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PREPARATION OF PVC HOLLOW FIBER MEMBRANE USING (DMAC/ACETONE)

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Abstract

Membrane manufacturing system was operated using dry/wet phase inversion process. A sample of hollow fiber membrane was prepared using (17% wt PVC) polyvinyl chloride as membrane material and N, N Dimethylacetamide (DMAC) as solvent in the first run and the second run was made using (DMAC/Acetone) of ratio 3.4 w/w. Scanning electron microscope (SEM) was used to predict the structure and dimensions of hollow fiber membranes prepared. The ultrafiltration experiments were performed using soluble polymeric solute poly ethylene glycol (PEG) of molecular weight (20000 Dalton) 800 ppm solution 25 °C temperature and 1 bar pressure. The experimental results show that pure water permeation increased from 25.7 to 32.2 (L/m^2.h.bar) by adding acetone to the dope solution, while rejection decreased from 91.8 to 63.2%.

Keywords: Polyvinyl chloride, (DMAC/Acetone) of ratio 3.4, ultrafiltration

Introduction

Membrane technology is presently an established part of several industrial processes. Well known is its relevance in the food industry, in the manufacture of dairy products as well as in the automotive industry for the recovery of electro-painting baths and wastewater treatment. Membranes make possible the water supply for millions of people in the world and care for the survival of the unnumerable people suffering from kidney disease. The chemical industry is a growing field in the application of membranes, which, however, often requires membrane materials with exceptional stability [1]. Ultrafiltration (UF) membranes are porous membranes with pore size ranging from 5 to 50 nm. The term ultrafiltration has been introduced to discriminate the process whose nature lies between nanofiltration and microfiltration [2]. Three modules of ultrafiltration can be obtained flat sheet, tubular and hollow fiber. For the hollow module the membrane is essentially a fiber with a hollow space (cavity) inside. A bundle of hollow fibers are assembled to gather in a module, with the free ends potted into a head plate The hollow fiber configuration is the favorite choice for modules in membrane separation because of the hollow fiber membranes having three major advantages over flat sheet membranes;

Hollow fibers have much larger ratio of membrane area to unit volume and hence higher productivity per unit volume of membrane module.

There is self supporting that can be back-flushed for liquid separation.
They have good flexibility in operation.
Therefore, the key properties determining membrane performance are high selectivity and fluxes, good mechanical strength, good chemical resistance, thermal stability under operating conditions, low fouling tendency, good compatibility with the operation environment, cost effective and defect free production [3].

Reverse osmosis and ultrafiltration membranes have been employed for the treatment of a variety of liquids ranging from seawater, to wastewater, to milk and yeast suspensions. Each liquid varies in composition and in the type and fraction of the solute(s) to be retained by the membrane. Complicating factors include the presence of substances such as, for example, oil in seawater and waste water. The presence of the oil normally necessitates an additional pretreatment step as well as further complicating the fouling process. The presence of humic acids in surface water and waste water also needs special attention. The fouling phenomena, the preventive means (i.e. pretreatment), and the frequency and type of membrane cleaning cycle are all dependent on the type of liquid being treated [4]. These two processes, ultrafiltration (filtration to 10 Angstroms for dissolved organic removal) and reverse osmosis (filtration to 5 Angstroms for dissolved organic and inorganic removal) are relatively new to the soft drink industry. Several reverse osmosis systems have been installed over the last five years and a few ultrafiltration units have been installed where only filtration and organic removal have been necessary [5].

Objective

Study the effect of using double solvent on performance and structure of hollow fiber membranes by using membrane performance system and scanning electron microscope (SEM).

Membrane Performance

The performance of a membrane is defined in terms of two simple factors, flux and retention or selectivity. Flux or permeation rate is the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time [5].

$$Flux = Q / A\,\Delta P \quad \ldots (1)$$

Where Q is the volumetric permeate flow rate (Lh^{-1}), A is the surface area of hollow fiber membranes (m^2) and ΔP is the transmembrane pressure (bar).

Selectivity is a measure of the relative permeation rates of different components through the membrane while retention is the fraction of solute in the feed retained by the membrane.

Ideally a membrane with a high selectivity or retention and with a high flux or permeability is required although typically attempts to maximize one factor are compromised by reduction in the other.

The simplest way to express the solute rejection characteristic of hollow fiber membrane is through observed/apparent rejection defined as the following relation [5].

$$R(\%) = \left(1 - Cp / Cf\right) \times 100 \quad \ldots (2)$$

Where C_p and C_f denote concentration of permeate and concentration of feed/bulk solution respectively and both can be measured.

Porosity Measurements

The membrane porosity, ε_m, can be defined as the volume of the pores divided by the total volume of the membrane. Briefly, hollow fibers, not previously treated with the glycerol solution, were dried and weighed with

a precision balance. The overall porosity was calculated as shown in table (2) according to the following formula [6]:

$$\varepsilon_m(\%) = (1 - \rho_{fiber} / \rho_{PVC}) \times 100 \quad \ldots (3)$$

Where ρ_{fiber} is the fiber density, ρ_{PVC} is the PVC density.

The fiber density was calculated from the mass and volume ratio:

$$\rho_{fiber} = 4m — \pi \cdot (OD2 - ID2) \quad \ldots (4)$$

Where *l* is the fiber length, *m* its mass, ID and OD the inner and the outer diameter, respectively.

Experimental Work

The polymeric membranes production is a complicated process since it involves many steps namely; material selection, drying process, dope solution preparation, casting or hollow fiber spinning, phase inversion process, and post treatment.

Materials

1. Polyvinyl chloride (PVC) powder as a membrane material, with K value 67, supplied by Gerhard Buchmann Kg Tuttlingen/Germany.

N, N Dimethylacetamide (DMAC) supplied by Seelze-

2. Hannover/Germany was used as a single solvent. N, N Dimethylacetamide and Acetone of purity 99.8% were used as double solvent to prepare polymer solution.
3. Poly ethylene glycol of molecular weight (Mw 20000 Dalton) supplied by Merck was used as a reference solution for characterizing the hollow fiber membranes performance.
4. Distilled water was used as internal coagulation fluid (bore fluid) and tap water as external coagulation one.

Dope Solution

Dope solution of 100g was prepared for both experiments, PVC powder which dried in an oven for 6 h at 70 °C to remove moisture content then dissolved in single solvent N, N Dimethylacetamide (DMAC) (17/83 wt/wt PVC/DMAC), for the second experiment PVC powder dissolved in a mixture of two solvents DMAC and Acetone at a ratio of 3.4 w/w keeping the ratio of(PVC/DMAC and Acetone) 17/83 wt/wt.

Spinning Process

Spinning process is a physical process, which involves the extrusion of a polymer solution through an annular spinneret (inner diameter 1mm, outer diameter 2mm) to form a hollow fiber. The dope solution entered the side opening of the spinneret No. 5 as shown in fig. (1) under an extrusion pressure of 0.1 bar of nitrogen, distilled water was used as an internal coagulant which pumped to the tube of the spinneret at a water flow rate (0.15 mL/s).The nascent hollow fiber membranes passed through a certain air gap 5 cm distance before entering the external coagulant bath (tap water at 25 °C).

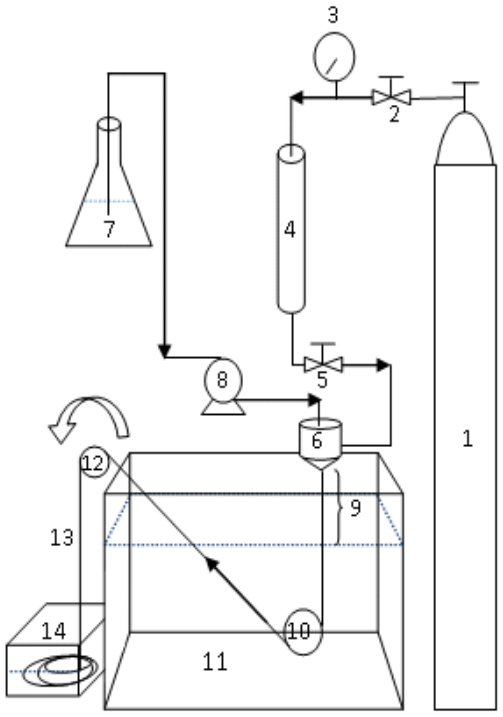


Fig. 1: Schematic diagram and manufacturing unit of the spinning system: 1- Nitrogen tube. 2-Pressure valve. 3-Pressure gauge. 4-Dope solution column. 5-Dope solution valve. 6-Spinneret. 7-Bore fluid container. 8-Bore fluid pump. 9-Air gap length. 10-Movable wheel. 11-Coagulation tank. 12-Take-up unit. 13-Hollow fiber membranes. 14- Hollow fibers reservoir container (fill with water)

Post Treatment

After the spinning of hollow fiber, the prepared membranes were put in a water bath at room temperature for at least one day to remove the residual solvent completely without further drying. After that they were kept in an aqueous solution of 25% glycerol (by volume) for 48 hour to avoid collapse of its porous structure and dried in air at room temperature.

Equipments

The cross sections and dimensions (inner diameter, outer diameter, and thickness) were determined using scanning electron microscope (Tescan performance in Nano space version 3.5.12.0). The feed and permeate solute concentrations were determined by using UV spectrometer (Thermo electric/Genesys 10UV).

Results

One of the important goals in membrane technology is to control membrane structure and thus membrane performance (flux and rejection). Membrane with higher flux leads to higher productivity and lower capital costs whereas membrane with higher rejection leads to higher recovery and lower power costs. [5]

Membrane Dimensions

Inner diameter, outer diameter and thickness were measured using SEM for the two system membranes single solvent (SS) and double solvent (DS) as shown in table (1).

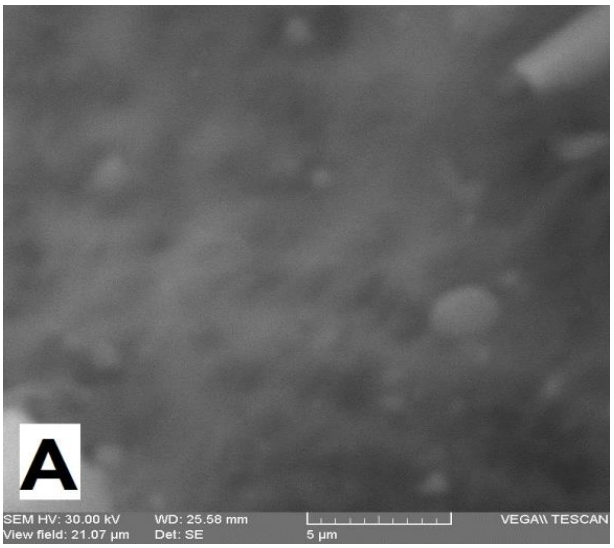
Table 1: Membrane dimensions

Membrane system	Inner diameter (mm)	Outer diameter (mm)	Average thickness (mm)
(SS)system membrane	0.80	1.10	0.15
(DS)system membrane	0.68	0.97	0.14

Table 2: Porosity of hollow fiber membranes prepared according to equation (3).

Membrane system	Porosity %
(SS)system membrane	21.6
(DS)system membrane	44.6

Porosity % doubled by adding small amount of acetone to the dope solution which can be observed from Fig. (2).



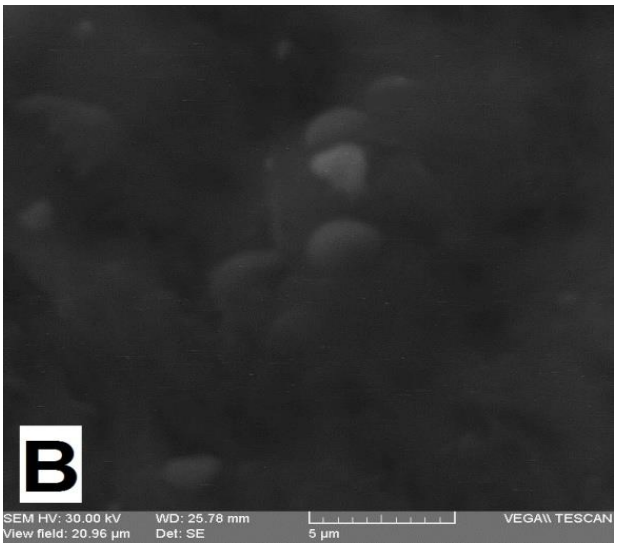
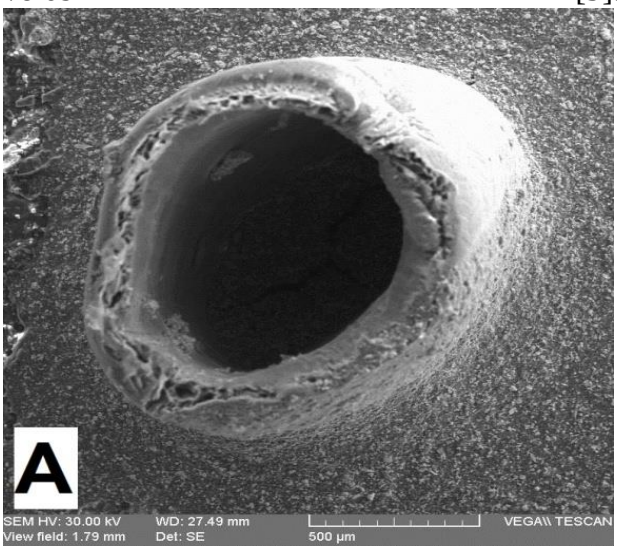


Fig. 2 SEM surface images (A) single solvent (SS) (B) double solvent (DS)

Effect of Using Double Solvent on Morphology and Flux of Hollow Fiber Membrane

Solutions using low solubility- parameter solvents, such as acetone are generally not appropriate. Such casting solutions precipitate slowly and give relatively nonporous membranes. Small amounts of these solvents may be added as casting solution modifiers [7]. However, PVC is insoluble in pure acetone [8]. Acetone acts as a non-solvent additive. It has been reported that the properties of polymer membranes could be improved by introducing non-solvent additives in the polymer solution [9]. Fig. 2 shows the structures of cross-sectional SEM pictures of hollow fiber PVC membranes. In Fig. (2) a-fiber without additives has a wide finger-like structure while Fig. (3) b-fiber with acetone additive show that the finger-like structure became thinner. Several authors reported that appropriate amount of non-solvent additives enhanced the formation of macro voids [9].



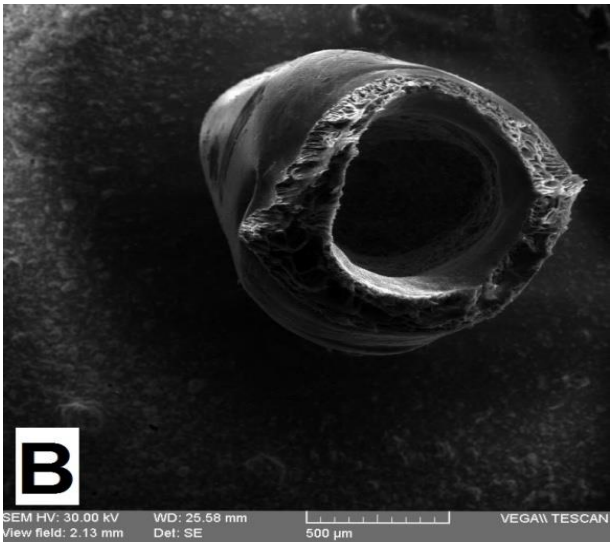


Fig. 3 SEM observations (A) single solvent (SS) (B) double solvent (DS)

As the macro-porous of the membrane increase the pure water permeation flow (PWPF) increase and rejection decrease as shown in table (3), pure water permeation fluxes (PWPF) were obtained from equation (1).

Table (3): Pure water permeation flow and rejection of PEG (20000 D) for PVC hollow fiber membrane at feed flow rate 10 L/h.

Membrane system	Polymer concentration (wt. %)	PWPF Jpwpf	Rejection R%
(SS) system	17	25.7	91.8
(DS) system	17	32.2	63.2

A feed solution of 800 ppm PEG (20000 D) was used to measure permeability and rejection of the prepared hollow fiber membranes. The feed flow rate was 10 L/h Fig. 3 and Fig. 4 shows the permeation flux decreased with time at operating temperature 25 °C and 1 bar pressure for horizontal hollow fiber module. Flux decreased according to accumulated solute (PEG).

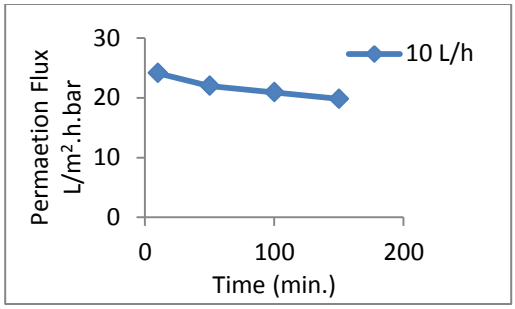


Fig. 4 Permeation flux of solution 800 ppm PEG (20000 Da) for single solvent (SS) system.

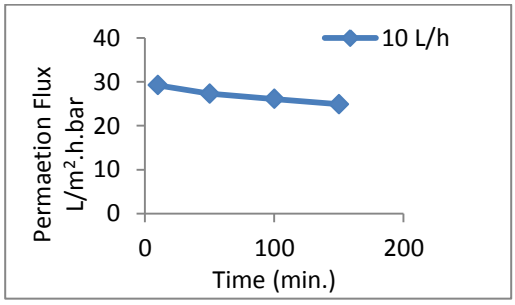


Fig. 5 Permeation flux of solution 800 ppm PEG (20000 Da) for double solvent (DS) system.

Conclusions

Hollow fiber ultrafiltration membranes were prepared using two solvents system, single solvent (SS) and double solvent (DS). According to the results, the following facts can be obtained:

High polymer concentration (17 wt. %) might result in a hollow fiber membrane with a dense skin layer in single solvent system.

SEM pictures illustrated that PVC membrane morphology changed from wide finger-like structure through a thin finger-like structure with some voids.

Macro-porous membranes were obtained in double solvent system.

According to the macro-porous, permeability was increased and rejection decreased.

Nomenclature

Symbol	Definition	Unit
ρ_{fiber}	Fiber density	g/ cm^3
ε_m	Membrane porosity	---
J	Pure water flux	L/(m^2·h·bar)
ρ_{PVC}	PVC density	g/ cm^3
R	Rejection	---
A	Surface area of hollow fiber	m^2
ΔP	Transmembrane pressure	bar
Q	Volumetric flow rate	L/h

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