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EFFECT OF MODIFIED COAL THROUGH CHEMICAL ACTIVATION PROCESS ON PERFORMANCE OF HETEROGENEOUS REVERSE OSMOSIS MEMBRANES

Heterogeneous reverse osmosis (RO) membranes have been prepared from cellulose acetate (CA) and modified coal through chemical activation. Nitric acid of various concentrations, sulfuric and acetic acids used for various time periods have been studied with respect to modification of structure of coal and consequently structure of RO membranes. The effect of these variables on the modification of coal was examined by IR spectroscopy. All membranes prepared in such a way showed improved performance in comparison with standard CA membranes. The volume flux of the best RO membranes at 94% level of solute separation was 3.87×10^{-2} m³/(m²·h) at 1.76 MPa using aqueous feed solution 400 mg/dm³ of sodium chloride. The performance improvement was related to increases of charge of groups of coal particles in the membrane, affecting their rheology and morphology resulting in better membrane productivity. The SEM of some membranes have also been presented. These membranes were tested also with 1:1, 1:2, 2:2 and 1:3 inorganic salt solutions. The agreement between the calculated and experimental data of solute separation for studied solutes was reasonably good.

1. INTRODUCTION

The performance of reverse osmosis is directly dependent on the properties of the membrane material, more specifically, the chemical nature of the membrane polymer and the structure of the membrane being the factors which determine the rejection and flux properties of the reverse osmosis system. Reverse osmosis (RO) membranes should offer high flux and high rejection, in addition to high strength and durability. In practice, however, high rejection and high flux have been two mutually exclusive goals that have eluded researches for decades of membrane development. Although in the last few years an increase in flux rates has been observed with no decrease in re-

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jection (and in some cases, a slight increase in rejection), most membranes represent a compromise between high rejection and high flux [1, 2]. High flux is important to reduce the size and cost of reverse osmosis system.

Reverse osmosis and ultrafiltration membranes made of cellulosics for water desalination and purification purposes nowadays are mostly replaced by polymer thin-film composite membranes. Cellulose acetate (CA) and its derivatives made them still suitable as membrane materials for specific purposes because of such advantages as moderate flux, high salt rejection properties, cost effectiveness, relative ease of manufacture, renewable source of raw material and non-toxicity. The RO membranes based on cellulose acetate–acetone–water system by wet phase inversion technique have been presented elsewhere [3, 4].

In order to obtain membranes with specific properties, additional additives can be added to the casting solution. Therefore, numerous investigations focused on exploitation of new membrane materials and on modification of existing ones for preparing RO membranes of enhanced properties. Some authors examined the possibility of using coal as additive material in preparation of RO membranes.

Heterogeneous RO membranes have been developed recently from cellulose acetate and coal. By inclusion of coal in casting solution of cellulose acetate, the product rate of membranes was improved in comparison with CA membranes. It is attributed to inclusion of coal particles into membrane, affecting active and porous layer, changing rheology of the membranes, as well as the morphology of polymer chains [5]. The method based on cellulose acetate modified with coal created by the phase inversion process seems to be a very promising method for preparation of heterogeneous RO membranes.

Many authors studied such parameters as composition of casting solution, evaporation time of solvent during film formation and gelation medium [3, 4, 10]. Considerable attention was paid to inclusion of modified coal into casting solutions. In comparison with previous published studies [6, 7], CA membranes modified with coal showed considerably better RO characteristics. Therefore, the interest was focused on selecting methods of modification of coal leading to increase in productivity of RO membranes [8, 9]. Carbon materials such as activated carbon, activated carbon from coal, from bituminous coal, etc. were prepared by various physical and chemical methods.

It has been concluded that chemical oxidation increased macro pore density, particle size, packing density, and decreased pH (indicating acidification by formation of acidic oxygen containing functional groups) attributed to the change in morphology etc. [11, 12]. Various oxidation processes (e.g. electrochemical, thermal and chemical) conducted either to study the reactivity of the carbon material or to modify the surface character of various carbon materials were studied [13]. A traditional approach for the modification of carbon surfaces involves the oxidative treatment for example, nitric acid or potassium permanganate resulting in the formation of various oxygenated functionalities [14].

Similarly as nitric acid, reused nitric acid is yet potentially valuable as oxidation agent for modification of coal [15, 16]. Most of these treatments include changes of morphological structures of coal, i.e. surface functional groups or tend to increase the number of oxygen-containing functional groups.

The objective of this work was preparation of the asymmetric heterogeneous RO membranes from CA and modified coal through chemical activation process (acid treatment). The effect of various acids, their concentration and modification time of coal with on the structure of coal and, consequently, on performance of membranes was investigated. The RO characteristics of resulting membranes are presented and discussed.

2. MATERIALS AND METHODS

Experiments. Cellulose acetate Eastman Kodak 398-3 with a degree of acetylation of 39.85% and Kosova's coal (Bardh i Madh), namely lignite was used for preparation of heterogeneous asymmetric RO membranes. First the coal specimens were treated with boiling water at 80 °C under stirring to remove all dissolved materials, i.e. inorganic part, color, etc. Then coal was treated with 0.5, 1 and 2 M nitric acid at 25 °C under stirring for 1, 3 and 6 h, and with 2 M sulfuric and acetic acids at 25 °C for 6 h. The reaction mixture was filtered with a 589 blue ribbon and then washed by successive aliquots of water. Finally, the modified coal was dried at 105 °C to the constant weight. The coal fractions of sieve size of 0.09 mm ca. 170 mesh were used in this study.

Film casting details. The film casting solutions contained 10 wt. % of cellulose acetate (E 398-3), 15 wt. % of coal with corresponding amounts of acetone (61.3 wt. %), water (12.25 wt. %) and magnesium perchlorate (1.45 wt. %) at 24 °C and ambient air (relative humidity 60%). The membranes made with modified coal with nitric, sulfuric, and acetic acids were named 318K-1 (K – Kosova's coal, 1 corresponds to the above weight ratios CA to coal). The films were cast on a clean glass plate (22×38 cm) with the use of a metal cylinder with uplifted edges to obtain the required film thickness (0.12 mm). The glass plate was kept at the same temperature (24 °C) as the casting solution. The casting solution temperature and the external conditions of solvent evaporation time (0 s) during film casting were the same for all series of films studied. The cast solution was immediately immersed into a gelation bath consisting ice-cold water (0 °C) for 1 h. Before the reverse osmosis experiment, the membranes were preshrunk under water at various temperatures and initially each film was subjected to pure water pressure treatment for 1 h at 20% higher pressure than that to be used in the reverse osmosis run.

Procedure of reverse osmosis. The membranes, five samples of each type, were tested in a laboratory RO apparatus shown schematically in Fig. 1.
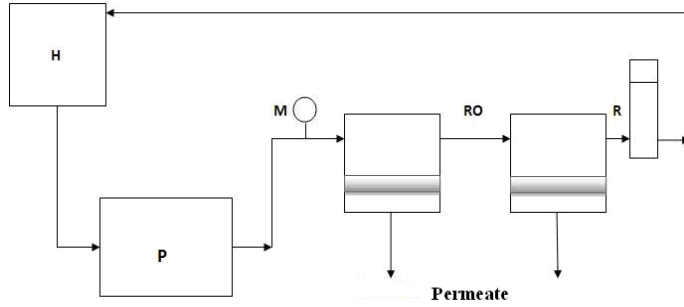
Fig. 1. Schematic representation of reverse osmosis set-up: H – hold tank,
P – high pressure pump, M – manometer, RO – RO cells, R – back pressure regulator

The metering pump Normandos N-K31 Bran & Lübbe, Hamburg, Germany deliv-
ered feed solutions to RO cells at a flow rate of 450 dm³/min. The home-made RO
cells of the same type and dimensions as described in [3] were connected in series.
The surface area of the membranes was 11.92 cm². All RO experiments with sodium
chloride solutions as a reference system were of the short-run-type for 2 h, and per-
formed at laboratory temperature and pressure of 1.76 MPa. The membranes were
tested about 6 months without changes of RO characteristics (solute separation or
product rate). The membrane performance data were obtained for conditions of feed
concentration and feed flow rate corresponding to the mass transfer coefficient k of
4.5×10^{-3} cm/s on the high-pressure side of membrane, using aqueous sodium chloride
feed solution of 400 mg/dm³ and aqueous solutions of NaF, Na_2SO_4, $CdSO_4$, Na_3PO_4
of the same concentration as the reference system.

The permeate flow rate Q, referring to the membrane permeated solution corrected
to 25 °C, and the rejection factor R, defined as:

$$R = 1 - \frac{C_p}{C_f}$$

where C_p and C_f, being the permeate and feed concentrations (mg/dm³), were deter-
mined in each experiment. Sodium chloride concentrations were determined using
a conductivity meter Radiometer CDM-3.

The solute transport parameter $D_{AM}/k\delta$ and pure water permeability constant were
calculated for sodium chloride for all films tested [3]. The $D_{AM}/k\delta$ solute transport
parameter was calculated from the experimental data of solute separation (f) and prod-
uct rate (PR) using following expression:

$$\frac{D_{AM}}{k\delta} = \frac{PR}{3600Sd} \frac{1-f}{f} e^{-PR/3600Skd} \tag{1}$$

where S – effective membrane surface area (cm^2), k – mass transfer coefficient on a high-pressure side of the membrane (cm/s), 3600 – time (s) and PR – product rate (g/h).

It has been shown [19] that for the case of completely ionized inorganic solutes in aqueous solutions, the solute transport parameter is related to the free energy parameter of ions involved by the expression:

$$\ln\frac{D_{AM}}{k\delta} = \ln C^* + \sum_i \Delta\left(\frac{\Delta G_i^\circ}{RT}\right) \tag{2}$$

where $\ln C^*$ is a constant, and the subscript i represents the ion involved. For a given membrane material, the $\ln C^*$ depends only on the porous structure of the membrane surface. For any given film, $\ln C^*$ can be determined from the experimental value of the reference solute transport parameter and free energy of ions in the reference system. Considering NaCl, the porous structure of the membrane can be represented by:

$$\ln C_{\text{NaCl}}^* = \ln\left(\frac{D_{AM}}{k\delta}\right)_{\text{NaCl}} - \left(\left(-\frac{\Delta G^\circ}{RT}\right)_{\text{Na}^+} + \left(-\frac{\Delta G^\circ}{RT}\right)_{\text{Cl}^-}\right) \tag{3}$$

For completely ionized inorganic solutes and taking ionic valences into consideration, Eq. (3) can be written in the more general form:

$$\ln\left(\frac{D_{AM}}{k\delta}\right) = \ln C^* + n_c\left(-\frac{\Delta G^\circ}{RT}\right)_c + n_a\left(-\frac{\Delta G^\circ}{RT}\right)_a \tag{4}$$

where n_c and n_a are the numbers of moles of cations (c) and anions (a) formed after dissociation of one mole of solute. For example, for symmetrical (1:1, 2:2, etc.) electrolytes, $n_c = n_a = 1$, for a 2-1 electrolyte, $n_c = 1$ and $n_a = 2$, etc. [3, 18, 19].

Characterization of coal. The composition of coals was examined using an IR spectrophotometer SHIMADZU, FTIR 8400S with KBr disc. The IR spectra of bare and modified coal with nitric acid are shown in Fig. 2a, IR spectra of bare and modified coal with nitric, sulfuric and acetic acids, in Fig. 2b. In coal modified with nitric acid, the presence of nitro group was observed in the region of 1420 cm^{-1}. The intensities of peaks of nitro groups in coal modified with 0.5 M and 1 M nitric acids slightly differ from each other with evident tendency of increasing from low to higher acid concentration. The intensity of the peak corresponding to nitro groups in coal modified with 2 M nitric acid was evidently higher. In the IR spectrum of coal modified with sulfuric acid, modes originating from sulfo groups were identified in the range of 1250–1300 cm^{-1}, and in that modified with acetic acid – from carboxylic groups in the range of 1705–1720 cm^{-1}.

Scanning electron microscopy. The structure of heterogeneous RO membranes was examined by means of SEM and is presented in Fig. 5. The samples were dewatered by gradual replacement of water by ethanol. The samples were sputtered with Au and measured with a scanning electron microscope, HITACHI S-3000N.

3. RESULTS AND DISCUSSION

The experimental data (solute separation f, pure water rate PWR and product rate PR) of CA and coal modified membranes (batch 318K-1) with nitric acid for all type films used in this work, tested with aqueous solution of sodium chloride as reference system are presented in Table 1, and with CA and modified coal with two other acids of the same concentration and modification time in Table 2. The pure water permeability constant A, mass transfer coefficient k, and solute transport parameter $D_{AM}/k\delta$, calculated using the Kimura and Sourirajan analyses [12] are also given in Tables 1 and 2.

Table 1

Performance of CA-modified coal membranes batch 318K-1 (I–V)

| Batch	Film No.	Film shrink. at temp. [°C]	$A \times 10^{-11}$ [g·mol H_2O /(cm²·s·Pa)]	$D_{AM}/k\delta$ 10^{-4} [cm/s]	f [%]	PR [g/h]	PWR [g/h]
1	2	3	4	5	5	7	8
HNO$_3$ 0.5 M, 6 h 318K-1 (I)	1	85	3.05	0.78	91.02	43.44	47.22
	2	85	3.42	1.37	86.15	47.74	52.91
	3	82	3.81	1.50	86.02	55.07	58.91
	4	82	4.00	2.00	83.07	57.07	61.84
	5	80	5.50	2.95	76.79	79.34	85.00
HNO$_3$ 1 M, 6 h 318K-1 (II)	1	85	3.13	0.91	90.55	49.00	49.45
	2	85	3.41	1.09	89.44	52.05	53.05
	3	85	3.53	1.15	88.95	52.86	54.60
	4	83	4.53	2.29	82.73	70.45	71.77
	5	80	5.88	4.63	73.89	90.76	90.81
HNO$_3$ 2 M, 6 h 318K-1 (III)	1	88	2.64	0.61	92.13	40.09	40.90
	2	88	3.82	1.23	89.02	58.05	59.19
	3	85	3.92	1.49	87.21	59.61	60.09
	4	84	5.60	3.40	79.21	86.13	87.23
HNO$_3$ 2 M, 3h 318K-1 (IV)	1	85	1.78	0.44	91.66	25.02	27.63
	2	83	2.30	0.84	89.57	34.92	35.67
	3	83	2.38	0.95	88.04	36.30	36.89
	4	80	3.59	1.31	88.04	55.29	55.50
	5	80	4.16	1.90	84.25	61.65	64.26

Table 1 continued

1	2	3	4	5	6	7	8
HNO₃ 2 M, 1 h 318K-1 (V)	1	85	1.29	0.35	92.17	19.42	19.98
	2	82	2.61	0.48	90.37	39.17	40.37
	3	82	3.52	0.83	85.94	50.56	54.40
	4	80	5.71	1.47	77.82	85.39	88.27
	5	80	6.45	3.54	70.72	95.72	99.70

T a b l e 2

Performance of CA modified coal membranes batch 318K-1 (VI, VII)

Batch	Film No.	Film shrink. at temp. [°C]	$A \times 10^{-11}$ [g·mol H_2O /(cm²·s·Pa)]	$D_{AM}/k\delta$ 10^{-4} [cm/s]	f [%]	PR [g/h]	PWR [g/h]
H₂SO₄ 2 M, 6 h 318K-1 (VI)	1	82	3.07	0.49	94.52	46.18	47.51
	2	79	3.40	0.91	90.80	50.96	52.62
	3	79	3.87	1.13	89.71	57.44	59.72
	4	79	4.26	1.66	86.52	63.99	65.84
	5	76	5.42	2.93	80.89	81.36	83.76
CH₃COOH 2 M, 6 h 318K-1 (VII)	1	85	2.97	0.82	90.99	45.71	45.88
	2	85	3.37	1.07	89.63	52.18	52.20
	3	85	3.99	2.00	87.06	58.60	58.77
	4	85	4.36	2.47	85.71	63.15	64.87
	5	79	5.82	3.78	76.97	88.54	90.03

Reactions of oxidation with nitric acid occurring in coal as suggested by Yidirim and Özbayoglu [15] and Alvarez et al. [16] are as follows. Basically, the reaction initiates with nitric acid providing nitro and nitroso groups as well as internal oxygen. These compounds attack on the aromatic rings leading to carboxylic, nitro and nitroso substitution [17].

$$2HNO_3 \rightarrow H_2O + 2NO_2 + 1/2O_2 \qquad (5)$$

$$2HNO_3 \rightarrow H_2O + 2NO + 3/2O_2 \qquad (6)$$
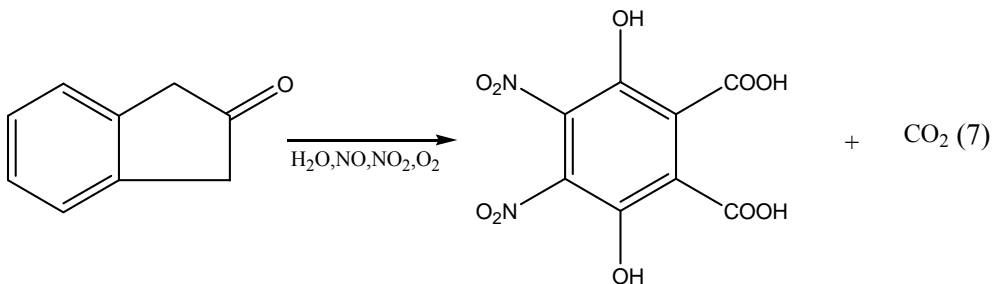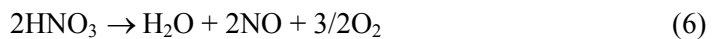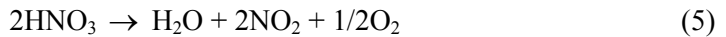
IR spectra of membranes prepared with nitric acid of various concentrations are given in Fig. 2a. It is evidenced from FTIR spectra in agreement with other experimental data (Table 1) that the intensity of the band at 1420 cm^{-1} ascribed to nitro groups increases with the concentration of nitric acid implying stronger attack of nitro and nitroso groups. These groups affect structure of membranes resulting in improvement of RO characteristics.
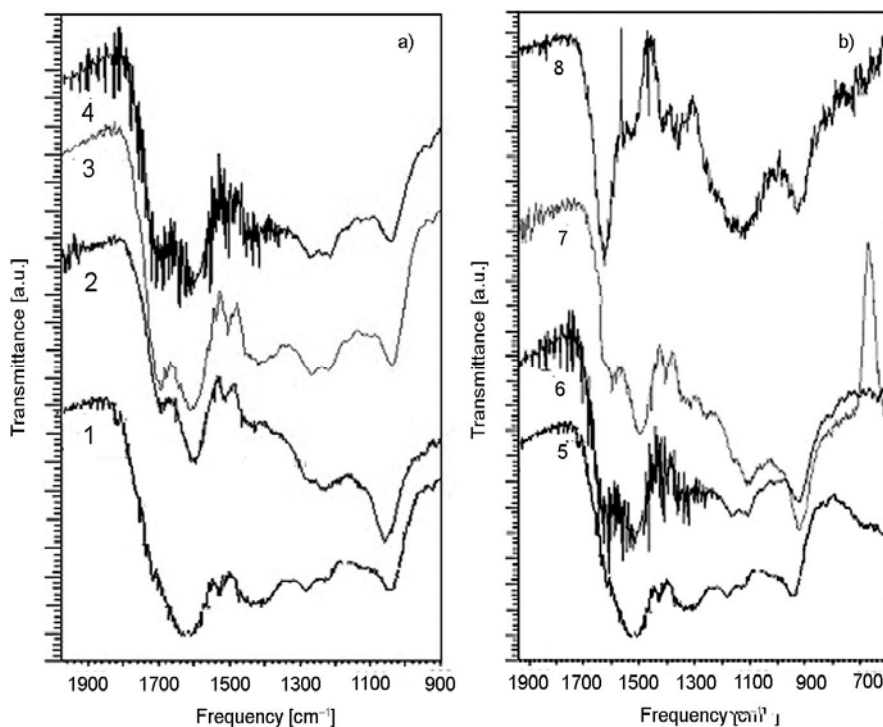

Fig. 2. IR spectrum of: a) bare (1) and modified coal with nitric acid
of the concentrations 0.5 M (2), 1 M (3) and 2 M (4), b) bare (5) modified coal
with nitric acid (6), sulfuric acid (7) and acetic acid (8)

The dependences of product rates and shrinkage temperatures on separation for batches 318K-1-coal modified with nitric acid of various concentrations are given in Fig. 3 and for those modified with 2 M nitric acid and various modification durations in Fig. 4. The data indicates that the initial size of pores on membrane surface in batches 318K-1 (III) is relatively bigger and more uniform than those in the other batches. Batches 318K-1 (III) showed simultaneously increased flux forming membranes of better productivity. These results indicate that higher acid concentrations and longer modification durations favoured the formation of more productive CA-coal RO membranes.
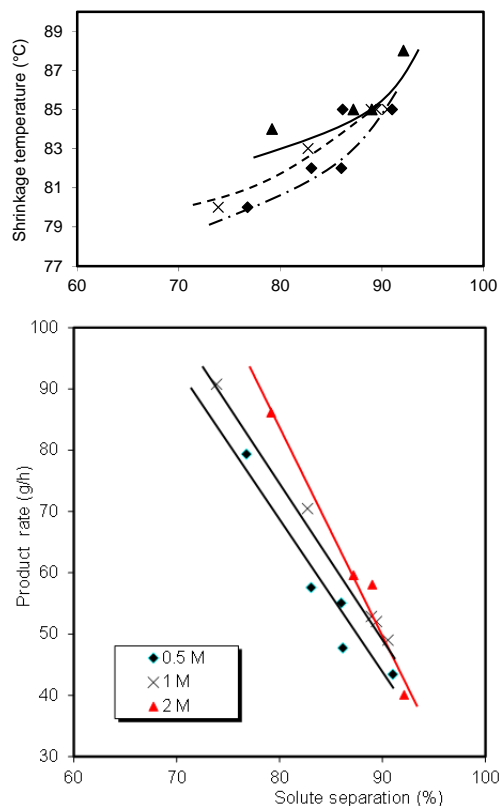
Fig. 3. Performance of membranes made from modified coal with nitric acid of various concentrations
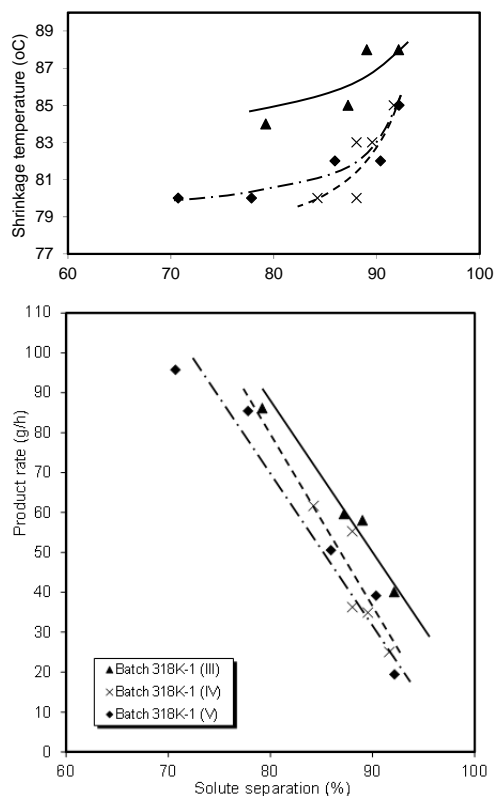
Fig. 4. Performance of membranes, made from modified coal with 2 M nitric acid at various durations of modification

Membranes with improved RO characteristics were obtained also of modified coal with sulfuric and acetic acids as a result of introduction of HSO_3^- and $HCOO^-$ groups. IR spectra of these membranes are shown in Fig. 2b.

Product rates vs. solute separation obtained for membranes with modified coal with various acids of the same concentration (2 M) and the same modification time (6 h) are presented in Fig. 5. The CA membranes (batch 316) film has also been examined to compare the data. It is evident that all CA membranes with modified coal (batch 318K-1) show considerably better RO performances than CA (batch 316) membranes, and slightly better than CTA membranes [7]. The best performance of all tested membranes was observed for the membranes batch 318K-1 (VI). This observation is important in terms of selecting the agents, methods of coal modification and quality control in making RO membranes. This improvement of product rate was attributed to inclusion of coal particles into membrane affecting the thickness of active layer of membrane. Changing viscosity or rheology of coal particles affects the poly-

mer rigidity and in consequence, compaction of porous layer. The improvement of performance of CA-modified coal membranes was also related to the effect of charged groups on the surface of coal particles, to the behavior of ions in coal particle–polymer interaction and the morphology of polymer chains [5]. In the case of modified coal through chemical process (acid treatment), the density of charged groups was increased influencing the properties of membranes.
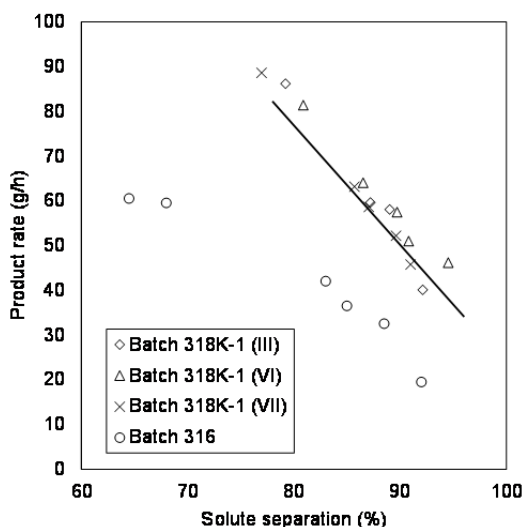

Fig. 5. Dependences of the product rates on separation obtained from coal modified
(6 h) with various acids of the same concentration (2 M) and batch 316

From the experimental values of $D_{AM}/k\delta$ of sodium chloride and values of $\Delta G°/RT$ of ions calculated by Matsuura et al. [18, 19], $\ln C^*_{NaCl}$ of three membrane types of different porosities was calculated from Eq. (3), and finally $\ln C^*$ of NaF, Na_2SO_4, $CdSO_4$, Na_3PO_4 from Eq. (4). The results of the calculations along with the actual experimental data are given in Table 3.

Table 3

Solute separation [%] for CA-modified coal membranes batch 318K-1 (VI)

Solute	Film 1, $\ln C^* = -11.29$		Film 2, $\ln C^* = -10.67$		Film 3, $\ln C^* = -10.45$	
	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated
NaCl	94.52	–	90.80	–	89.71	–
NaF	94.88	96.63	87.84	91.30	90.92	93.28
CdSO_4	97.64	99.89	95.56	99.50	95.08	99.97
Na_2SO_4	97.66	99.71	96.16	99.22	96.57	99.49
Na_3PO_4	99.33	99.99	98.88	99.99	99.00	99.99

RO performances of membranes are consistent with the membrane specification data. The agreement between the calculated and experimental data of solute separation for studied solutes was reasonably good.
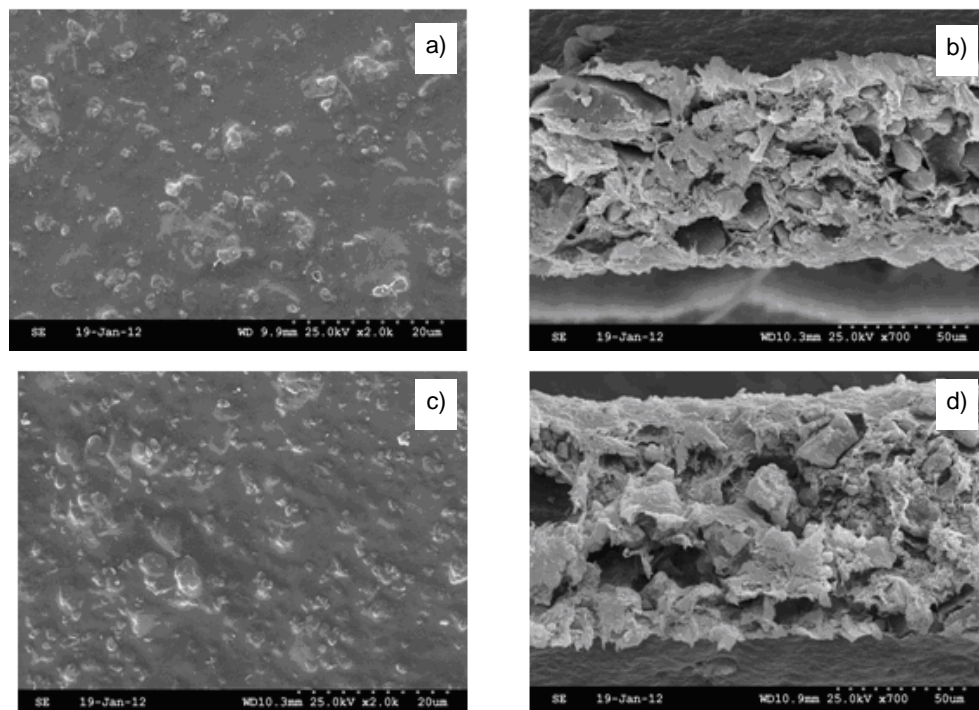

Fig. 6. SEM of surfaces (a), (c), and cross sections (b), (d),
of membranes 318K-1 (III) (upper row) and 318K-1 (VII) (lower row)

The electron micrographs of heterogeneous RO membranes batches 318K-1 (III) and 318K-1 (VII) annealed at 353 K are shown in Fig. 6. The membranes presented in Fig. 6a, c and 6b, d corresponds to a skin layer on the top surface and the cross-section in the bottom. The porous supporting framework (matrix) exhibits specific irregularity of the pore structure. The porosity of the supporting matrix increases from the top to the bottom and pore forms are more rounded and widely distributed in comparison with CA membranes [5].

4. CONCLUSIONS

Heterogeneous RO membranes from cellulose acetate and modified coal have been prepared through chemical activation and the effects of various parameters on membrane performance were investigated.

A considerable influence on RO characteristics of resulting membranes was noticed by altering the structure of coal by the form of modification. The best performance showed RO membranes prepared from CA and coal modified with nitric acid at higher concentrations and longer modification times, and for those made from coal modified with sulfuric acid. This is attributed to the presence of charged groups whose concentration increased upon time and concentration of acid. The agreement between the calculated and experimental data fot solute separation for some inorganic salts was reasonably good.

The reverse osmosis characteristics (increased flux without rejection of solute separation) of these membranes at low pressure and low cost make them interesting for further development.

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