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PREPARATION AND PROPERTIES OF CELLULOSE ACETATE –COAL HETEROGENEOUS REVERSE OSMOSIS MEMBRANES

The heterogeneous asymmetric reverse osmosis membranes made from a blend of cellulose acetate and powdered coal prepared from two different composition of casting solvent solutions have been studied. Blends of cellulose acetate–coal of the following proportions by weight (1:1), (1:1.25) and (1:1.5) are tested with the first solvent mixture (acetone–dioxane), and the composition of cellulose acetate–coal in ratio (1:1.5) with three different types of coal and the second solvent (acetone) is also verified under the same casting solution, temperature, solvent evaporation time and gelation medium. The difference in performances caused by changes of solvents as well as by various amounts and types of coal are presented. At 86–90% level of solute separation and feed flow conditions corresponding to a mass transfer coefficient of $45 \cdot 10^{-4}$ cm/sec the productivities of the membranes are 49.89–30.99 g/(h/cm^2) at $17 \cdot 10^5$ Pa using 6.86 mol/dm^3 of NaCl in the feed. The reverse osmosis separation of other 10 inorganic salt solutions under the same conditions as in permeability tests have also been tested. The scanning electron micrographs of membranes with overaged reverse osmosis characteristics are given.

1. INTRODUCTION

During the last decades the cellulose acetate has been found as the best membrane material for most applications of reverse osmosis. By varying the composition of the casting solution, solvent evaporation rate during film formation, the precipitation medium and precipitation temperature, different asymmetric reverse osmosis membranes of high performances have been produced. The mechanism of formation of these membranes has been already investigated and is well known [1]–[8]. In addition to these achievements there have been numerous attempts to prepare asymmetric reverse osmosis membranes from different polymers or by addition of other additives to cellulose acetate casting solution. The introduction of the new additives (often native materials) as clay minerals, fly ash and coal with little or without any pretreatment becomes very common [21]. Most of such trials had a simple intention to make a better, usually more productive and selective reverse osmosis membranes, but only few of them were successful [9]–[11].

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The aim of this study was to prepare highly productive cellulose acetate–coal heterogeneous reverse osmosis membranes able to operate at low pressures.

2. EXPERIMENTAL

2.1. MATERIALS

Cellulose acetate Eastman Kodak 398-3 with 39.85% degree of acetylation and coals of Kosova (Bardh and Madh), Bosnia (Tuzla) and Poland were used for preparation of heterogeneous asymmetric reverse osmosis membranes.

2.2. COAL PREPARATION

The coal specimens were treated with boiling water under stirring conditions. The residual coal after filtering was dried at 105 °C to constant weight, ground and sieved. The coal fraction of >0.09 mesh particle size was used in this study.

2.3. FILM CASTING DETAILS

The composition of the casting solution and the conditions for membrane preparation are given in table 1.

Table 1

Film casting details of 6 different batches

Casting solution	Concentration (wt. %) Batches		
	602-1	602-2	602-3
Cellulose acetate (E 398-3)	10	10	10
Coal (K)	10	12.5	15
Acetone	56.2	55	52.2
Dioxane	10	8.7	9
Magnesium perchlorate	1.45	1.45	1.45
Water	12.35	12.35	12.35
Casting solution	Batches		
	316-K	316-B	316-P
Cellulose acetate (E 398-3)	10	10	10
Coal (K, B, P)	15	15	15
Acetone	61.30	61.30	61.30
Magnesium perchlorate	1.45	1.45	1.45
Water	12.25	12.25	12.25

The letters K, B, P mean Kosova, Bosnia and Poland coals, respectively.

Conditions of membrane preparation:

Temperature of casting solution:	24 °C.
Temperature of casting atmosphere:	24 °C.
Casting in ambient air:	(RH-60%).
Solvent evaporation time:	zero min.
Duration of film-setting in ice-cold water ~0 °C:	1h.

Films were cast on a clean glass plate using a metal cylinder with uplifted edges to obtain the same film thickness. After being cast the membranes were allowed to remain in gelation bath for one hour and subsequently were treated by immersion in a water bath of the desired temperature for 10 min. The membranes shrunk at different temperatures (88, 80, 75 and 60 °C) were used to give different levels of solute separation at a given set of operating conditions. The temperature of this water bath was controlled to within ±0.5 °C. The membranes were initially subjected to a pressure of $20 \cdot 10^5$ Pa by passing pure water for 1 h before subsequent use in reverse osmosis.

2.4. REVERSE OSMOSIS PROCEDURE

Reverse osmosis experiments were carried out at an operating pressure of $17.63 \cdot 10^5$ Pa using a standard reverse osmosis apparatus and conventional experimental procedures [15]. Aqueous feed solution containing sodium chloride at a concentration of 6.8 mol/dm^3 were tested to obtain data on membrane specification and to specify the mass transfer coefficient on the high pressure side of the membrane. A feed flow rate of 450 dm^3/min was used giving a mass transfer coefficient $K = 45 \cdot 10^{-4}$ cm/sec. Mass transfer coefficient K was kept constant in all experiments. The concentrations of sodium chloride and the other single salts (sodium nitrate, sodium fluoride, sodium sulphate, magnesium sulphate, zinc sulphate, cadmium sulphate, copper sulphate, manganese sulphate, lead nitrate and sodium phosphate) in the feed and the product solution were determined by specific resistance measurements.

In each experiment the solute separation f is defined as:

$$f = \frac{\text{solute concentration in feed} - \text{solute concentration in product}}{\text{solute concentration in feed}}.$$

Pure water permeation rate PWR (g/h) and product rate PR (g/h) per a given area of 11.95 cm^2 were determined. The membrane performance data were obtained for conditions of feed concentration and feed flow rate corresponding to a mass transfer coefficient K of $45 \cdot 10^{-4}$ cm/sec on the high pressure side of the membrane using aqueous sodium chloride feed solutions.

2.5. PREPARATION OF MEMBRANES FOR SCANNING ELECTRON MICROSCOPE EXAMINATION OF THE MEMBRANE STRUCTURE

The structure of heterogeneous asymmetric membranes was investigated by the use of scanning electron microscope. The micrographs of heterogeneous asymmetric

membranes cast from batch 316-B were examined. The samples were dewatered by gradual replacement of water by ethanol. Then the membranes were placed in liquid N_2 and fractured. Thin layers of graphite and gold were subsequently deposited on them in vacuum. Micrographs were done with a Cambridge Instrument Co. Ltd. U.K. Stereoscan 180 scanning electron microscope at 20 kV. The micrographs of heterogeneous asymmetric membranes annealed at different temperatures are presented in figure 1.

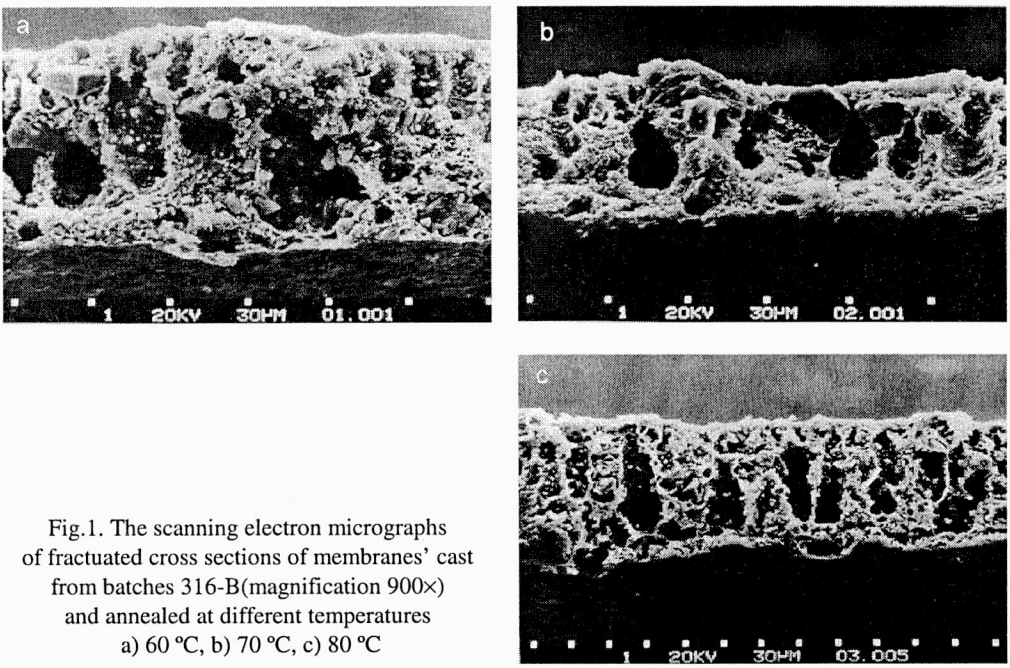

Fig.1. The scanning electron micrographs of fractuated cross sections of membranes' cast from batches 316-B(magnification 900×) and annealed at different temperatures a) 60 °C, b) 70 °C, c) 80 °C

3. RESULTS AND DISCUSSION

The properties of heterogeneous asymmetric membranes are characterised by scanning electron microscopy and separation characteristics. These membranes exhibit a specific irregularity of the pore structure and therefore it is very difficult to compare such a structure with regular geometric forms. The membranes show a skin layer on the top surface. Generally, although not invariably, there is a gradual increase in the size of pores in the substructure progressing from the top to the bottom surface of the membrane. At a temperature of 60 °C the pores appear more rounded in comparison with those at a temperature of 80 °C which are more elongated, i.e. the pores look more narrow and long (figure 1).

Two sets of experimental data (*f*, PWP, PR) obtained using two different types of heterogeneous asymmetric membranes and aqueous solution of NaCl as reference

system are presented in tables 2 and 3. The membrane performance data were obtained for conditions of feed concentration and feed flow rate corresponding to a mass transfer coefficient K of $45 \cdot 10^{-4}$ cm/sec on the high pressure side of membrane. Every membrane used is completely specified in terms of its pure water permeability constant A, and solute transport parameter $D_{AM}/K\delta$ (D_{AM} is the diffusivity of the solute in the membrane phase and δ is the effective thickness of the membrane) at the operating pressure given in tables 2 and 3 (SOURIRAJAN and KIMURA [14]). The calculated values of A and $D_{AM}/K\delta$ for aqueous sodium chloride solution as a reference system and the above membranes show an interesting difference in their properties and behaviour. The solute transport parameter $D_{AM}/K\delta$ for membranes (batches 602 and batches 316), as expected, is increased with decreasing solute separation, lower values of $D_{AM}/K\delta$ for reference solute indicate a relatively smaller average pore size on the membrane surface, less solute transport through the membrane and hence higher solute separation (tables 2 and 3).

Table 2

Comparative performance of membranes (batches 602) at $17.63 \cdot 10^5$ Pa.
Solution system: sodium chloride–water, feed concentration: 6.8 mol/dm^3,
membrane area: 11.92 cm^2, $K = 45 \cdot 10^{-4}$ cm/sec

Film type batches (602-K)	Film No.	Film shrinkage (temp. °C)	$A \cdot 10^{-11}$ (g·mole H_2O $\times cm^{-2} \cdot s^{-1} \cdot Pa^{-1}$)	$D_{AM}/K\delta \times 10^{-5}$ ($cm \cdot sec^{-1}$)	f solute (sep. %)	PR (g/h)	PWR (g/h)
602-1	1	88	2.4279	12.20	82.6	33.01	33.10
	2	88	3.3632	17.77	80.51	44.27	45.85
	3	80	3.4754	26.10	74.16	45.55	47.38
	4	80	4.4833	61.33	58.82	58.50	61.12
602-2	1	88	3.4908	15.84	83.20	47.34	47.71
	2	88	4.257	24.89	78.11	56.43	58.71
	3	80	4.7449	37.32	76.3	6279	64.85
	4	80	4.8339	36.80	72.73	65.65	65.90
	5	80	6.6567	78.89	60.0	88.39	90.75
602-3	1	88	6.1200	51.96	9.54	88.66	94.53
	2	88	4.7740	47.0	68.48	69.5	73.74
	3	80	4.9000	57.5	64.71	71.42	75.69
	4	80	5.0830	63.33	62.85	75.05	78.51
	5	75	8.2814	125.8	51.18	108.64	112.9

The letter K means the Kosova coal.
f – solute separation coefficient, DWR – pure water permeation rate, PR – product rate.

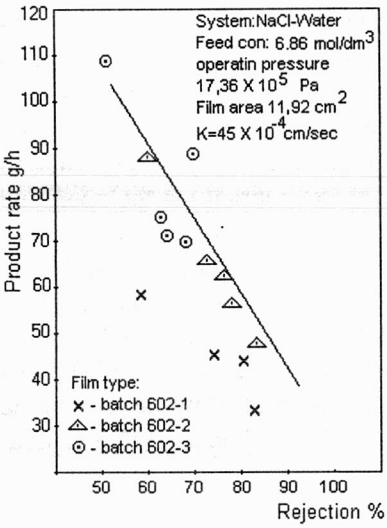

Fig. 2. Comparative performance of membranes (product rate vs. rejection)

Different membranes prepared from the same casting solvent, i.e. batches 602-1, 602-2 and 602-3, vary widely in product rate, for the same or nearly the same rejection of sodium chloride as the ratio of coal to cellulose acetate is increased. However, while comparing membranes of batches 602-3 and 602-2 of the same rejection, it can be seen that those membranes have better properties (especially in product rate) than membranes cast from batch 602-1. Batches 602-3 and batches 602-2 generally show nearly the same characteristics, but some of the former type membranes are better (figure 2).

These improvements of product rate are attributed to the inclusion of coal particles into membrane structure, since all other parameters which determine the performance of membranes are identical for all the six types of the films studied. This can be explained on the basis of the effect of coal on the thickness of active layer of a membrane. By changing viscosity or rheology, coal particles affect the polymer rigidity and, in consequence, compaction of porous layer.

Table 3

Comparative performance of membranes (batches 316) at $17.63 \cdot 10^5$Pa. Solution system: sodium chloride–water, feed concentration: 6.8 mole/dm^{-3}, membrane area: 11.92 cm^2, $K = 45 \cdot 10^{-4}$ cm/s

Film type batch 316	Film No.	Film shrinkage (temp. °C)	$A \cdot 10^{-11}$ (g·mole H_2O ×cm^{-2}·s^{-1}·Pa^{-1})	$D_{AM}/K\delta \times 10^{-5}$ (cm·sec^{-1})	f solute (sep. %)	PR (g/h)	PWR (g/h)
	1	88	2.3648	4.6556	92.17	30.99	32.24
	2	75	3.5040	12.015	86.31	46.08	47.83
316-K	3	75	3.5069	18.9155	80.43	47.63	47.93
	4	60	5.2198	33.8900	75.15	69.99	71.34
	5	60	4.8788	44.6060	68.99	66.70	66.71
	1	88	2.2294	10.8621	83.18	30.27	30.47
	2	75	3.6884	17.3147	82.37	50.20	50.41
316-B	3	88	2.9603	18.0355	77.62	36.29	40.46
	4	75	4.6050	45.9122	67.45	62.73	62.78
	5	75	5.0734	66.3552	60.13	67.53	69.34
	1	88	1.0148	16.5956	93.80	13,01	13.87
	2	88	1.5855	55.0681	87.70	21.17	21.67
316-P	3	88	3.3928	30.7831	70.20	43.58	46.37
	4	80	4.3381	51.7054	62.08	53.33	59.28
	5	75	5.0158	71.0271	57.50	63.64	68.38

The letters K, B, P mean the Kosova, Bosnia and Poland coals, respectively.

The improvement in performances of these membranes is also related to the effect of charged groups on the surface of coal particles, on the behaviour of ions in the coal particle–polymer interaction; on the morphology of polymer chains, i.e. hydrophobic parts of cellulose acetate bind to coal particles and turn hydrophilic parts (of both substances) into arrangements which aid hydrogen bonding with moving water flux.

The experiments governed by these conclusions have been carried out in the second solution with acetone as solvent and proportions of cellulose acetate–coal as 1:1.5 using three different types of coal (table 1). These membranes were named batches 316 and characterised in the same way as films batches 602. The performances of these membranes are presented in table 3 and figure 3.

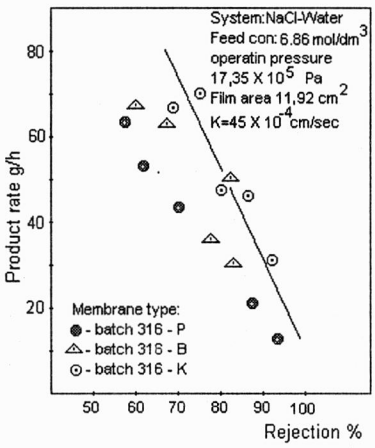

Fig. 3. Comparative performance of membranes(product rate vs. rejection)

While comparing the performances of the batches 316.K, 316.B and 316-P it can be seen that these membranes made by some casting solution show different characteristics. The productivity of the batches 316-K type membranes is higher than those of the batches 316-B and 316-P (figure 3).

These results indicate that the casting solution composition with the Kosova powdered coal gives the best membrane performances. A slight difference between the films of the same type of coal and different casting solvents was noticed when compared with films made of casting solvent with different types of coal. The membranes batches 316-K, 316-B and 316-P do not show any big difference in order of rejection, but it is noticed that there is a difference in the product rate, i.e. the batches 316-K and 316-K are slightly better than the batch 316-P.

The results clearly prove that different types of coal, i.e. different countries of origin, in casting solution composition affect membrane performance significantly.

The changes of composition of casting solvent solution, the evaporation rate during film formation, the precipitation medium and precipitation temperature are also important parameters affecting the performances of membranes and are the object of further study.

The heterogeneous asymmetric membranes were used for determining the reverse osmosis characteristics such as: product rate and solute separation of the following salt solutions: sodium nitrate, sodium fluoride, sodium sulphate, magnesium sulphate, zinc sulphate, cadmium sulphate, copper sulphate, manganese sulphate, lead nitrate and sodium phosphate. These data are given in table 4.

Table 4 gives the performances (solute separation and product rate) data for one film from each of four types of membranes, i.e. film No. 1 for batch 602-3 and film No. 2 for batches 316-K, 316-B and 316-P for aqueous solutions of each of the above

Table 4

Separation and product rate of salts for membranes cast from batches 602-3 and 316-K, 316-B, 316-P

Systems	Batch 602-3		Batch 316-k		Batch 316-B		Batch 316-P	
	f solute (sep. %)	PR (g/h)	*f* solute (sep. %)	PR (g/h)	*f* solute (sep. %)	PR (g/h)	*f* solute (sep. %)	PR (g/h)
NaCl	70.0	88.66	86.31	46.08	82.37	50.2	87	21.67
$NaNO_3$	67.18	91.34	66	75.88	–	–	84.20	20.7
NaF	71.0	97.98	89.93	51.45	89	41.75	91.9	20.32
Na_2SO_4	–	–	97	52.01	95.13	50.44	97.19	20.2
$MgSO_4$	86.30	97.92	95.04	50.73	95	48.94	96.34	20.43
Na_3PO_4	95	95.0	98.63	51.72	97.7	47.96	97.9	20.4
$ZnSO_4$	86	90.0	94.8	53.96	94.16	48.91	95.44	20.87
$CdSO_4$	87.06	90.0	93.25	50.20	94.21	48.69	96.40	20.72
$CuSO_4$	84.18	91.37	95.	45.44	93.04	50.5	95.15	21
$MnSO_4$	86	90.2	96.12	53.32	91.1	49.51	96.26	21.13

systems. The results, such as product rate and rejection, are consistent with the membrane specification data. For all types of membranes used in this study the order of rejection of salts is similar, i.e. three-valent and di-valent salts are rejected better than monovalent ones. The performance tests of the batches 602-3 and 316-K give better results than the test with reference membrane types [12]. The results of treatment of industrial effluents and waste waters by these membranes are already published [18].

4. CONCLUSIONS

The analyses and conclusions obtained show that performances of heterogeneous asymmetric membranes made from cellulose acetate and powdered coal are improved in comparison with those of asymmetric cellulose acetate membranes. The results prove that productivity improvement is achieved due to addition of coal to casting solution. Both the amount and the type of coal are the variables which contribute to the formation of membranes of high productivity. The performance data obtained with heterogeneous asymmetric membranes suggest that these membranes seem promising for the treatment of industrial effluents and waste waters. The development of these membranes is of a great importance to a wide variety of the low pressure reverse osmosis application.

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WŁAŚCIWOŚCI I OTRZYMYWANIE HETEROGENICZNYCH MEMBRAN TYPU OCTAN CELULOZY–WĘGIEL STOSOWANYCH DO ODWRÓCONEJ OSMOZY

Badano heterogeniczne, asymetryczne membrany do odwróconej osmozy, które wykonano z mieszanki octanu celulozy ze sproszkowanym węglem przygotowanej z dwu różnych mieszanin roztworów rozpuszczalnika służących do odlewania membrany. Testowano mieszaniny octanu celulozy z węglem aktywnym (w proporcji 1:1, 1:1,25 i 1:1,15), do których dodawano acetonu z dioksanem, a następnie mieszaninę octanu celulozy z trzema różnymi odmianami węgla (w stosunku 1:1,5), do której dodawano acetonu. W obu przypadkach zachowano ten sam skład roztworu do wylewania, taką samą temperaturę, ten sam czas parowania rozpuszczalnika i to samo medium żelujące. Pokazano, że różnice w wydajności membran zależą od rodzaju rozpuszczalnika oraz ilości i rodzaju dodanego węgla. Gdy rozdzielenie substancji rozpuszczonych wynosiło 86–90%, a warunki przepływu cieczy przez membranę odpowiadały współczynnikowi przenikania masy $45 \cdot 10^{-4}$ cm/s, wtedy sprawność membran wynosiła 49,89–30,99 $g \cdot h^{-1} \cdot cm^{-2}$ pod ciśnieniem $17 \cdot 10^5$ Pa dla roztworu NaCl o stężeniu 6,86 $m \cdot dm^{-3}$. Testowano także w tych samych warunkach separację w wyniku odwróconej osmozy 10 innych roztworów soli nieorganicznych. Zaprezentowano zdjęcia membran wykonane za pomocą mikroskopu skaningowego.

membrany hetero... asymetryczne
octan celulozy
węgiel
osmoza odwrócona