PERVAPORATION OF AQUEOUS ETHANOL SOLUTIONS THROUGH PURE AND COMPOSITE CELLULOSE/BIOCELLULOSE MEMBRANES

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Abstract.
The pervaporation performance in terms of total permeate flux, separation factor with respect to the separation of ethanol/water was assessed for composite membranes based on composite cellulose, obtained from solutions containing dissolved cellulose in NaOH - thiourea solutions, biocellulose and tetraethyl orthosilicate (TEOS). The phase inversion method was employed for membrane preparation using cellulose/bio cellulose/TEOS solution. The casting solution was spread as a thin film on to a glass plate (for non-supported membranes) or on a paper support (for supported membranes) and then exposed to ambient air for 24 h. NaOH and thiourea were removed from the film by treating with 1M HCl solution and rinsing with distilled water to a neutral pH. The rinsed membrane was kept in distilled water for 24 h and further dried at room temperature. Three content of biocellulose, 0% ,10% and 30%, with different operation temperature has been used in experiment. Pervaporation performances, which were evaluated in terms of total permeate flux and pervaporation separation factor, strongly depended on membrane biocellulose content, on ethanol concentration and operation temperature. The experiment showed that the flux increases with decreasing the ethanol content and with increasing the operation temperature.

Key words: alcohols dehydration, cellulose membrane, biocellulose membrane, permeate flux, pervaporation, separation factor

1. Introduction

The following four process, namely liquid- liquid extraction, extractive distillation, chemical adsorption and azeotrope distillation, are used in separation of mixtures containing organic compounds and water. The disadvantages of these techniques are represented by demand of external entrainer, extensive amount of energy and downstream processing to recover key component [1]. In the last year's pervaporation is considered a promising process for dehydration of solvent [2, 3]. The process was already mentioned in the early of the 20th century; first major research efforts were made by Binning et al. beginning with 1950 year at the American Oil Company [4]. Pervaporation (PV) is an emerging membrane separation technology with the merit of low operating costs. The disadvantages of

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the pervaporation are the high capital cost and the low maximal capacity [5]. In PV process, the feed liquid mixture is placed in contact with one side of non-pours membrane and one of these liquids is removed as permeate from other side as vapor at low-pressure [6, 7]. In recent decades, the world's present economy is highly dependent on various sources of fossil energy production such as, coal, natural gas, oil etc. but these sources are non-renewable [8]. Ethanol is one of the most renewable promising future fuels due to its simplicity of production process, high energy value and environmentally friendly comportment.

The ethanol derived from fermentation has received a wide popularity as a fuel [9, 8, 10]. Pervaporation is one of the good processes that are used to reduce the effect of product inhibition and improve the sugar utilization and solvent productivity in fermentation process [11]. Repeat units characterizing the structure of some pure membranes widely employed for pervaporation of organics (hydrophobic membranes) or water (hydrophilic membranes) from organics-water mixture, especially from ethanol-water system, are shown in figure 1 [12].

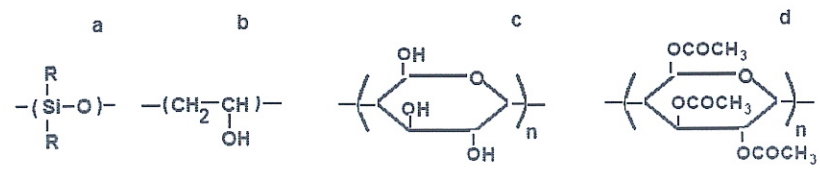

Fig. 1. Repeating units in membranes for processing water-ethanol system (a- polydialkylsiloxane (hydrophobic), b- polyvinyl alcohol (hydrophilic), c- cellulose (hydrophilic), d- cellulose triacetate (hydrophilic))

Cellulose is called biocellulose (BC) when it is obtained by mean of some bacteria through biosynthesis, using glucose as substrate. The most efficient producer of bacterial cellulose is *Acetobacter xylinum* (or *Gluconacetobacter xylinus*), a gram-negative strain of acetic-acid-producing bacteria [13, 14]. The BC can be used with many polymers as composite membrane due to its good mechanical properties, high water absorption capacity, very low porosity, high adsorption capacity for some compounds, stability; properties due to a highly crystalline material structure [15].

Composite organic-inorganic membranes based on TEOS ($Si(OCH_2CH_3)_4$), as an inorganic precursor, have been widely applied to separate aqueous-organic systems [16, 17]. In synthesis of these membranes the silanol groups (–Si–OH), obtained by TEOS hydrolysis, give siloxane bonds (–Si–O–Si–) by dehydration reaction with other silanol groups or dealcoholizes reaction with ethoxy group (–Si–O–CH_2CH_3). For cellulose membranes, siloxane structures are dispersed among cellulose chains resulting in a more open network of hybrid membrane, *i.e.*, exhibiting a larger free-volume [12].

This work has aimed at preparing and characterizing cellulose based hybrid membranes with biocellulose as well as at their testing for pervaporation separation of ethanol-water system. The effect of, ethanol concentration and operation temperature on pervaporation performances, expressed as total permeate flux, separation factor was evaluated.

2. Experimental

Materials

Cotton cellulose powder (50 μm diameter, 0.600 g/cm^3 density), tetraethyl orthosilicate (TEOS) min 98 % as well as crystals of urea ($C_2H_4N_2O$) and thiourea ($C_2H_4N_2S$) were supplied by Sigma-Aldrich Chemie (Germany). NaOH pellets were purchased from Merck (Germany). All reagents were used without further purification. A porous paper support was used to prepare supported pure and composite membranes

Casting solution preparation

For the synthesis of pure cellulose membranes, a casting solution was prepared according to the following procedure: (i) an alkaline solution containing 9 wt. % NaOH and 5 wt. % urea/thiourea was selected as solvent for cellulose; (ii) cellulose powder (CE) was added to the alkaline solution forming a slurry with 8.5 wt. % cellulose, (iii) never dried biocellulose fibres (BC) were added to the solution at 3 values (0 %, 10 %, 30 %) expresses as BC mass percentage relative to total mass of cellulose, which was stirred for 3 hours at a temperature up to 30°C; (iv) the stirred slurry was frozen at about -18 °C for minimum 24 h; (v) the frozen solution was thawed at room temperature and a hydrogel (casting solution) was obtained. For the synthesis of composite cellulose membranes, the casting solution prepared conforming to (i)-(iv) steps was mixed for 10 min with TEOS with 10% mass relative to CE.

Membrane preparation

Supported and non-supported composite/cellulose membranes were synthesized by the phase-inversion method, as follows: (i) the casting solution with/without BC was spread as a thin film onto a glass plate (for non-supported membranes) or a paper support (for supported membranes) and then exposed to ambient air for 24 h; (ii) NaOH and urea/thiourea were removed from the film by treating with 1M HCl solution and rinsing with distilled water to a neutral pH; (iii) the rinsed membrane was kept in distilled water for 24 h and further dried at room temperature.

Optical microscopy (OM) analysis

Casting solutions with/without BC were analysed by means of IOR ML-4M optical microscope (IOR, Romania) in order to observe in these the quality of dissolved cellulose and the distribution of BC fibrils.

Pervaporation tests

Pervaporation experiments were carried out in a batch stirred cell operated under vacuum. The supported membrane was put on a sintered steel disk, 5 μm average pore diameter, welded to the top of the lower compartment. The upper compartment containing the feed ethanol-water mixture was closed in order to stop any loss from feed. Before starting an experiment, the membrane was equilibrated for 30 minutes with a liquid mixture of the same composition as that of the feed. The swollen membrane was then placed in the pervaporation device and the feed liquid was charged to the upper compartment, wherein a magnetic stirring was used to mix the ethanol-water solution. This stirring aimed at minimizing the mass transfer resistance between the feed liquid and membrane. A vacuum of 100 mbar was applied to the lower compartment by means of a vacuum pump (Sartorius, Japan) and the permeate was collected in an ice trap.

The liquid temperature in the feed compartment and the system mass were measured before starting (t_i , m_i) and after finishing (t_f , m_f) an experiment. Total pervaporation flux, j_p, was estimated using Eq. (1), where m is the mass of the permeate collected during the pervaporation time, $\Delta\tau$, and A the effective membrane area.

$$j_p = \frac{m}{A\Delta\tau} = \frac{m_i - m_f}{A\Delta\tau} \quad (1)$$

Ethanol concentrations in the permeate and feed samples were estimated using an Atago Abbe refractometer (Atago, Japan). Separation factor relative to water and ethanol, $\alpha_{w/eth}$, was calculated with Eq. (2), where X and Y represent the mass fractions of species in the feed and permeate, respectively.

$$\alpha_{w/eth} = \frac{(Y_w / Y_{eth})}{(X_w / X_{eth})} \quad (2)$$

3. Results and discussions

Optical microscopy images of casting solutions with and without biocellulose, shown in figure 2, indicates the appearance of a basic uniformed structure with some local agglomeration of dissolved cellulose (figure 2a) in which the biocellulose fibrils are orderly distributed (figure 2b and 2c). It can be appreciated that the membrane will result from these type solutions will have a homogenous structure.

The pervaporation experimental measurements are performed in term of total permeate flux j_p, and separation factor $\alpha_{w/eth}$. For that in pervaportion experiments

has been used 7 values of water content in feed (c_w in 17.2-80.6 % range), 3 values of biocellulose mass content in swelled membrane (c_{BC} in 0-30% range), and three values of operation temperature (t in 25-45 °C range). The results, presented in figure 3, show an increase in total permeate flux with all process operational parameters (process factors). Increasing water content in the feed increases the permeate flux due to increase the swelling of membrane and this give more flexibility of membrane chains. On the other hand, the permeate flux getting bigger with temperature due to increase the mobility of the chain molecules of membrane. This phenomenon led to increase the diffusion of components inside of gel membrane.

Fig 2. Optical microscope images of casting solutions with and without BC at 100x magnification: a - without BC, b- 10 % BC, c- 30 % BC;

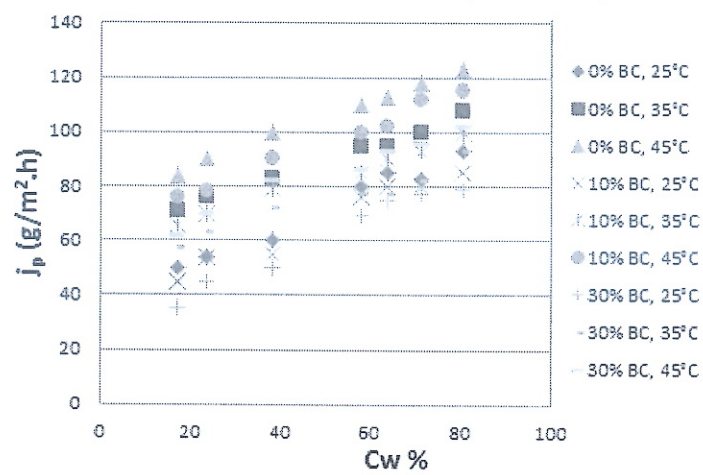

Fig. 3. Effect of water mass percentage in the feed (C_w) on pervaporation flux (j_p) for CE-TEOS-BC membrane

As shown in figure 3, the separation factor, $\alpha_{w/eth}$, is strongly dependent on c_w and c_{BC}. From figure 3 one can observe that $\alpha_{w/eth}$ for pure cellulose membrane drops from (11.9-13.5) to (4.5-5.1), for 10% BC membrane from (12 -13) to (4.3-5), where for 30% BC membrane from (13.8 -14) to (4.8-5.8). Accordingly, to these data $\alpha_{w/eth}$ decreases with increasing of c_w and decreasing the BC percentage.

This behaviour of composite cellulose membrane suggested that membrane is strongly hydrophilic due to the high hydrophilicity of biocellulose. An enhancement of membrane swelling by an increase in c_w, which has negative influence on separation factor and this swelling allows some of ethanol molecules to diffuse through the membrane with water molecules.

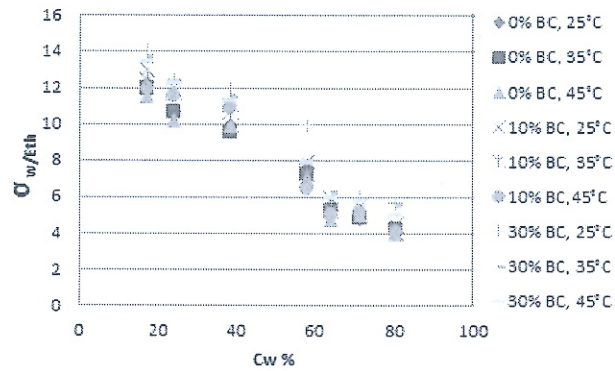

Fig. 4. Effect of water mass percentage in the feed, c_w, on separation factor, $\alpha_{w/eth}$, for CE-TEOS-BC membrane

The data from figures 3 and 4 can be used to obtain the relations describing the dependency of pervaporation flux and separation factor upon process factors (water content of the feed, c_w, biocelluose concentration in the membrane, c_{BC}, and temperature, t) by these using in completing of one factorial experimental plan type 2^3[18]. The dimensionless factor values in Table 1 were computed as it is shown by relationships (3). They serve in rapid determination of characteristic coefficients of regression relationship for 2^3 factorial plan that connects the response process with process factors [18].

Table 1

Matrix of factors influence on pervaporation flux and separation factor for CE-TEOS-BC composite membranes (c_{wc}= 0.5, Δc_{wc}=0.3, c_{BCc}=0.15, Δc_{BC}=0.15, t_c=35, Δt = 10)

No. exp.	c_w kg w/kg m	c_{BC} kg BC/kg CE	t ^{0}C	X_1	X_2	X_3	j_p g/(m^{2}h)	$\alpha_{w/eth}$
1	0.2	0	25	-1	-1	-1	51	12.3
2	0.2	0	45	-1	-1	+1	85	11.5
3	0.2	0.3	25	-1	+1	-1	38	14.1
4	0.2	0.3	45	-1	+1	+1	62	13.8
5	0.8	0	25	+1	-1	-1	93	4.2
6	0.8	0	45	+1	-1	+1	125	3.9
7	0.8	0.3	25	+1	+1	-1	77	5.7
8	0.8	0.3	45	+1	+1	+1	105	5.1
9	0.5	0.15	35	0	0	0	77	4.95
10	0.5	0.15	35	0	0	0	78	4.85
11	0.5	0.15	35	0	0	0	77.5	5.05

$$X_1 = \frac{c_w - c_{wc}}{\Delta c_w}, X_2 = \frac{c_{BC} - c_{BCc}}{\Delta c_{CB}}, X_3 = \frac{t - t_c}{\Delta t} \quad (3)$$

The processing of data from table 1 for obtaining the j_p and $\alpha_{w/eth}$ as functions of c_w, c_{BC} and t goes to relationships (4) and (5). They quantitatively argue all comments above given refering to figures 3 and 4. Except the X_2X_3 interaction, that slowly affects the total pervaporation flux, no other interaction between factors are important in determining j_p and $\alpha_{w/eth}$. It is noteworthy that the linear influences of water concentration in processed mixture (X_1 as dimensionless expression), BC membrane concentration (X_2 as dimensionless expression) and temperature (X_3 as dimensionless expression) are in opposition inside of relations for j_p and $\alpha_{w/eth}$. In other words, if a highly selective membrane is wanted then it will operate with low pervaporation flux.

$$j_p = 79.5 + 20.5X_1 - 9X_2 + 14.75X_3 - 1.75X_2X_3 \quad (4)$$

$$\alpha_{w/et} = 8.825 - 4.1X_1 + 0.85X_2 - 0.25X_3 \quad (5)$$

6. Conclusions

Cellulose membrane was prepared by phase inversion process and tested in pervaporation of water-ethanol mixtures. Composite membranes were obtained on a casting solution by adding biocellulose and TEOS. Total flux j_p and separation factor $\alpha_{w/eth}$, were studied with different operational parameters (mass content of water in feed, c_w= 17.2-80.8%), biocelluose mass loading, c_{BC}= 0-30%, TEOS mass content 10%, operation temperature, t = 25-45 ^{0}C). Experimental results showed an increase in permeate flux j_p of 10 and 30 % bicelluose with all operational parameter, moreover decrease of $\alpha_{w/eth}$ with increasing water content and operational temperature. Analytical expressions for j_p and $\alpha_{w/eth}$ upon pervaporation process factors has been established. The experimental results show that these composite membranes are hydrophilic membrane.

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