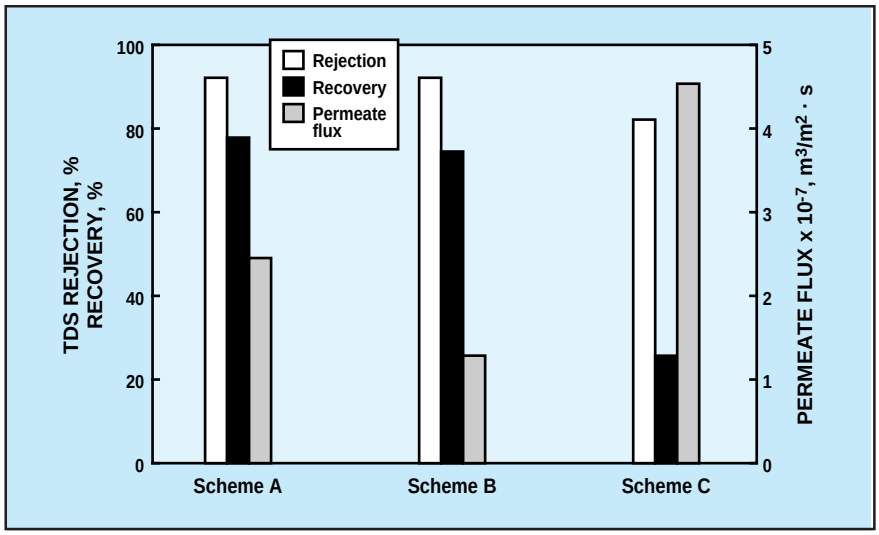
$$J = k \ln[(c_m - c_p)/(c_0 - c_p)] \quad (7)$$

where the mass transfer coefficient k is a function of cross flow velocity, system geometry and physical properties of the solution.

Flux decline with time for all the schemes is shown in **Figs. 8, 9, and 10** for feed concentrations 55, 73, and 90 kg/m^3, respectively. Since the UF membrane has larger pore sizes, its flux is always higher but it decreases because of the concentration polarization. The decline in flux is gradual for scheme B and C in all the cases, whereas that for scheme A is rapid. This is because, in scheme A, membrane polarization is minimized and the steady state is attained quickly. For example, in Fig. 8, for scheme A, steady-state flux is reached within 10 min whereas, for scheme B and C, it was 25 and 20 min, respectively. Flux prediction of such behavior has already been attempted *(27-30).* It is interesting to note that the flux decline (Figs. 8–10) is more gradual in NF runs than that in UF experiments. This suggests that besides concentration polarization, there exists some reversible fouling (pore blocking) of the membrane during the operation. But this fouling of the membrane is not permanent because it is observed that the membrane permeability remains unchanged after washing of the membrane.

Quality of the product permeate of NF. The quality of the NF

12. Performance of different schemes



permeate can be specified in terms of tds rejection. Rejections, in membrane terminology, are of two types, namely, observed and real rejection. Observed rejection is defined as:

$$R_0 = 1 - c_p/c_0 \quad (8)$$

and real rejection is defined as:

$$R_r = 1 - c_p/c_m \quad (9)$$

However, in this study only observed rejection is considered. Rejection of tds versus feed concentration for different schemes is shown in **Fig. 11.** Here, scheme C shows the minimum and A shows the maximum rejection. The permeate having low tds content consists mainly of low molecular weight organic coloring compounds. The quality of the permeate was also observed from the color of the final permeate, i.e., of NF. The color of the permeate in scheme C was yellow, that in B was light yellow, and that in A was almost white with a slight yellowish tinge, which indicates the permeate in scheme C contains the maximum amount of the organics and that in scheme A contains the minimum amount of the organics. The color of the permeate of UF, in scheme A, was observed to be black.

To summarize the overall performances of the three schemes, they are shown schematically in **Fig. 12.** It shows that the flux is less in scheme A compared to that in C, whereas recovery of the inorganics and rejection of the organics are maximum in scheme A.

The enhancement of the permeate flux in any membrane separation process is a major research interest in various membrane research laboratories. Although increase in applied pressure seems to be logical to increase the driving force and therefore flux, this leads to more concentration polarization due to the osmotic pressure buildup. Therefore, introduction of turbulence *(12)* or turbulent promoters like spacers *(27)* reduces the concentration polarization to a significant extent. Studies on pressure pulsation *(26)* may prove significant increases in permeate flux. Negative transmembrane pressure pulsing also results in an increase in flux in presence of irreversible membrane fouling as well as reversible concentration polarization *(31).* Using such techniques, the permeate flux in scheme A can be improved to make the process economically viable.

Causticization and color removal

The final permeate can be treated in a conventional causticizer with lime, so that all the sodium carbonate is converted to sodium hydroxide. The trace amount of color in the permeate can also be removed by adsorption of coloring compounds by lime, which was confirmed by earlier work *(32, 33).* The causticized permeate can then be recycled back to the digester.

I. Analysis of black liquor

Total dissolved solids, %	15
Organics (dry basis), %	68
Inorganics (dry basis), %	32
Na_2S, g/L as Na_2O	0.88
NaOH, g/L as Na_2O	0.14
Na_2CO_3, g/L as Na_2O	2.05

Energy consumption

In an attempt to illustrate the viability of scheme A, a simple energy consumption calculation for carbonation under stirring and membrane separations was carried out. The calculations are simple presentations of energy consumption and should not be taken as a complete illustration of the process calculations. It was observed that energy consumed in carbonation is insignificant compared to the pumping energies in the membrane modules. Energy consumption for scheme A is around 300 kJ/kg and that for B and C is around 280 kJ/kg.

Experimental

Materials

Asymmetric cellulose acetate membrane, used for ultrafiltration, was obtained from Permionics (India) Ltd. and was of 1000 molecular weight cut-off (MWCO). For NF, a thin film composite (TFC) membrane of cellulose acetate was used, supplied by Hydranautics India Ltd., which was of 500 MWCO as specified by the manufacturer. The membranes were anisotropic, hydrophilic and of flat rectangular sheet type with an operating pH range of 2–12.

The membrane was supported on a porous sheet. BL was procured from Central Pulp Mills, Surat, and was diluted with distilled water for different concentrations in terms of tds.

Apparatus

Carbonation. A cylindrical pressure vessel of 800 mL (fitted with a pressure gauge) capacity was used for carbonation with the help of a carbon dioxide gas cylinder. A stirrer was attached to it to provide stirring. Stirrer speed was measured with the help of a stroboscope.

Membrane separation. For membrane separation, a rectangular cross flow cell was used. It was cast in gun metal, and to avoid corrosion, nickel plating was done. The cell was of 0.4 m in length and 0.06 m in width. A neoprene rubber gasket of width 0.01 m was placed inside the cell. The channel height was determined by the thickness of the gasket which was 1.5 mm. In order to allow the flow to be fully developed in the channel, a minimum length was required from the entrance. Depending on the maximum Reynolds number used *(34)*, it was determined to be 0.05 m. Hence, the entrance length of 0.05 m was kept blank with a plastic sheet. Therefore, effective membrane area, after deducting gasket width, became 0.33 m x 0.04 m. The cross flow cell was connected to a reciprocating pump of capacity 0.33 m x 0.04 m. The cross flow cell was connected to a reciprocating pump of capacity 5 L/min. An Elico pH meter (model no. LI-120) was used to measure pH of the solutions.

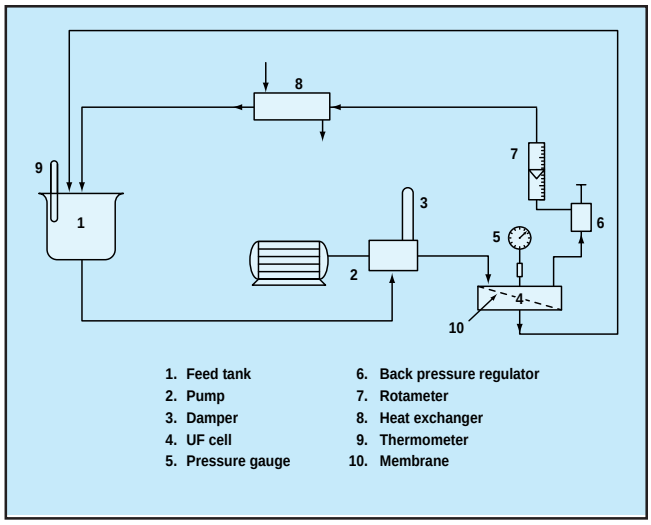
Analysis. The black liquor analysis is given in **Table I.** The major inorganic contents for different sample streams were calculated by a pH metric triple titration method *(35)*. Total dissolved solids in black liquor was determined gravimetrically by evaporating the sample in an oven at 105± 3°C.

Experimental design

Carbonation. It was observed that during carbonation for lower concentrations, pH drops very fast with time. Hence, a little higher concentration (119 kg/m^3) of BL was chosen for study of the carbonation of BL. BL of this concentration was subjected to carbonation for different contact times. At the end of each run, the carbonated solution was analyzed. It was observed that pH reached a steady value for a contact time of 15 min. Therefore, to ensure complete carbonation, BL solution was carbonated for half an hour, at 206 kPa, 30°C, and at a stirrer speed of 180 rpm, in order to prepare the feed solutions for UF and NF runs. For preparation of the feed carbonated solution for the runs of UF and NF, BL solution was carbonated for half an hour. Carbonation was carried out at 206 kPa and 30°C and at a stirrer speed of 180 rpm. To carbonize about a 2.0-L solution the solution was treated with carbon dioxide in batches. The concentrations of feed BL solutions, before carbonation, chosen for the membrane separations were varied as 55, 73, and 90 kg/m^3.

Membrane separation. The operating pressure for all UF runs was chosen as 689 kPa and that for NF was 1723 kPa. The recirculation flow rate for both UF and NF was chosen as 2.22 x 10^{-5} m^3/s. To observe the effectiveness of different schemes (as described in Results), experiments were carried out as scheme C, B, A, in that order.

13. Experimental setup



Procedure

First, a solution of fixed concentration of BL was prepared. It was carbonized in the pressure vessel in batches. Membranes were compacted at 824 kPa (for UF) and at 1895 kPa (for NF), which are higher than the highest operating pressure at 2.22 x 10^{-5} m^3/s for 6 h with distilled water. At the same flow rate, water flux was measured at four different pressures to determine the membrane permeability. For scheme C, BL was directly treated by NF. The feed tank was filled with 2.5–3.0 L feed solution and the pump was made operative. Instantaneous pressure difference was reached (within 10 s). Cumulative volume of permeate was measured as a function of time at fixed operating conditions. This was continued till a steady-state flux value was reached. Steady-state flux was attained within 25 min. However, the run was continued for 1 h. For scheme B, carbonated BL was subjected to NF and the run was taken as described previously. For scheme A, carbonated BL was first treated by UF. UF runs were very long, ranging from 12 to 16 h to collect sufficient volume (around 3 L) of permeate to carry out subsequent NF runs. The data for these UF runs are not presented in detail in Figs. 8–10 because the fluxes and rejec-

Nomenclature

A	= membrane permeability, $m^3/N \cdot s$
BL	= black liquor
c	= concentration, kg/m^3
CFUF	= cross flow ultrafiltration
k	= mass transfer coefficient, m/s
M	= molecular weight
NF	= nanofiltration
P	= pressure, Pa
Q	= recirculation flow rate, m^3/s
RO	= reverse osmosis
R	= universal gas constant J/mol. °K
R'	= resistance, m^{-1}
R_0	= observed rejection
R_r	= real rejection
T	= temperature, °K
t	= time, min
tds	= total dissolved solids, %
UF	= ultrafiltration

Greek symbols

ΔP	= pressure differential, Pa
$\Delta\Pi$	= osmotic pressure differential, Pa
ω	= stirrer speed, rpm
μ	= viscosity, Pa·s

Subscripts

ad	= adsorption
bl	= boundary layer
g	= gel layer
m	= membrane surface
o	= bulk condition
p	= permeate

tions did not vary after reaching the steady state (i.e., within 15 min). Samples were collected from all the streams for analysis. All the experiments were carried out between 26°C and 31°C. Hence, all properties and data were corrected and calculated at 30°C. After each run, the feed tank and the set-up including the membrane were washed by recirculating distilled water at the lowest pressure and highest flow rates for nearly 30 min. After that, the membrane permeability was checked. The above procedure was followed for different feed concentrations. The schematic diagram of the experimental set-up is shown in **Fig. 13.**

Conclusions

From the present study, it can be concluded that carbonation of BL with membrane separation may be a possible route to recover water with inorganics without destroying the organics. The process outlined here may replace expensive as well as polluting equipment used in the conventional kraft process plant.

Carbonation of BL helps in releasing bound alkali chemicals to the bulk. Study of the carbonation of BL reveals that the overall decay of concentration of active alkali obeys a first-order-type rate law. This may help to estimate the time required to attain an extent of carbonation.

Carbonation followed by UF and NF proved to be better than carbonation with NF or direct NF of BL. Scheme A shows better results in terms of inorganic recovery and permeate quality. Inorganics recovery can further be increased by choosing a suitable NF membrane with pores slightly bigger than the one used in this study. This should enhance permeate flux at the expense of slight permeate quality (tds may increase). ■

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