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Preparation of heterogeneous reverse osmosis membranes undergoing modification process

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ABSTRACT

This paper gives more insight about the role of aryl diazonium salt (DS) grafted on coal surface prior to use in the membrane making process, which brings better membrane separation. The surface of coal particles was modified by chemical reduction of 4-nitrobenzenediazonium salt of different concentrations at millimolar level in aqueous acid solution (hypophosphoric acid, sulfuric, hydrochloric, nitric, and phosphoric) and aprotic (acetonitrile) medium. The attenuated total reflectance-Fourier transform infrared spectra showed that the nitrophenyl groups were strongly bonded on the surface of coal particles. The use of the modified coal for the preparation of reverse osmosis (RO) membranes, alter their characteristics as shown by RO parameters as well as scanning electron microscopy images. The current paper provides the data that shows evidence of the DS's effect on the modification of coal and better separation of RO heterogeneous membranes.

Keywords: Reverse osmosis; Heterogeneous membranes; Modified coal; Diazonium salt

1. Introduction

The productive reverse osmosis (RO) membranes should offer simultaneously high solute rejection, good water permeability, chemical stability, and good compaction resistance particularly for aqueous separations of different species. The resulting membranes are made mainly of cellulosic and polyamide materials. The cellulosic membranes today are mostly replaced by a new generation of thin composite polyamide membranes. Although cellulose acetate (CA), cellulose triacetate, and cellulose acetate–cellulose triacetate blend membranes prepared generally in asymmetric form give relatively lower flux compared with last one, they are still important materials for preparation of RO membranes. They have many industrial applications and specific purposes to date, owing to their abundant availability, excellent hydrophilicity, and low cost [1].

Therefore, it seemed of interest to some new development of these membranes. The important RO parameters are (1) water adsorption, (2) hydrophilic/hydrophobic character, (3) impact resistance, (4) compatibility and stability, (5) pH sensitivity, etc., which influenced the CA membrane performance. This could be achieved also by introduction of charged groups into CA. These specific future characteristics give rise to good permeability and permselectivity.

CA membranes prepared from CA powder, formamide, and acetone by phase inversion, have been used to separate substances in fluid mixtures under high pressure between 5.6 and 10.5 MPa for seawater desalination and 1.4–4.2 MPa for brackish water desalination, filtering methanol, ethanol, and urea in RO process [2]. The CA membranes modified with polyacrylic acid, using various plasticizers and coated with polyaniline showed larger pore size. The electrical conductivity of modified membranes coated with polyaniline increased by two orders of magnitude when the plasticizer triphenylphosphate was used. The CA–polyaniline membranes are effective adsorbents of AuI_2^- complex and represent

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a promising alternative for gold recovery process without the use of cyanide solutions [3].

Room-temperature development of thin film composite (CA TFC) membrane was developed by direct casting of CA onto an ultrafiltration membrane support. A combined swelling and annealing treatment was found to improve salt rejection level (~94%), without significant flux deterioration. The incorporation of silver nanoparticles onto the active surface of the CA TFC significantly enhanced the membrane's resistance to biofouling [4].

The methods used for the modification of material surfaces involve both physical and chemical process. These methods include surface grafting [5–7], surface coating [8,9], surface crosslinking [10,11], plasma treatment [12,13], blend method, etc. Currently considerable attention has been given to the preparation of CA RO membranes by blend method.

Heterogeneous membranes for RO made by CA and modified coal have shown very good RO characteristics. The coal modified through chemical activation with concentration aqueous solutions (2 M) of nitric and sulfuric acid during 5 h showed improved RO performance [14].

Electrochemical reduction of aryl diazonium salts (DSs) on various carbon electrodes in organic mediums leads to the covalent grafting of the organic groups to the electrode surface [15,16]. The same electrografting reaction can be performed in acidic aqueous solution in the case of carbon, iron, mild steel, and other coinage metals [17].

The grafting can also take place spontaneously without any electrochemical assistance in the aprotic medium onto carbon, copper, iron and zinc, palladium [16], and semiconductors (Si and Ga, As) [18]. The attachment of aryl groups on coal particle surfaces through the spontaneous reduction of the corresponding aryl DS in acidic or neutral medium is now an alternative method for the modification of coal used for RO heterogeneous membranes. Modified coal is considered an enhancing agent for high flux without perturbation of rejection [19].

The role of several parameters such as composition of casting solution, cellulose acetate–coal ratio, modification time of coal in aprotic medium, evaporation rate of solvent during the film formation, and gelation medium, for performance development of RO membranes is already investigated [20,21].

The aim of this paper is to study the impact of modified coal with aryl moieties, achieved at different concentrations of aryl DS in aqueous medium of different acids, through chemical grafting, and to improve the properties of such membranes.

The introduced changes in the morphology and the performances of RO membranes enable more information about the optimization of their key parameters such as flux and rejection.

2. Materials and methods

2.1. Experimental

CA from Eastman Kodak 398-3 with a degree of acetylation of 39.85%, and Kosovo's coal obtained from locality Bardh i Madh, namely lignite was used for preparation of heterogeneous asymmetric RO membranes.

2.2. Coal modification

Coal surface modification in aqueous solution was performed as follows: the coal specimens were treated with boiling water under stirring conditions to remove all dissolved materials, that is, inorganic part and color. The residual coal after filtering was dried at 105°C to constant weight. Typically, 8 g of this coal was dispersed in 100 cm^3 acetonitrile, and the same volume of aqueous solutions (H_3PO_2, H_2SO_4, HCl, HNO_3, and H_3PO_4 of the same concentration 0.01 M), and 5, 10, 15, 20, 50 mM of $^+N_2C_6H_4NO_2BF_4^-$ under stirring at the temperature <5°C for 5 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 constant weight, ground, and sieved. The coal fractions of sieve size of ≈170 mesh were used in this study.

The attenuated total reflectance infrared (ATR–IR) spectra of modified coal particles were recorded with a germanium ATR accessory (Jasco ATRPR0470-H). For each spectrum, 1,000 scans were accumulated with a spectral resolution of 4 cm^{-1}. The background recorded before each spectrum was that of a native (nonmodified) coal substrate.

2.3. Film casting details

The film casting solutions contained 10 wt.% of CA (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 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 RO experiment, the membranes were preshrunk under water at various temperatures (in the range 80°C–88°C), and initially each film was subjected to pure water pressure treatment (2.112 MPa) for 1 h at 20% higher pressure than that to be used in the RO run (1.76 MPa).

The membranes were tested in the RO setup already described elsewhere [14].

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

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

where C_p and C_f, being the permeate and feed concentrations (mg/dm^3) were determined 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 (A) were calculated for sodium chloride as referent system for all films tested. The pure water permeability constant A was calculated using the following equation:

$$A = \frac{\mathrm{PWR}}{M_B \times S \times 3{,}600 \times P} \tag{2}$$

where PWR is product water rate (g/h), M_B – molecular mass of water (g/mol), S – effective membrane surface area (cm^2), and P – pressure (Pa).

The solute transport parameter $D_{AM}/k\delta$ was calculated from the experimental data of solute separation (f) and product rate (PR) of sodium chloride for all films tested by the following expression:

$$\frac{D_{\mathrm{AM}}}{k\delta}=\frac{\mathrm{PR}}{3{,}600S\rho}\frac{1-f}{f}e^{\frac{-\mathrm{PR}}{3{,}600Sk\rho}} \tag{3}$$

where S – effective membrane surface area (cm^2), k – mass transfer coefficient on a high pressure side of the membrane (cm/s), 3,600 – time (s), PR – product rate (g/h), and ρ is density of solution g/cm^3.

3. Results and discussion

The modification of the surface of coal particles is performed by the chemical reduction of 4-nitrobenzenediazonium salt. The nitrophenyl grafted layer is introduced in order to improve the hydrophilic properties of asymmetric heterogeneous RO membranes [18]. ATR-IR spectra were recorded in the samples of coal particles modified with nitrophenyl moieties derived from 4-nitrobenzenediazonium salt at different concentrations in aqueous acid solution.

The spectrum of modified coal particles with nitrophenyl groups in H_3PO_2 recorded by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) is shown in Fig. 1 in the region between 1,200 and 1,800 cm^{-1}.

One can see the apparition of two broad bands at 1,350 and 1,530 cm^{-1} which are attributed undoubtedly to the asymmetric and symmetric stretching vibrations of nitro groups linked with benzene ring [21].

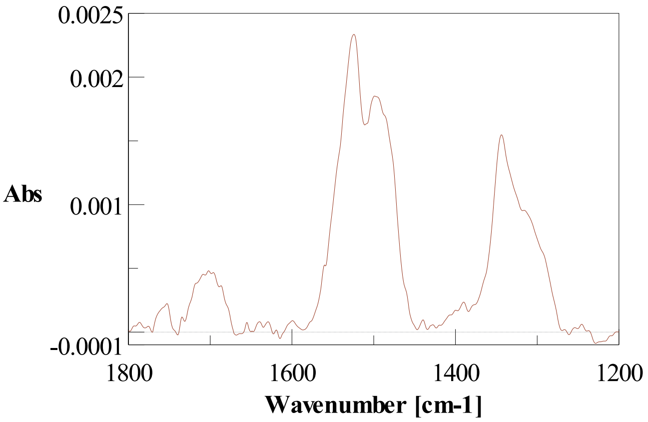


Fig. 1. ATR-FTIR spectra of modified coal with nitrophenyl groups in H_3PO_2 (0.01 M).

The peak absorbance is at the range of thin nitrophenyl films that are obtained when glassy carbon. Vulcan particles and metal surfaces were modified electrochemically or chemically with 4-nitrobenzenediazonium salt. The broadness of the peaks is due to the modification of different coal particles at different extent, like in the case of polished glassy carbon surface [22].

The chemical reduction reaction takes place spontaneously due to the ability of coal to reduce the aryl DSs to aryl radicals, which in turn, very reactively attack the coal surface and are attached on it (Fig. 2).

The grafted films remain stable even after 1 h extraction in boiling toluene as in the case of glassy carbon surface modified with alkyl chains [21].

It is well known that rejection factor and permeate flux are influenced by many factors: membrane intrinsic characteristics and their porosity, physicochemical properties of system, solute and casting solution concentration, and operating pressure. The chemical attachment of the aryl groups derived from the DS onto the coal surface permits change to the structure, the morphology and the porosity of heterogeneous RO membranes. The impact of these changes is tested in the following experiments.

The experimental data of pure water permeability (PWR, g/h), product rate (PR, g/h), and solute separation (f, %), of aqueous solution of $NaCl\text{-}H_2O$ as referent system of different types of heterogeneous RO membranes batches 317K-1, I (5 mM); II (10 mM); III (15 mM); IV (20 mM); and V (50 mM) are presented in Tables 1 and 2.

The RO membrane made with coal particles covered with aryl groups show different performance, data presented in Tables 1 and 2. The results obtained with membranes of CA-modified coal at the range concentrations of DS 10–20 mM, (batches 317K-1, II; III; and IV) show better product rate compared with those (batches 317K-1, I; and V) for the same level of solute separation.

RO performances of resulting membranes were specified in terms of pure water permeability constant, A, solute transport parameter $D_{AM}/k\delta$ (D_{AM} is the diffusion of the solute in the membrane phase), δ is the effective thickness of membrane. One can observe the lower values of solute transport parameter $D_{AM}/k\delta$, which indicate a relatively smaller average pore size on membrane surface, less solute transport through the membranes and hence higher solute separation [19].

Having in mind that all other parameters remain almost constant, the change in membrane porosity expressed by the pore size distribution and effective number of pores in the active layer of membrane would provide experimental evidence for the observed rejection factors and permeate flux changes.

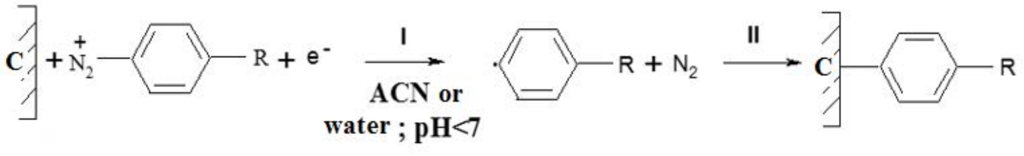


Fig. 2. Scheme of aryl diazonium salt reduction on coal surface.

Table 1
The performance data of membranes (batches 317K-1, II; III; and IV)

	Film type batches	Film no.	Film shrink. temp. (°C)	$A \times 10^{-11}$ gmol H_2O/cm^2 s Pa	$D_{AM}/k\delta$ (10^{-4} cm/s)	*f*, solute sep. (%)	PR (g/h)	PWR (g/h)
Batch 317K-1, II	H_3PO_2 10 mM DS	1	88	3.96	1.19	89.55	60.86	61.26
		2	85	5.24	2.84	83.21	79.89	80.94
	HCl 10 mM DS	1	88	2.74	0.54	93.40	40.93	42.34
		2	85	4.28	1.56	87.28	64.83	66.23
	H_2SO_4 10 mM DS	1	88	2.85	0.67	92.23	42.99	44.07
		2	85	3.79	1.52	86.71	57.67	58.62
	HNO_3 10 mM DS	1	88	2.99	0.69	92.28	45.27	46.32
		2	85	3.35	1.20	88.23	50.79	51.82
	H_3PO_4 10 mM DS	1	88	2.69	0.67	91.85	40.62	41.50
		2	85	3.67	1.53	86.39	55.79	56.72
Batch 317K-1, III	H_3PO_2 15 mM DS	1	88	3.75	1.01	90.78	57.48	57.92
		2	85	4.01	1.21	89.45	60.24	61.98
	HCl 15 mM DS	1	88	2.71	0.68	91.90	41.25	41.89
		2	85	3.19	1.06	89.30	49.32	50.51
	H_2SO_4 15 mM DS	1	88	2.00	3.76	94.07	30.10	31.02
		2	85	3.27	7.76	91.88	48.89	50.63
	HNO_3 15 mM DS	1	88	2.52	0.54	93.08	38.33	38.98
		2	85	2.77	0.64	92.38	41.75	42.93
	H_3PO_4 15 mM DS	1	88	2.64	0.60	92.49	39.43	40.87
		2	85	3.78	1.85	84.38	57.81	58.43
Batch 317K-1, IV	H_3PO_2 20 mM DS	1	88	3.34	0.52	94.55	50.82	51.69
		2	85	3.76	0.88	91.82	57.14	58.06
	HCl 20 mM DS	1	88	2.99	0.87	90.58	45.71	46.20
		2	85	4.62	1.55	87.94	69.97	71.38
	H_2SO_4 20 mM DS	1	88	2.49	0.59	92.39	37.89	38.54
		2	85	2.82	0.73	91.55	42.93	43.65
	HNO_3 20 mM DS	1	88	3.05	0.87	90.38	45.29	47.09
		2	85	4.39	2.57	81.05	66.80	67.95
	H_3PO_4 20 mM DS	1	88	2.04	0.34	94.67	30.93	31.59
		2	85	3.85	1.49	87.03	58.59	59.60

DS, aryl diazonium salt.

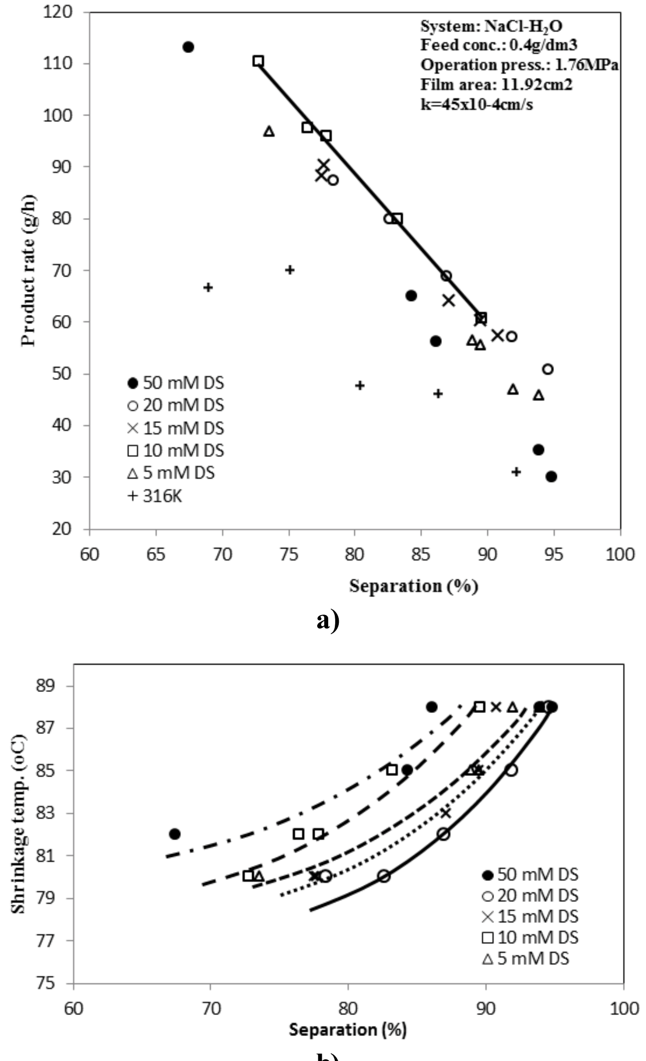
Table 2
The performance data of membranes (batches 317K-1, I and V)

Film type batches	Film no.	Film shrink. temp. (°C)	$A \times 10^{-11}$ gmol H_2O/cm^2 s Pa	$D_{AM}/k\delta$ (10^{-4} cm/s)	*f*, solute sep. (%)	PR (g/h)	PWR (g/h)
Batch 317K-1, I	1	88	2.99	0.54	93.88	45.85	46.23
H_3PO_2 5 mM AD	2	85	3.62	1.14	89.44	55.64	56.04
Batch 317K-1, V	1	88	2.00	0.32	94.82	30.16	30.97
H_3PO_2 50 mM AD	2	85	4.29	2.01	84.29	65.12	66.27

The performance data (product rate vs solute separation) for a set of different films cast under the same conditions, with hypophosphoric acid (batches 317K-1, I (5 mM); II (10 mM); III (15 mM); IV (20 mM); and V (50 mM)) along their shrinkage temperature profiles are given in Figs. 3(a) and (b).

RO membranes made with modified coal at the range of concentrations (10–20 mM) of aryl DSs look more optimal for preparation of asymmetric CA-modified coal membranes (Fig. 3(a)).

The resulting performance differences in membranes originated from the introduction of nitrophenyl groups of



a)

b)

Fig. 3. (a) Product rate and solute separation results of RO membranes made with modified coal particles at different concentrations of aryl diazonium salts: batches 317K-1, I; II; III; IV; and V and (b) shrinkage temperature versus solute separation.

DS grafted onto coal surface particles, which is related to the concentration of the DS in the solution.

The attachment of nitrophenyl groups onto coal particles surface has an impact on their rheology and morphology in general, respectively, on the morphology of polymer (CA) chain, and its wettability because the nitrophenyl groups are hydrophilic groups [21]. That's why the resulting membranes show the better performance.

The relative porosity can be also assessed by relative positions of the membrane shrinkage temperature profiles, that is, shrinkage temperature versus solute separation curves determined in RO experiments [23,24].

The shrinkage temperature versus solute separation curves for membranes (batch 317K-1, V; Fig. 3(b)) are located at the highest temperature that indicates the presence of the biggest pores on the membrane surface in the as-cast conditions. The shrinkage temperature profile curves of membranes (batches 317K-1, I; II; III; and IV) are located at lower temperature, indicating that the surface pores are evidently smaller and polydisperse because they should be shrunk at the lower temperatures to give the same level of solute separation. As the casting solution compositions differ only in concentration of aryl DS used, and since the membrane preparation procedure is the same for all the membrane types, the variations observed in relative porosities of the membrane surface region can be attributed only to the influence of aryl DS concentrations, which in turn produces different porosities and consequently different separation characteristics.

The performance correlation data of membranes in different aqueous acidic, and aprotic (acetonitrile) mediums [19] are given in Fig. 4.

The separation characteristics (product rate vs separation) of membranes that contain the modified coal with nitrophenyl groups issued from the nitrobenzenediazonium salt solution in different acid mediums show this order of productivity: $H_3PO_2 \geq HCl > H_2SO_4 > HNO_3 > H_3PO_4$. The best results were obtained with modified coal in H_3PO_2 medium membranes (batch 317K-1, IV), and acetonitrile medium membranes (batch 316K-5h) [19]. The improvement of separation characteristics is attributed to the presence of H_3PO_2 which is the most reductive agent in comparison with other acids, so it makes spontaneous reduction of the aryl DS easier. When characteristics of RO membranes are compared (batch 317K-1, IV) with those previously prepared with unmodified coal (batches 316K) [25], at about the same level of solute separation and feed flow conditions (corresponding to mass transfer coefficient of 45 × 10^{-4} cm/s), the RO membranes with coal modified in H_3PO_2 showed superior

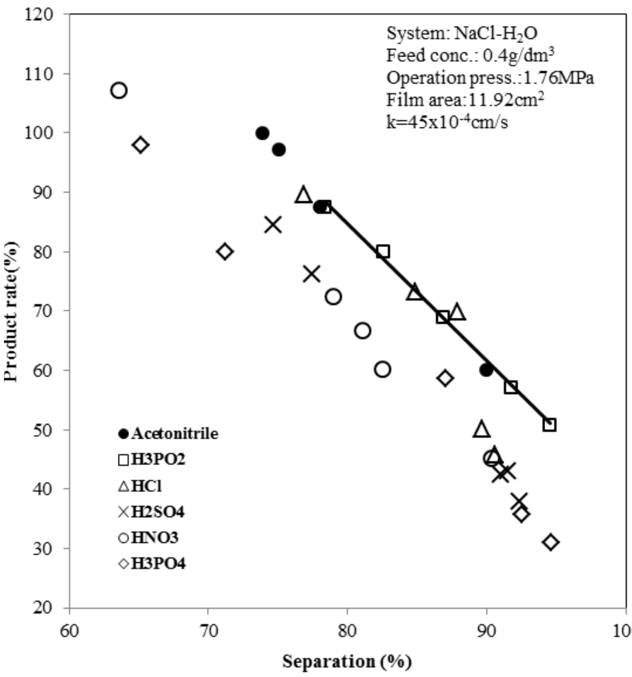


Fig. 4. Product rate and solute separation results of RO membranes (batch 317K-1, IV) made with modified coal particles of DS (20 mM) in different aqueous acidic mediums of the same concentration 0.01 M and acetonitrile.

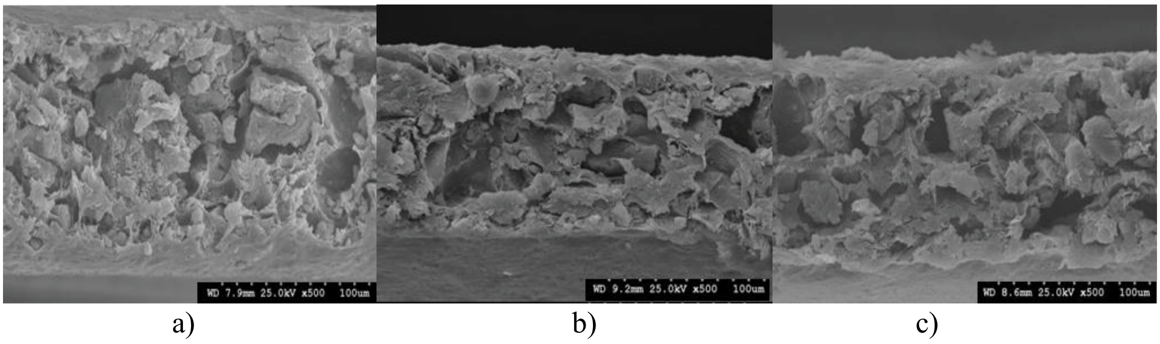


Fig. 5. SEM images of HAROM membranes: (a) batch 317K-1 II, (b) batch 317K-1 III, and (c) batch 317K-1 IV in aqueous acid medium (H_3PO_2 0.01 M).

productivity (4.262×10^{-2} m^3/hm^2) in comparison with last types (2.59×10^{-2} m^3/hm^2).

In addition these membranes show good impact resistance, stability, and antifouling properties (enhanced hydrophilicity). According to our unpublished results, during 4 years testing of these membranes with standard solution of NaCl-H_2O as referent system, sewage and heavy metal polluted waters at pH 5–8, was observed that RO characteristics of membranes were changed within 1%–2%.

3.1. Morphological analysis by scanning electron microscopy

The morphology of heterogeneous asymmetric RO membranes was characterized by scanning electron microscopy (SEM) method. The SEM images of the membranes which highlight the morphology changes of membranes: (1) (batch 317K-1 II), (2) (batch 317K-1 III), and (3) (batch 317K-1 IV) in acid medium H_3PO_2 are shown in Fig. 5.

From the observed images, the morphology changes of membranes by the surface modification of coal particles could be seen. We observe that the heterogeneous asymmetric membrane has a porous structure in the surface and very porous structure underneath. Pores are enlarged from the top to the bottom in the more rounded-like form and near similar for all membranes in comparison with finger-like form pores of heterogeneous CA-nonmodified coal [25]. These changes were the result of the introduction of modified coal particles in the skeleton of CA. These results are consistent with supposition that modified coal was successfully introduced onto heterogeneous asymmetric RO membrane surfaces.

4. Conclusions

Spontaneous grafting of aryl DSs on coal surface particles can be achieved in aqueous acid and aprotic solution at different concentrations of DS. Best results are obtained with DS concentrations at the range of 10–20 mM. This parameter is shown to be an important casting solution constituent for preparation of heterogeneous RO membranes.

The aryl groups strongly bonded in the coal particle surface had a significant impact on the rheology and morphology of the membranes, and these changes have influenced solute separation and solute-solvent permeation rate. RO membranes made of modified coal in aqueous solution of hypophosphoric acid have superior characteristics; significant enhancement of flux without deterioration of solute separation compared with CA bare coal membranes.

The resulting membranes with enhanced hydrophilicity, look promising for improvement of impact resistance, stability, and antifouling characteristics.

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