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Performance Evaluation of Nanofiltration Membrane for Separation of Primary Alcohols from Dilute Solutions

Kundan Baruah, Rajiv Goswami, Monti Gogoi and Swapnali Hazarika*

Engineering Science and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat- 785006, Assam, India

Abstract

Membranes for separation of alcohols from aqueous solutions were prepared from α, β, γ- cyclodextrin separately and characterized for Membrane thickness, Pore diameter, Pure water permeability, Water uptake, Contact angle and membrane morphology study. Permeation performance of the membranes was tested for primary alcohols such as methanol, ethanol and butanol. Effect of process parameters on flux and rejection of the membranes were studied and permeation models were analyzed. It was observed that β-CD membranes give 99% separation of alcohols from 1.73 molL^{-1} - 0.766 molL^{-1} solution at pressure 3 bar. Highest flux value was found to be 91.3 Lm^{-2}hr^{-1} - 87.3 Lm^{-2}hr^{-1}.

Keywords: Cyclodextrin; Nanofiltration; Permeation flux; Dilute solution

Introduction

Industrial effluents contain organic solvents in low concentrations, most notably in the process stream of polyester, ethanol, chemical, petrochemical, food, and pharmaceutical industries. Several methods are available to remove them from the process stream. Examples of such processes include distillation, extraction, neutralization, over-liming, vacuum evaporation, stream stripping, charcoal adsorption, ion exchange resin adsorption etc. [1,2]. However, separation of these solvents from the process effluents encounters difficulties because of their presence in lower concentration. Although membrane technology proves to be an efficient process in the removal of alcohols, yet it holds an outset position. As reported in the literature, on downstream processing there are only insufficient works done on alcohol separation using NF system [3]. When the solute size is somewhat bigger than the pore size of the membrane, NF membranes testifies itself as an effective technology for the removal of such organic compounds [4-6]. In these cases, comparatively compounds with higher molecular weight or of hydrophobic nature have been taken into account and the evaluation of rejection of small uncharged organic compounds is infancy [7-9]. Considering the dependence of solute transport on physic- chemical properties of the solvent, membrane and solute, a detail analysis of the permeation of small organic compounds by means of NF membrane is a confronting issue. Several recent studies focusing on the transport of organic solute through the membrane depends on the pore size and the charge of the membrane. Thus, NF technique seems to be an improved process in membrane separation for recovery of organic solvents from solutions and hence enhancing its application in the last decade.

Herein, an extensive study on NF membrane is done for recovery of primary alcohols from its dilute aqueous solutions. α, β and γ-cyclodextrin composite with polysulfone membrane have been prepared. The membranes have been characterized using various spectroscopic techniques and evaluated the performance of the membrane for separation of alcohols from dilute aqueous solutions. Cyclodextrin has unique characteristics features such as uniform macromolecular structure, molecular self-assembling etc. which determines its efficiency to form uniform membrane structure with control pore size [10]. It can also be used for studying host guest chemistry as it has the tendency to form host guest complexes with organic moiety having relevant diameter and physical interactions [10].

Previously, various solute, solvent and membrane parameters affecting the transport model were determined experimentally and certain models were developed [7-9]. As the transport models for NF system are quite limited therefore further research and improvement of transport models are highly necessary with validation [11-18]. In our work, we have evaluated the performance of the membrane for recovery of primary alcohols such as methanol, ethanol and butanol using indigenously developed membrane. Permeation results were analyzed through a suitable permeation model and the effects of solvent membrane parameters were identified.

Materials and Methods

Commercial grade Polysulphone (average molecular weight 22000, purity 99%) was supplied by Aldrich chemical Company, USA. Polyethyene glycol (1500) was obtained from G.S. Chemical testing and allied industries, Delhi. Lithium Nitrate (99% extra pure) and α, β and γ cyclodextrin hydrate (purity 99%) was procured from Acros organic-USA. N-methylpyrolidone (NMP, purity>99.5%) was purchased from Rankem-India.

Membrane preparation

Flat sheet membranes are prepared by phase inversion method. Polysulfone (PSf)is mixed with a definite amount of α-Cyclodextrin, polyethylene glycol, LiNO₃ and then dissolved in different solvents viz NMP, DMF, DMAc and DMSO separately at room temperature (28-32°C and relative humidity about 78%) to make the casting solution. The polymer solution is stirred for about 6 hours at room temperature (28°C-27°C) using a magnetic stirrer until a homogeneous solution was achieved. Flim was cast on a glass plate with a casting knife of thickness 0.5 mm maintaining the same temperature as in the solution and are exposed for about 5 minute to ambient before immersion into a

*Corresponding author: Swapnali Hazarika, Engineering Science & Technology Division, CSIR-North East Institute of Science and Technology, Jorhat- 785006, Assam, India, Tel: ++913762370012; Fax: ++913762370011; E-mail: shrrljt@yahoo.com

coagulation bath that contains ice-cooled water (maintained at about 6°C). When the cast films 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. Finally the membranes were characterized by using different analytical methods and kept ready for permeation experiments [19].

Membrane characterization

The prepared polymeric membranes were characterized by various instrumental techniques. Membrane thickness, pure water permeability and water uptake were determined by the method reported earlier [19]. Pore diameter and porosity of the membranes were determined by Capillary Condensation flow porometer (PMI, Model CCFP/5A). The morphology and the cross section of the membranes were examined by Field Emission Scanning Electron Microscope (LEO 1400VP, UK) and High Resolution Transmission Electron Microscope (JEM 2100 PLUS). The average pore size, surface porosity and pore size distribution of the membrane were obtained from the SEM images using Image J software. Contact angles of the membranes were determined by contact angle meter (DM-501, Kyonea Interface Science).

Evaluation of performance of the membrane

The efficiency of the membrane for alcohol separation was assured by performing the permeation experiment in a disproportionate two component membrane cell whose compartment volume on the feed side and permeate side was 1 litre and 0.5 litre respectively. The polymeric film was placed between the two-compartment cell containing silicon-rubber packing. The cell was fabricated with the membrane of area 15 cm^2 and was connected to a reservoir containing 1 litre feed solution. The feed solution was stirred and circulated by peristaltic pump continuously through the membrane cell. The experiments were performed under various conditions changing pressure, flow rate, temperature and concentration. The permeation experiments were performed in the batch mode for 2 hours. The samples were collected in every 30 minutes interval and analyzed the samples by a refractometer. The concentration of permeates were determined using calibration curve obtained from the standard sample analysis. The operating conditions such as concentration, temperature, pressure and flow rate plays a vital role in the separation performance of NF membrane [18]. The schematic representation of the experimental setup is shown in Figure 1.

Theoretical Background

The permeation flux and percentage rejection were evaluated for each alcohols separately on the basis of operating conditions like operation time, flow rate, pressure and concentration using the equations mentioned in our earlier work [19,20]. The separation performance of the prepared membrane was ascertained on the basis of the above mentioned factors. The permeation model for the NF system has been examined by using different models namely Pore Flow Model and Solution Diffusion Model [19-21]. The simplified version of the two models has been given below. Equation 1 corresponds to the pore flow model and equation 2 refers to solution diffusion model.

$$N_v = -\frac{d_{particle}^2}{180(1-\varepsilon)^2 \eta} \frac{\varepsilon^3}{\tau d} \nabla p \qquad (1)$$

$$N_i = P_{i,m}^{molar} \left(x_{i,f} - \frac{\gamma_{i,p}}{\gamma_{i,f}} x_{i,p} \exp\left(-\frac{\bar{V}_1 \Delta p}{RT} \right) \right) \qquad (2)$$

Results and Discussion

Characterization of membrane

Before going to the separation experiment, it is very essential to determine the physical properties of the membrane. Physical properties such as membrane thickness, pore diameter, contact angle, surface porosity and pure water permeability of membranes were determined by instrumental technique discussed in Section 2.2. The values of such properties are given in Table 1.

Figure 2 shows the top surface of the prepared membranes obtained from the SEM analysis. The top layer of the membrane is expected to form due to spinodal demixing which occurs because of the instability of the polymeric solution during the fast diffusion process [22]. SEM image of β-CD shows better morphology in comparison to the others (α- and γ-CD membranes). Figure 3 shows the cross-sectional image of α-CD, β-CD, and γ-CD membranes. It is observed that the membranes have asymmetric structures consisting of a dense top layer and a
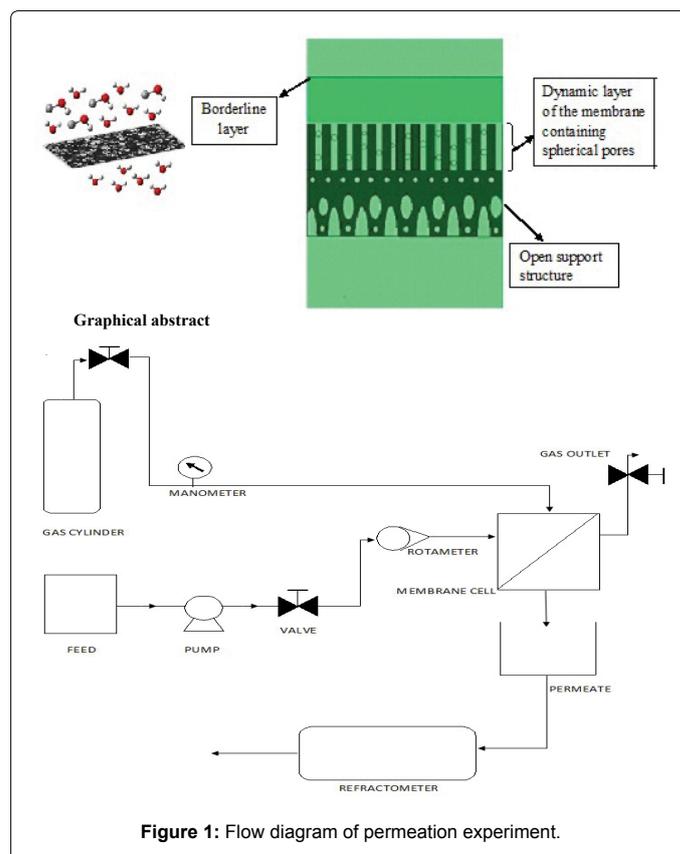

Figure 1: Flow diagram of permeation experiment.

Membrane material	Membrane thickness (μm)	Pore diameter (nm)	Surface porosity (ε%)	Pure water permeability (L m^{-2} h^{-1})	Water uptake (%)	Contact angle (°)
α-CD	57.40	5.12	0.44	55	14.32	78
β-CD	12.30	4.78	0.87	46	18.91	75
γ-CD	64.80	8.49	0.82	82	12.32	87

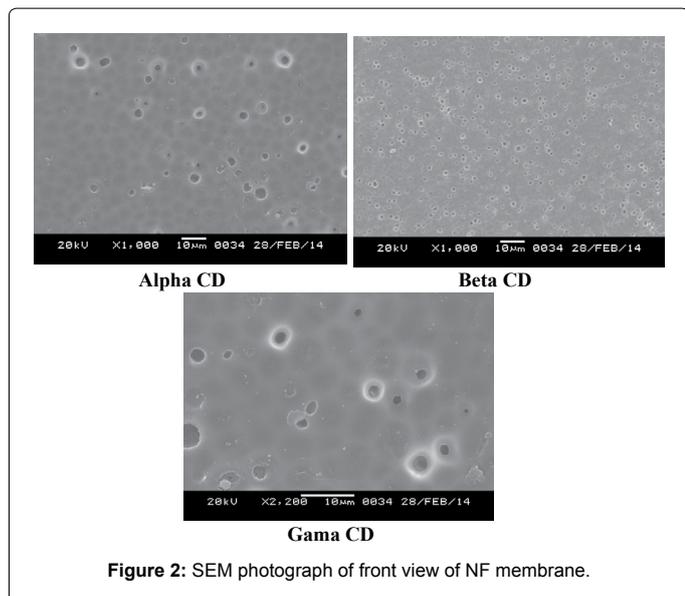**Table 1:** Physical properties of the composite NF membranes.

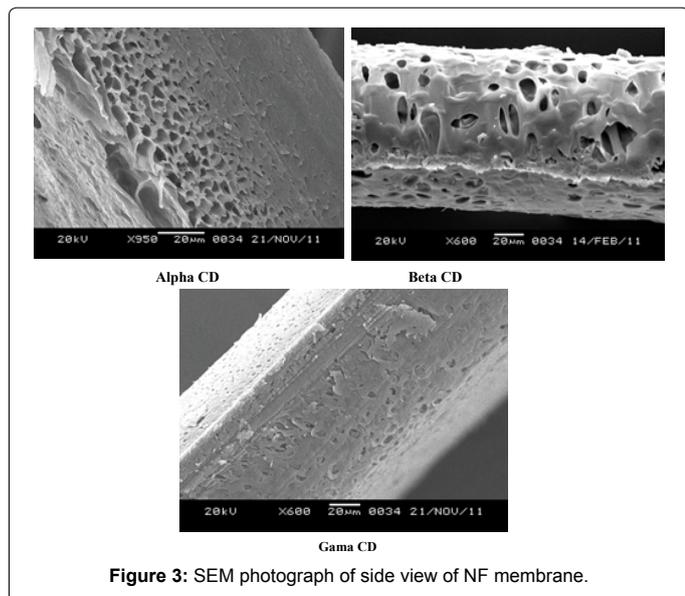**Figure 2:** SEM photograph of front view of NF membrane.

Figure 3: SEM photograph of side view of NF membrane.

porous sub layer. The sub layer seems to have finger-like cavities as well as macrovoid structure. This finger like cavity is due to instantaneous demixing of membrane material in the solvent [23].

SEM analysis unveiled numerous pores of β-CD membrane of diverse sizes. Overall 800-1100 pores were ascertained from the relative cross-section areas which were determined with the help of image-analysis program. The numerical mean of the pore sizes were noted and represented as the pore diameter distribution curve as shown in Figure 4. It was observed that the pores were homogenously distributed in case of β-CD membrane. Its pore size distribution is narrowest amongst the three membranes discussed here. For α-CD and γ-CD membranes the distribution curves are not so representative due to uneven distribution of pore size and hence not plotted.

TEM images of the membranes are shown in Figure 5. TEM pictograph distinctly reveals the conglomeration of the active layer of the membrane. β-CD fills the cavities of the Polysulfone support.

Therefore, it is observed that the upper surface of the membrane is much uniform than the meld of β-CD-Polysulfone. The circular patches in the micrograph of β-CD membrane indicate the pores or cavities of the membrane. The interstitial cavities of β-CD are interconnected forcing channels throughout the entire thickness of the membrane. Certain big pores are present in α-CD and γ-CD membranes which show the non-uniformity of the pores on the membrane surface.

Permeation of Methanol, Ethanol and Butanol through α-CD, β-CD, γ-CD

Membrane performances for separation of methanol, ethanol and butanol were studied differently using three types of membrane (α-CD, β-CD and γ-CD). Experiments were conducted using certain variable
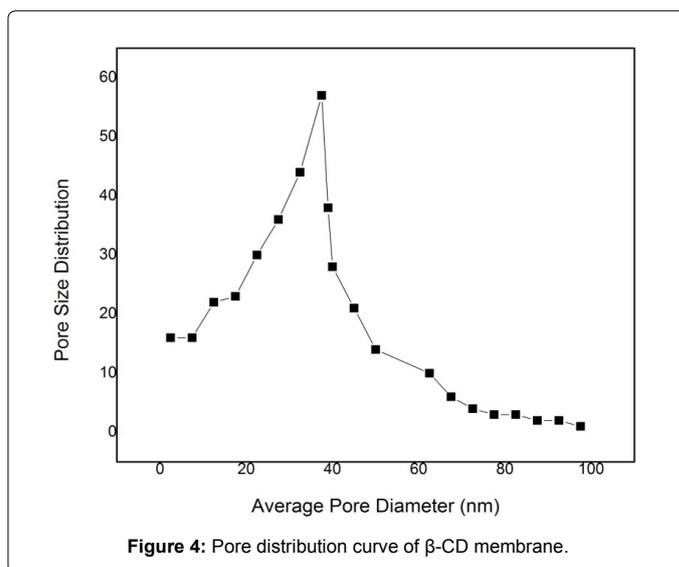

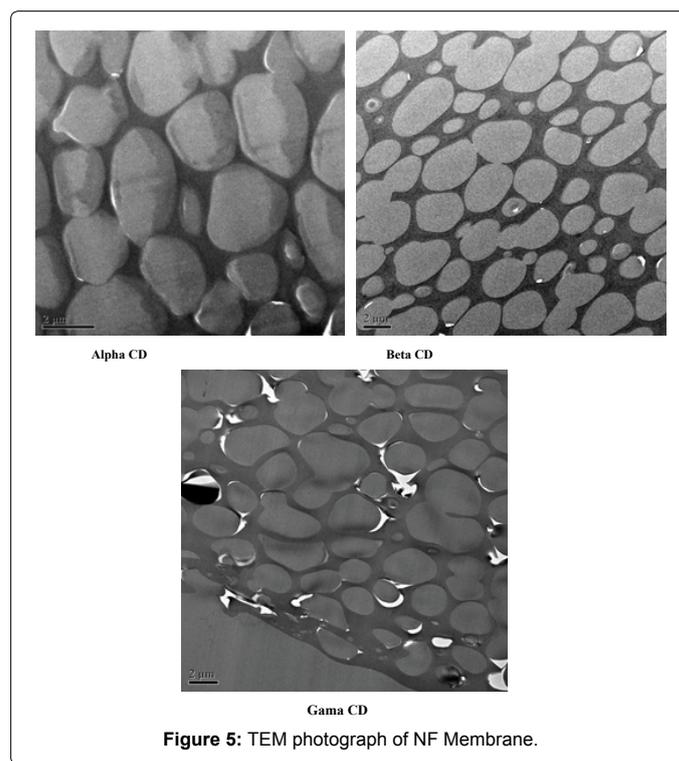**Figure 4:** Pore distribution curve of β-CD membrane.

Figure 5: TEM photograph of NF Membrane.

parameters such as concentration of feed solution, operating pressure, feed flow rate and time. Detailed results are discussed below.

Effect of concentration

In order to study the effect of concentration of the three alcohols on permeation process of β-CD membranes, experiments were carried out in the concentration range from 0.247 molL^{-1} to 1.73 molL^{-1} (7 wt %) for methanol, 0.171 molL^{-1} to 1.20 molL^{-1} for ethanol and 0.109 molL^{-1} to 0.766 molL^{-1} for butanol. Figure 6 shows that the permeation flux declined slowly before the concentration reached at 4 wt%. From this result it is observed that concentration of feed solution has a great influence on the separation performance of membranes. The steady permeation flux reached at 86.9 Lm^{-2}hr^{-1}, 84.9 Lm^{-2}hr^{-1} and 83.2 Lm^{-2}hr^{-1} for methanol, ethanol and butanol respectively at high concentration, shows that the membrane is suitable for this application [20]. In the same way, the rejection is high (over 99%) and is partially affected by the concentration of alcohols as shown in the same Figure 6.

Effect of pressure

Fouling is expected on the membrane surface at a low transmembrane pressure (TMP) because some of suspended solids did not receive high driving force to be pushed to the retentate side. Fouling refers to an increase in membrane resistance during a process. It is an undesirable phenomenon which is usually caused by adsorption and deposition of material on the membrane. As TMP is increasing from 10 to 20 bars, the percentage of Total Dissolved Solids rejection is also increases with increasing in exposure time. Studies show that the solute flux depends on concentration gradient across the membrane. Thus, when transmembrane pressure increases, solute passes through the membrane as water pushes the solute at a faster rate and it can be transported. Hence rejection increases with increasing pressure.
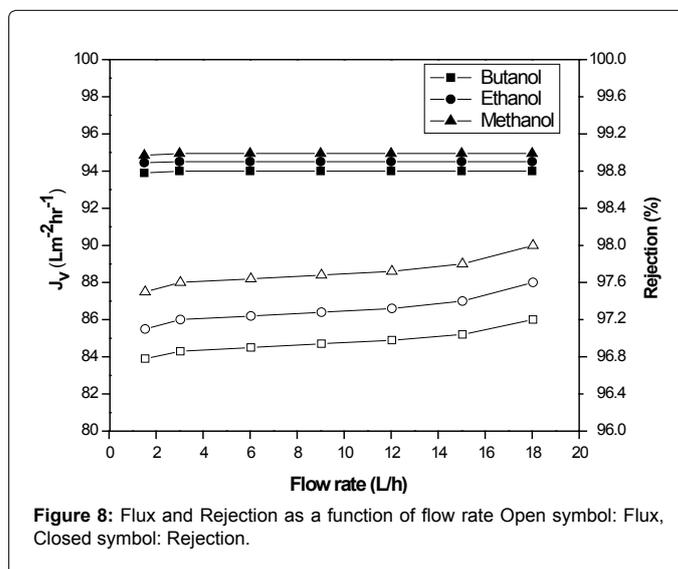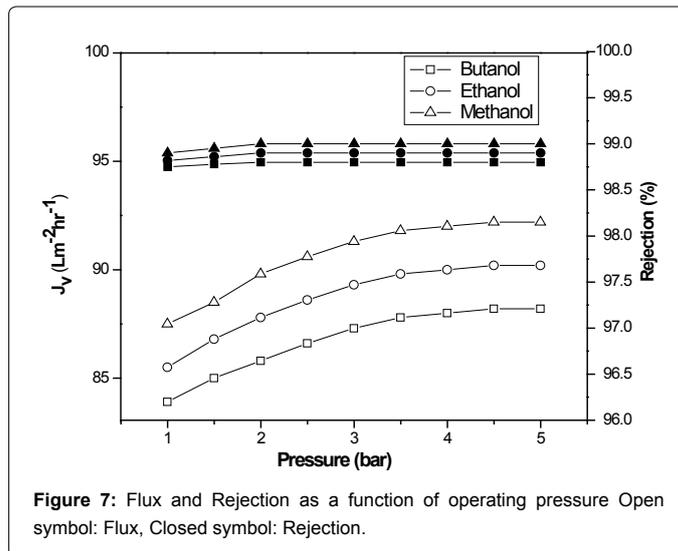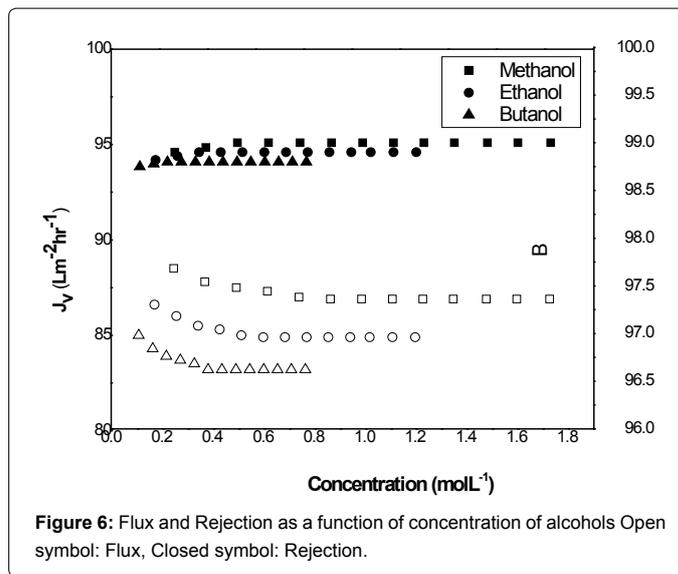
A suitable operating pressure for β-CD membrane separation system is found to be 3 bar. Permeation flux at 3 bar is observed to be 91.3 Lm^{-2}hr^{-1}, 89.3 Lm^{-2}hr^{-1} and 87.3 Lm^{-2}hr^{-1}. Slightly less permeation flux is observed compared to that observed at 5 bar, which is also large enough for commercial application. The rejection of alcohols was as high as 99% as in evident from Figure 7. The pressure was found to have little influence on the rejection for this separation process as the rejection is over 99%, even if at low pressure range [20].

Effect of flow rate

The effect of flow rate of alcohol solution on the separation performance of β-CD membrane is shown in Figure 8 wherein the rejection is also shown. The change in flow rate has not influenced the rejection; however it has little impact on permeation flux. The permeation flux increases when the feedstock flow rate goes up, which indicates that the mass transfer resistance exists in the boundary layer, and a high flow rate can reduce the resistance; but the range of permeation flux from 87.5 to 90 Lm^{-2}hr^{-1}, 85.5 to 88 Lm^{-2}hr^{-1} and 83.9 to 86 Lm^{-2}hr^{-1} for methanol, ethanol and butanol respectively is narrow, which means the boundary layer conditions is not very thick. Thus, the change of the flow rate has no significant impact on the variation of the thin boundary layer [20].

Effect of operation time

Experiments were carried out to study membrane stability in three alcohols and tested the performance of the membranes over a period of 4 months. From Figure 9, it is seen that, the separation performance was kept at a high level after a long period of work. Permeation flux decreased from 87.5 to a steady state of 86.5 Lm^{-2}hr^{-1} for methanol,

Figure 6: Flux and Rejection as a function of concentration of alcohols Open symbol: Flux, Closed symbol: Rejection.

Figure 7: Flux and Rejection as a function of operating pressure Open symbol: Flux, Closed symbol: Rejection.

Figure 8: Flux and Rejection as a function of flow rate Open symbol: Flux, Closed symbol: Rejection.

85.5 to 84.5 Lm^{-2}hr^{-1} for ethanol and 83.9 to 83.2 Lm^{-2}hr^{-1} for butanol. The slight decline of flux is due to membrane compaction at 4 months. The densification of the membrane under pressure reduced the flux through the membrane. Long-term operation has little influence on the rejection of alcohols as shown in the same figure, which indicates the solvent-resistant performance of the membrane [20].

Effect of temperature on permeate flux

The effect of solution temperature on permeate flux of the membrane at optimal conditions is shown in Figure 10. It can be observed that the temperature change from 10°C to 50°C modified the permeate flux of the membrane at other constant optimal conditions ([alcohol]: 0.494 moll^{-1}, 0.343 moll^{-1}, 0.218 moll^{-1} for methanol, ethanol and butanol respectively, flow rate: 100 ml/min and pressure 2 bar). Higher temperatures reduced the viscosity of the feed solution, and then the solution became easier to transfer through the membrane [24]. Thus, temperature is expected to have a fairly significant effect on permeate flux (Figure 11).
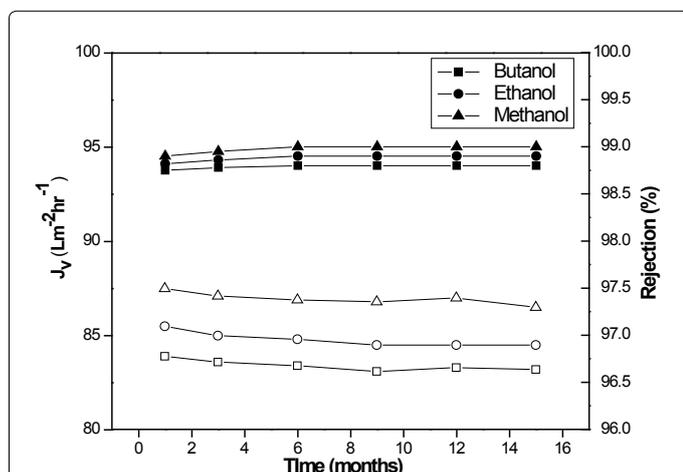

Figure 9: Effect of operation time on permeation flux and Rejection (Pressure 2 bar, flow rate: 100 ml/min, [alcohol]: 0.494 moll^{-1}, 0.343moll^{-1}, 0.218 moll^{-1} for methanol, ethanol and butanol respectively) Open symbol: Flux, Closed symbol: Rejection.
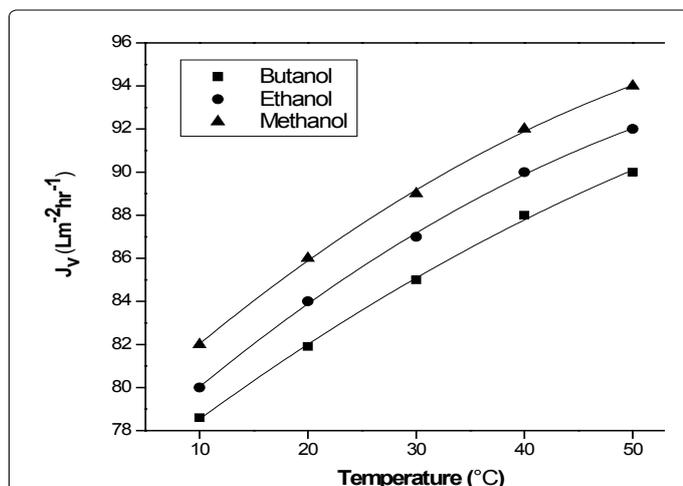

Figure 10: Effect of temperature on permeation flux and Rejection (Pressure 2 bar, flow rate: 100 ml/min, [alcohol]: 0.494 moll^{-1}, 0.343moll^{-1}, 0.218 moll^{-1} for methanol, ethanol and butanol respectively).
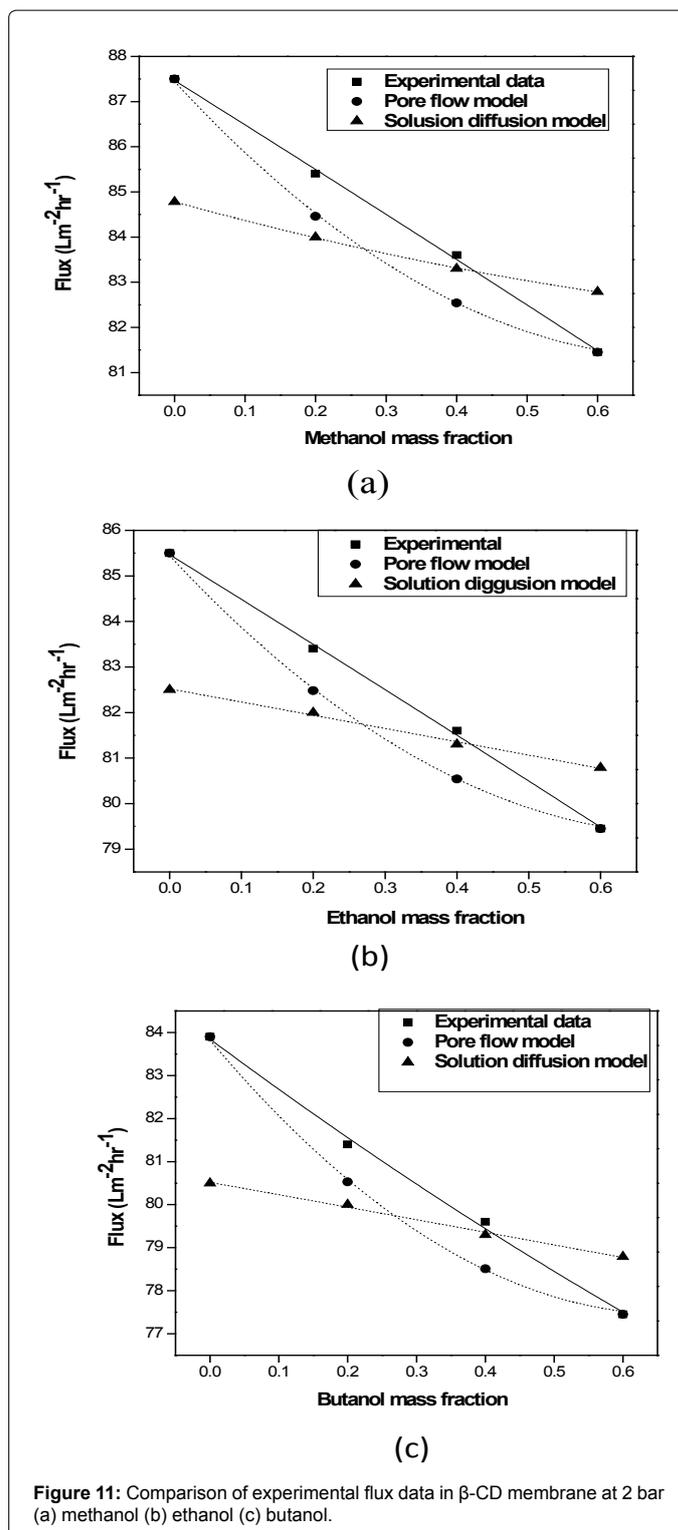

Figure 11: Comparison of experimental flux data in β-CD membrane at 2 bar (a) methanol (b) ethanol (c) butanol.

Transport model fitting and statistical analysis

It is incongruous to cogitate the same magnitude of viscosity for solvents concomitant with NF membrane and the solvents associated with the bulk system. Discrepancy may arise on incorporating the bulk solvent viscosity, while plotting the flux of different groups of solvents as a function of bulk viscosity. Orientation of the solvents molecules

in the vicinity of the tiny nano pore wall drastically abridged the solvent permeability [25-27]. Diverse hydrophilic and hydrophobic interactions between the solvent and the membrane are the origin for this permeation blocking alignment. Dias et al. [27] put emphasis to explore the structure of water inside the NF/RO membrane and concluded that feebly H-bonded water molecule clustered around a hydrophobic membrane and perturbed the permeability performance. A well-known fact about viscosity is that it decreases with decrease in pore dimension, however the minuscule pore of the NF membrane make it challenging to evaluate the viscosity precisely. Brown at el. [28] concluded that a tenfold increment in viscosity is observed when a mono layer of water molecule (d=0.28 nm) get endorsed at the pore of the NF membrane.

Pore Flow model was used to analyze the flux data. The predicted values using both pore flow and solution diffusion models are shown in Figures 11(a-c). The transport of alcohol through β-CD NF membrane follows in accordance to the pore flow model and can be implemented for the development of separation device for separation of alcohols from aqueous solution.

Conclusion

The efficiency of the NF membrane which were prepared from α, β and γ cyclodextrin embedded with polysulfone were analyzed experimentally for recovery of alcohols from its dilute aqueous solution. The ideal conditions were firmly ascertained by studying the effect of flow rate, pressure, operation time and concentration on the obtained permeation flux and percentage rejection. The optimum operating pressure for alcohol separation from its dilute aqueous solution with the help of polymeric composite membrane is 3 bar which is a convenient pressure range for its application. At this pressure β-CD membranes give 99% separation of alcohols from 1.73 molL^{-1} - 0.766 molL^{-1} solution. Highest flux value was found to be 91.3 Lm^{-2}hr^{-1} - 87.3 Lm^{-2}hr^{-1}. There is an increment in permeation flux due to the deduction in mass transfer resistance as a result of which high flow rate was obtained which evidently explains the decrease in the rejection when the feed stock flow rate goes up. There is no change in the activeness of the prepared membranes upto four months. The experimental results established that the pore flow model is best fitted for recovery of alcohols from aqueous dilute solution using membrane.

List of Symbols:

J — permeation flux (Lm^{-2}hr^{-1})

R — rejection

c — molar concentration (moll^{-1})

d_{pore} — pore diameter (nm)

$d_{particle}$ — particle diameter (m)

l — membrane thickness (nm)

n — mass flux (kgm^{-2}s^{-1})

N — molar flux (mol m^{-2}s^{-1})

N_v — total volume flux (m s^{-1})

J_v — Solvent flux (lm^{-2}hr^{-1})

Δp — Applied pressure (bar)

Π — Osmotic pressure (bar)

n — Number of moles of alcohol

R — Universal gas constant

V — Volume of permeate in time t (ml)

$P^{mass}_{i,m}$ — mass permeability (kgm^{-2}s^{-1})

p^{molar}_{im} — molar permeability (mol m^{-2}s^{-1})

R — ideal gas constant (Pa m^3 mol^{-1} K^{-1})

t — time (s)

T — temperature (K)

w — mass fraction

x — molar fraction

A — Membrane area (cm^2)

ΔC — Concentration variation in the corresponding aqueous solution at the time interval Δt

R_{obs} — observed Rejection

C_f — Concentration of the feed ((moll^{-1})

C_p — Concentration of the permeate side (moll^{-1})

T — absolute temperature

μ — chemical potential (Jmol^{-1})

ρ — density (kg m^{-3})

τ — tortuosity factor

$\alpha^{/}$ — viscous flow characterization parameter

β — membrane viscous flow characterization parameter

γ — molar activity co-efficient

δ — Hilderband solubility parameter (MPa$^{1/2}$)

ε — porosity

ζ — friction co-efficient (J s m^{-2} mol^{-1})

η — viscosity (Pa s)

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