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A Novel Separation Process of Lignocellulose by Nanofiltration Membrane

ABSTRACT : ***Dissolution of lignocellulose was studied in ionic liquid at room temperature. Dissolution of lignocelluloses was confirmed by microscopic observation and SEM analysis of the sample before and after treatment. Recovery of ionic liquid was performed by using indigenously developed and characterized beta-cyclodextrin Nanofiltration membrane. The effect of applied pressure (DP) and concentration of lignocellulose on the rejection, membrane fouling and water flux was studied in a membrane cell. The solution flux increases with pressure indicate the effect of concentration polarization is not significant.***

A separation process is any mass transfer process used to convert a mixture of substances into two or more distinct product mixtures, where at least one of which is enriched in one or more of the mixture's constituents. In some cases, a separation may fully divide the mixture into its pure constituents. Separation processes occupy a key position in many industries like food, pharmaceuticals, biotechnology, textiles, and other industries in addition to their enormous applications in water and wastewater treatments. In fact, separation technologies are integral parts of chemical processes and dictate process economics/ profitability. Membranes are primarily used for separation, and is such a separation process which is operated without heating and thus are energetically usually lower than conventional thermal separation processes like distillation, sublimation or crystallization. This separation processes are purely physical and for its gentle separation, the use of both fractions (called permeate and retentate) is possible. The widely used membrane processes include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, electrolysis, dialysis, electrodialysis, gas separation, vapor permeation, pervaporation, membrane distillation, and membrane contactors[1]. Microfltration and ultrafiltration is widely used in food and beverage processing. Nanofiltration and reverse osmosis membranes are mainly used for water purification purposes. Nanofiltration (NF) is a relatively new membrane separation technique which is a pressure driven membrane process and pore size between 0.5 and 2 nm, normally applicable for separation of dissolved components. The specialty of NF membrane is water softening, treatment of industrial effluents contaminated with organics or heavy metals[1-3]. The process is regarded as an innovative and promising water treatment technique, and a potential alternative to conventional water treatment approaches[4-6]. Nanofiltration is used to achieve a separation between sugars, other organic molecules and multivalent salts on one hand and monovalent salts and water on the other. In this study we have reported the separation of lignocellulose after its dissolution in ionic liquid.

Lignocellulosic biomass is renewable, environmentally friendly and abundant in the natural world. It is mainly consisted of cellulose (15-25%), lignin (23-33%) and hemicelluloses 16-25%). With lignin, cellulose occurs as main part of every lignocellulosic biomass. Lignocellulose is the major structural component of woody and non woody plants such as grass and represents a major source of renewable organic matter. Lignocellulose consist of lignin, hemicelluloses and cellulose. Large amount of Lignocellulose waste are generated through forestry and agricultural practices, paper and pulp industries, timber industries and many agro industries. Among potential alternative bioenergy resources, lignocellulosics have been identified as the prime source of biofuels and other value added products[3]. North East region of India is rich in natural resources and biomass which provides feedstock for fuels, fine chemicals, speciality chemicals, foods and functional foods, nutraceuticals etc. Some reported work indicates that coir fibre of this region contains large amount of lignin which we considered as the lignocellulosic biomass for our present study[7]. 1-n-Butyl-3-methylpyridinium tetrafluoroborate ionic liquid was used for dissolution of lignocellulose as dissolution of lignocellulose is better in this ionic liquid[8].

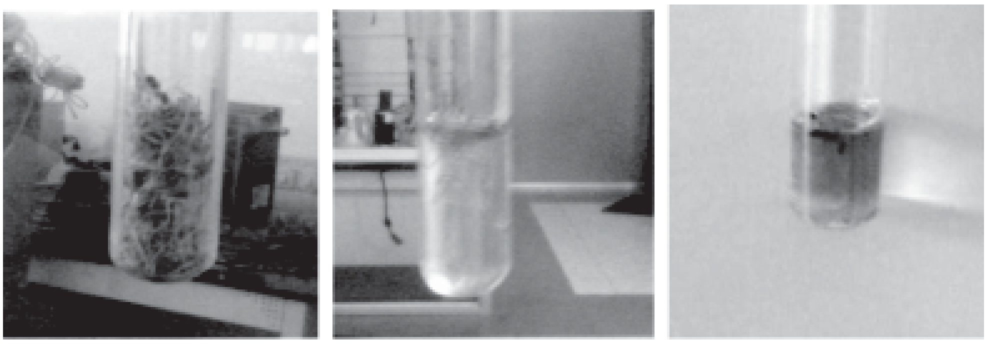

Fig. 1. (a) Coir fibre (b) Before IL treatment (c) After IL treatment

Materials and Methods : For our study we used coir fibre obtained from NE Region of India and it Contains : Cellulose: 35-36%, Lignin: 36-40%, Ash content : 2.10%, Silica: 0.02% as reported earlier[7]. 1-n-Butyl-3-methylpyridinium tetrafluoroborate, was obtained from Sigma Aldrich, Mumbai, India. Polysulphone (average molecular weight 22,000) was obtained from Aldrich Chemical Company, USA in pellet form. Polyethylene glycol 1500 was supplied by G.S. Chemical testing Lab & Allied industries-India. α, β and γ-Cyclodextrin hydrate (purity 99%) and Lithium Nitrate (99% extra pure) were supplied by Acros Organics-USA. N- methyl pyrrolidone (purity>99.5%) was procured from Rankem- India. All reagents were used without any further purification. Other solvents were taken from RENKEM. Membrane was prepared by dissolving Polysulfone (PSf) in NMP as solvent at room temperature ($28\text{-}32^0$C and relative humidity about 78%) and then mixed with definite amount of Polyethylene glycol (PEG-1500), $LiNO_3$, and β-Cyclodextrin to make the casting solution. The polymer solution is stirred for about 6 hours at room temperature (28^0C-30^0C) using a magnetic stirrer until a homogeneous solution was achieved. Films were cast on a glass plate with a casting Knife maintaining the same temperature as in the solution and are exposed for about 5 minute to ambient before immersion into a coagulation bath that contains ice-cooled water (maintained at about 6^0C). When the cast films were changed their colour from transparent to white, immediately immersed into the coagulation bath and separates out of the glass plate after sometime. The prepared membrane sheets were washed under running water and kept in deionized water bath overnight. Then the sheets were dried at room temperature.

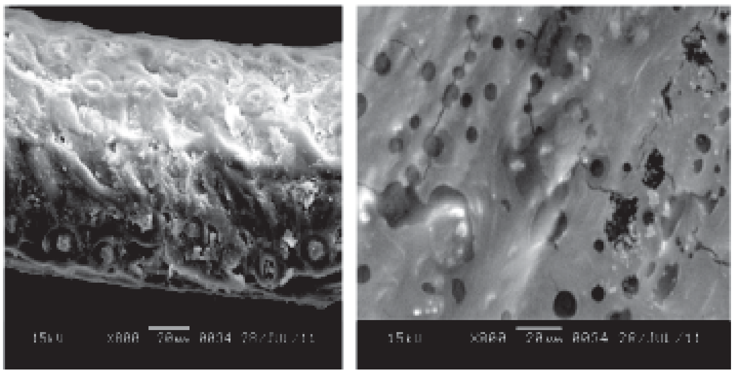

Fig. 2. SEM photograph of Coir fibre, (a) : Before treatment, (b) : After Treatment

The lignocellulose part of the biomass was dissolved in ionic liquid by constant stirring for 10 hr at room temperature and precipitated by adding water. The filtrate is used for membrane separation process, which contains trace amount of dissolved component. By using β-CD nanofiltration membrane ionic liquid was recovered in pure form and can be used for commercial application.

Results and Discussions : Dissolution of lignocellulose was observed by the change in colour of the ionic liquid solution before and after treatment (Figure 1) which is also confirmed by the Scanning Electron Micrograph (SEM) of coir fibre sample (Figure 2).

Most of the cellulosic content of the lignocellulosic biomass can be separated from the ionic liquid solution. We used indigenously developed beta cyclodextrin nanofiltration membrane for separation of lignocellulose. The membrane was prepared by mixing beta cyclodextrin with polysulfone in N-methyl pyrrolidone (NMP). Most NF membranes are composite in nature, with a selective layer on the top of the microphorous substrate[9-11]. Scanning Electron Micrograph (SEM) and Transmission Electron Micrograph (TEM) of beta-CD membrane are shown in Figure 3. SEM photographs indicate that the membrane contains pores of almost similar shape but the pore diameters are not uniform. Surface roughness as visualized from SEM photographs seems to be low resulting in relatively low fouling. The TEM micrographs of CD membranes suggest that CD exists mainly with polysulfone and CD distributed exclusively in polysulfone.

The pore size of the membrane was determined by Capillary Condensation flow porometer (PMI, Model

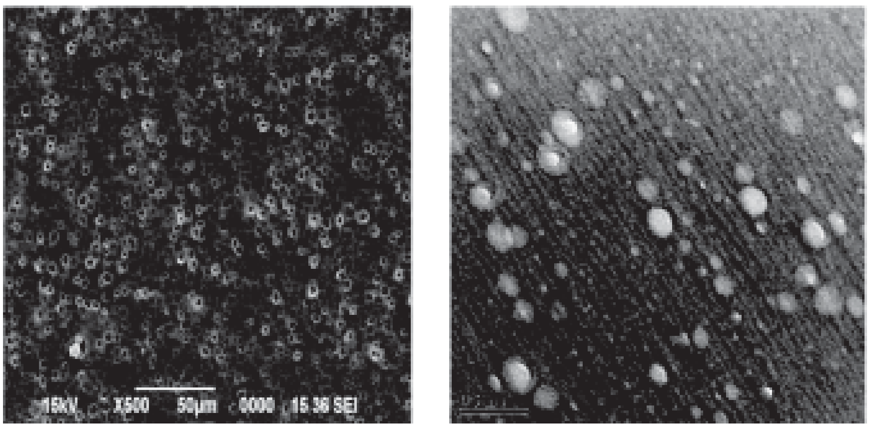

Fig. 3. Scanning Electron Micrograph (SEM) and Transmission Electron Micrograph (TEM) of β-CD membrane

CCFP-5A) and was found to be 66 nm. Porosity and pure water permeability was 66% and 3.55 x 10^5 $cms^{-1}bar$ respectively.

For the membrane permeation experiment a two compartment membrane cell was used with the experimental system shown in Figure 4. Volume of each compartment of the cell was 50 ml. The polymeric membrane was placed between the compartments with silicone–rubber packing and the cell was connected with a reservoir of 250 ml. The solution of dissolved lignocelluloses in ionic liquid was stirred continuously and circulated by peristaltic pump that was connected to the reservoir. The sample solutions were collected from the permeate side after a permeation period and analyzed by UV-VIS spectroscopy. The measurements were made at the maximum wavelength (280 nm) in the visible range. Effect of applied pressure and lignocellulose concentrations were observed on the separation phenomenon.

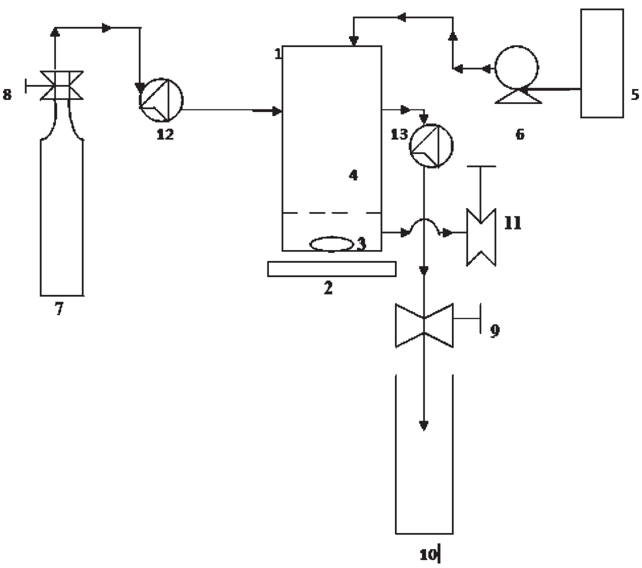

Fig. 4. Flow diagram of permeation experiment

1.Membrane cell 2. Magnetic stirrer 3. Magnetic capsule 4. Membrane 5. Feed tank 6. Peristaltic pump 7. N_2 gas 8. Gas valve 9. Gas valve 10.Water vessel 11. Sample collecting valve 12. Pressure gauze 13. Pressure gauze

The permeation flux was calculated by the equation,

$$j = \frac{V \quad C}{A \quad t} \qquad (1)$$

Where V is the volume of permeate in time t, A Membrane area, ΔC the concentration variation in the corresponding aqueous solution at the time interval Δt.

The rejection percentage was defined as

$$R\% \quad \frac{C_f \quad C_p}{C_t} x100 \qquad (2)$$

where C_f and C_p are the concentration in feed and permeate respectively.

Effect of applied pressure on separation of lignocelluloses was observed by changing pressure as NF is a pressure driven process. The effective pressure for this particular membrane was 2 bar to 5 bar. Another important factor of the membrane is rejection and was calculated by equation (2). Figure 5 shows the variation of percentage rejection as a factor of pressure and concentration. The

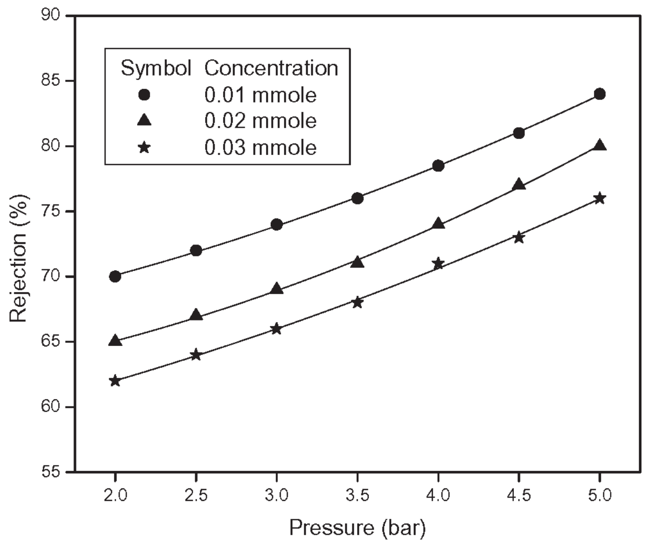

Fig. 5. Rejection of lignocellulose at different operating pressure

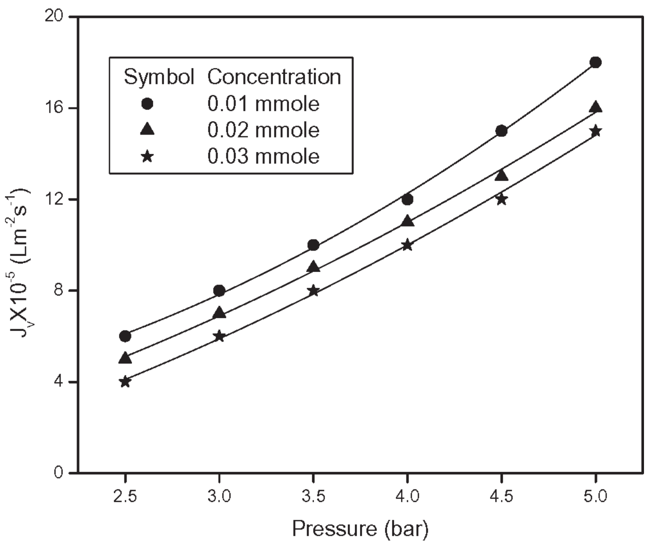

Fig. 6. Variation of solvent flux with pressure at different lignocellulose concentration

percentage rejection increases with increasing pressure and decreases with increase in concentrations. With increase in pressure, convective transport becomes dominant causing rejection to increase[12]. However, concentration polarization which is the effect caused by the change in concentration across the membrane will also increase with increase of pressure, results in decrease in rejection. Solvent flux increases with applied pressure indicating little effect of concentration polarization or fouling in this pressure range as shown in Figure 6.

Figure 7 shows that the decrease in permeate flux with time is insignificant. This implies that in the range of pressure studied, the membrane does not suffer much compaction effects which would reduce its pores and consequently the permeate flux[13].

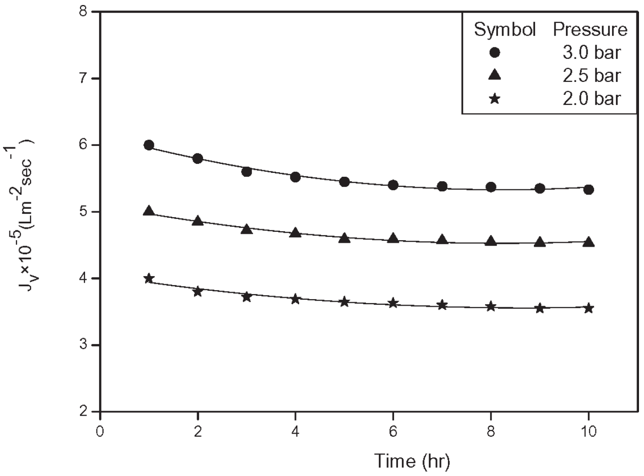

Fig. 7. Variation of flux with time at different pressures at constant lignocellulose concentration of 0.01 mmole L^{-1}

Conclusion

Recovery of ionic liquid was studied with indigenously developed nanofiltration membrane in which the cellulose was obtained as the reject component in high concentration. Due to the high cost, recovery and recycle of ionic liquid is important for commercial application. Thus, separation of lignocellulose from lignocellulosic biomass by nanofiltration membrane is expected to occupy a key position in membrane research. Further investigation in this work is in progress. ❒

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