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Application of novel surface-modified PES membranes for removal of heavy metals from aqueous solutions

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ABSTRACT

Plasma-treated poly(ether sulfone) (PES) membranes were functionalized with gama-mercaptopropyltriemethoxysilane (MPTMS) in order to increase their affinity for heavy metals during filtration of aqueous solutions. The influence of effective parameters concerning the modification process such as concentration and pH of the silane solution on both surface properties and performance of the membranes were investigated. ATR-FTIR, contact angle, SEM, and EDS measurements were carried out to characterize the membranes. After plasma treatment, the hydrophilicity of the membranes increased which resulted in an increase in the adsorption of silanol groups on the membranes surfaces. By decreasing the pH level of the silane solutions to 3.5, the adsorption of silanol groups on the surface of plasma-treated PES membranes increased. The MPTMS-modified membranes showed a significant increase in heavy metal adsorption and a decrease in flux. Moreover, MPTMS-modified membranes showed a high selectivity for Hg^{2+} ions as well as good stability and recovery during filtration process.

Keywords: Polyethersulfone membrane; Surface functionalization; Heavy metal; Separation; Adsorption; Mercapto silane

1. Introduction

Heavy metals are well-identified contaminants for public health, plants, and animals because of their toxicity [1]. Hg^{2+} and Pb^{2+} ions are known as the most hazardous metals, and are on the US Environmental Protection Agency's list of priority pollutants. According to the guidelines, the concentration of mercury and lead in drinking water should not exceed 6 and 10 μg/L, respectively [2]. Nowadays, the concentration of these heavy metals may exceed 50 μg/L in wastewaters [3]. Precipitation process is a conventional method for removing heavy metals from aqueous solutions [1], while the most useful technique is filtration with membranes [4]. Membrane filtration was earlier used in order to retain metallic cations. The filtration was commonly performed in combination with using chelating reagents as additives in the feed [5]. Starov and Arthanareeswaran [6] used PES membranes to separate the metal ions, Ni(II), Cu(II),

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and Cr(III), from aqueous solutions using two complexing polymer ligands: polyvinylalcohol (PVA) and poly(diallyldimethylammonium chloride) (PDDA). The presence of ligands leads to the accumulation of complexes and subsequently with an increase in the size of the solute, the big accumulated complexes can be separated by a membrane. These ligands are recyclable and need to be regenerated before reusing. In order to improve the process of wastewater treatment, the recent studies involve membranes incorporated with chelating groups which can be blended into the membrane matrix or grafted on the membrane surface [7,8]. Common chelating agents like poly(acrylic acid), PVA, chitosan, and ect are physically absorbed (usually with electrostatic interaction), which imposes some limitations such as low selectivity and pH sensitivity on the separation properties of the membranes. Besides, the stability of the modification during the separation processes is always a point of concern [9].

The use of different silane coupling agents with various functionalities is a general approach to functionalizing ceramic membranes [10] and silica nanoparticles [11,12] which are employed to separate heavy metal ions from aqueous solutions. Huang and Hu [13] prepared silica magnetic nanoparticles modified by mercapto silane. They showed that the modified particles had a good adsorption capacity for Hg, Pb, Cu, and Cd ions, and had higher selectivity for Hg ions. Zhang and coworkers [14] synthesized a thioether-functionalized mesoporous fiber membrane for Hg^{2+} removal and showed that their membrane exhibited high selectivity and capacious adsorption of Hg^{2+}. Xu and coworkers [15] prepared thiol-functionalized silica for sorption of Pb^{2+} and Cd^{2+} ions, and according to Pearson theory for hard and soft acids and bases [16] they concluded that chemical bonding between thiol groups and metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} is the dominant mechanism of metal ion adsorption. Thus, they deduced that Cd^{2+} removal should not be as efficient as Pb^{2+} removal because of the weaker bonding strength between Cd^{2+} and thiol groups. Their results showed that thiol-functionalized particles had high selectivity for adsorption of softer metal ions like Hg^{2+} and Pb^{2+}.

Functional silane coupling agents present novel materials with high selectivity and adsorption properties in separation of heavy metal ions. Incorporating these functional groups into the membranes can improve the separation properties of membranes. Poly (ether sulfone) (PES) is one of the most important polymeric materials and is widely used in separation fields due to its good mechanical and chemical properties, and easy preparation by phase inversion method [17]. In spite of its wide use, there are some disadvantages to PES and PES-based membranes. The main disadvantage of these membranes is connected to their relatively hydrophobic character and non-selective separation. Many kinds of modifications such as blending and surface grafting have been used on PES membranes, which are reviewed by Zhao et al. [18] and Nady et al. [9]. Generally, the aim of these modification methods is to improve the membrane hydrophilicity, which decreases fouling problems and increases biocompatibility. However, these methods have less focus on increasing the PES membrane affinity for heavy metal ion separation. Accordingly, the use of functional silane coupling agents can introduce a new way to improve selectivity character of PES membranes in heavy metal separation processes. Hydrophobic membranes such as PES that are approximately chemically inert usually need a pretreatment prior to grafting of adsorbent groups on them. The common pretreatments of PES are chemical modifications such as sulfonation [19], radiation treatment with gamma ray [20], electron beam-induced grafting [21], plasma treatment and plasma-induced grafting [22], and corona treatment [23]. Plasma treatment can also be used as a source of radicals for initiating graft polymerization. The active components generated in plasma can activate the upper molecular layers of the membrane surface to increase the hydrophilicity, without affecting the bulk of the polymer [24]. Plasma treatment generates a variety of oxygenated groups such as –OH, –OOH, –COOH on the membrane surface, which facilitate the linkage between PES and silane molecules and subsequently improve the immobilization of silane molecules on the membrane surfaces.

Due to the weak separation and selectivity properties of neat PES membranes for separation of heavy metal ions, the sorption or repulsion ability of these membranes is supposed to modify. In this study, gama-mercaptopropyltriemethoxysilane (MPTMS) coupling agent as a novel material with high affinity for heavy metal ions such as Hg^{2+} and Pb^{2+} was directly deposited on the surface of plasma-treated PES membranes. MPTMS-modified PES membranes were used for absorption of heavy metal ions from aqueous solutions. ATR-FTIR, Raman spectroscopy, and EDS techniques were used for chemical analysis of modified membranes. SEM and contact angle measurement were carried out for morphology and wettability investigation. The pure water flux and heavy metal ion rejection tests were performed to study the membrane performance.

2. Experimental

2.1. Materials

Polyethersulfone (PES) was purchased from BASF, Germany (E6020, MW = 58,000) and 3-mercaptoporpyltrimethoxysilane (MPTMS) was provided by Wacker Company. N,N-dimethylacetamide (DMAC) as solvent and polyvinylpirolidone (PVP) as pore former were supplied from Merck. Other raw materials including $HgCl_2$, $NiCl_2$, $Pb(NO_3)_2$, HCl, H_2SO_4, ethanol (EtOH), and HNO_3 were purchased from Merck and used as received.

2.2. Membrane preparation

PES membranes were produced through phase inversion method. A homogenous polymer solution containing 18 wt% PES, 1 wt% PVP as pore former, and DMAC as solvent was cast using an adjustable casting knife. A layer of the polymer solution with a thickness of 150 μm was cast on a glass plate and immediately immersed into deionized water (DI-Water) at the temperature of 25˚C. After the coagulation process finished, all proto-membranes remained in DI-Water for one week and then dried for 24 h at 25˚C.

2.3. Surface modification

To generate polar groups on the surface of PES membrane, plasma treatment in Ar/O_2 (50/50) atmosphere was used. The treatment was carried out in a tubular low density RF (13.56 MHz) at a pressure of 70 mtorr, power of 25 W, and gas flow rate of 40 ml/min for one minute. Silane solutions were prepared by solving different concentrations of MPTMS in a mixture of EtOH/DI-Water (95/5). The silane concentration was 2–8 wt%. These silane solutions were set in two pH levels; natural (pH 6.5) and acidic (pH 3.5), as described in Table 1. The plasma-treated PES membranes masked in backside were immersed in the silane solutions and kept for one minute. The treated membranes were then dried for 24 h at 25˚C and washed with water to remove weakly adsorbed silanes. The schematic representation of membrane preparation method is shown in Fig. 1.

2.4. Membrane characterization

2.4.1. Chemical analysis

Fourier transform infrared (FTIR) and Raman spectra of modified and unmodified PES membranes were obtained for investigation of chemical groups formed on the surface of membranes. The attenuated total reflection (ATR) technique using Bruker-IFS 48 FTIR spectrometer (Etlingen, Germany) with horizontal ATR device (Ge, 45o) was used. Thirty-two scans were taken with a 4 cm^{-1} of resolution in the range of 4,000–500 cm^{-1}.

Raman spectroscopy technique using Bruker—SENTERRA (Germany, 2009) with high-energy laser diodes was employed over a spectral range of 80–3,500 cm^{-1} and a spectral resolution of 3 cm^{-1}.

Energy dispersive X-ray spectroscopy (EDS) analysis was employed for elemental analysis of surface and bulk of the modified and unmodified PES membranes using Philips ESEM X130 from FEI Company, Netherland.

2.4.2. Hydrophilicity

The contact angle of water was measured on the membranes surfaces using tensiometer, G10 KRUSS, Germany. DI-Water was used as the probe liquid in all measurements. To minimize the experimental error, the contact angles were measured at five random points of each sample and the average number was reported. By using the contact angle data, the hydration free energy of the membranes was calculated by the following Young–Dupre equation (Eq. (1)) [25].

$$(1 + \cos\theta)\gamma_{w}^{TOT} = -\Delta G_{sw} \tag{1}$$

where γ_{w}^{TOT} is the total surface tension of water, equal to 73 mJ/m^2. The hydration free energy ($-\Delta G_{sw}$) of membranes was calculated in order to quantify the membranes relative hydrophilicity [26].

2.4.3. Morphological studies

In order to study the surface and cross section of membranes, E-SEM (Philips-X130, Netherland) was employed. The membranes were cut into pieces of small sizes. These pieces were immersed in liquid nitrogen for 15–20 s and then broken. The fractured samples were gold sputtered for producing electric conductivity, and photomicrographs were taken under very high vacuum at 15 kV.

2.4.4. Membrane performance

All filtration experiments were carried out in a self-made dead-end stirred cell with operating pressure of 3 bars as shows in Fig. 2. The capacity and the

Table 1
Description of sample preparation conditions

Sample	PES (wt%)	PVP (wt%)	Treatment	Concentration of MPTMS	pH	Deeping time (min)	Curing
Neat PES	18	1	Non	–	–	–	–
MPES/C2/A	18	1	Ar/O_2Plasma	2	Acidic	1	24 h at 25°C
MPES/C2/N	18	1	Ar/O_2Plasma	2	Natural	1	24 h at 25°C
MPES/C5/A	18	1	Ar/O_2Plasma	5	Acidic	1	24 h at 25°C
MPES/C2/N	18	1	Ar/O_2Plasma	5	Natural	1	24 h at 25°C
MPES/C8/A	18	1	Ar/O_2Plasma	8	Acidic	1	24 h at 25°C
MPES/C8/N	18	1	Ar/O_2Plasma	8	Natural	1	24 h at 25°C

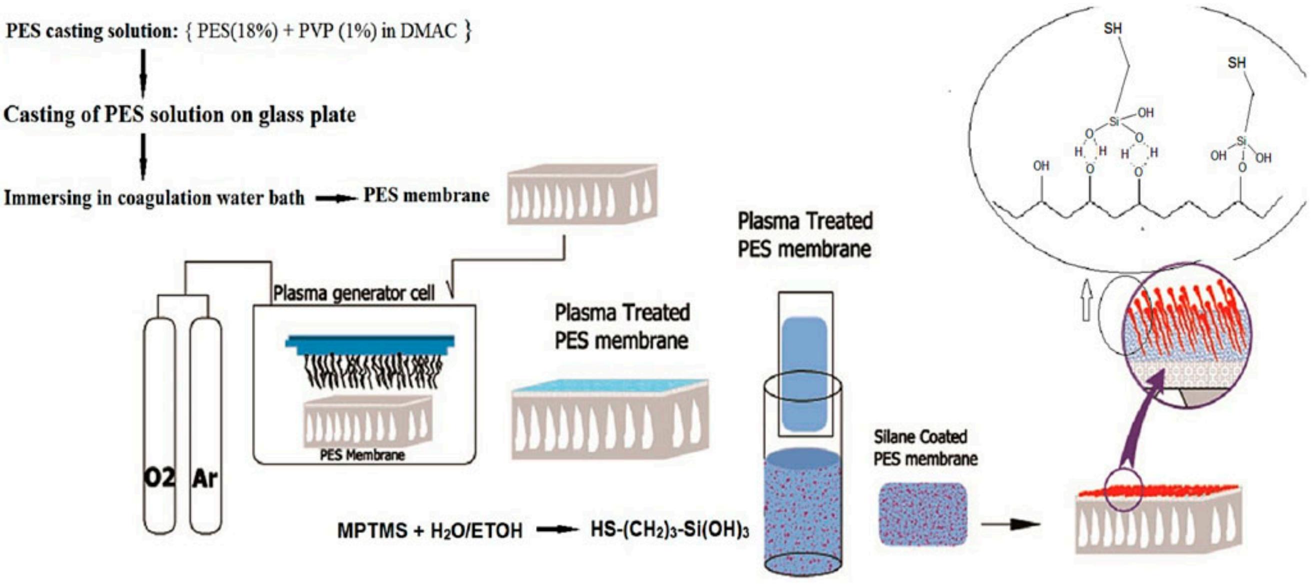

Fig. 1. Procedure of preparation of mercapto functional PES membrane.

effective surface area of the module were 200 ml and 3 cm^2, respectively. The top of the cell was equipped with a gas inlet for pressurizing the cell using nitrogen.

The flux (J_w) of diffusing water across the membrane is described by (Eq. (2)).

$$J_w = \frac{m}{A\Delta t} \tag{2}$$

where m and A are the mass of the permeated water and the membrane area, respectively, and Δt is the permeation time. After pure water flux measurement (J_w), the solution reservoir was refilled with a 10, 20, and 40 ppm $HgCl_2$ and $Pb(NO_3)_2$ solution and the rejection of all membranes were determined under a 3-bar trans membrane pressure (TMP) at 25°C and a fixed stirrer speed of 500 rpm. The heavy metal rejection ratio was calculated by (Eq. (3)).

$$R\ \% = \left(\frac{C_{\text{Feed}} - C_{\text{Permeate}}}{C_{\text{Feed}}}\right) \times 100 \tag{3}$$

where C_{Feed} and C_{Permeate} represent the heavy metal ion concentration (Pb^{2+} and Hg^{2+}) in feed and permeated solutions, respectively, measured using inductively coupled plasma mass spectroscopy (ICP).

3. Results and discussion

3.1. Chemical analysis

The absorbance spectra of the surface of unmodified PES, plasma treated, and modified PES

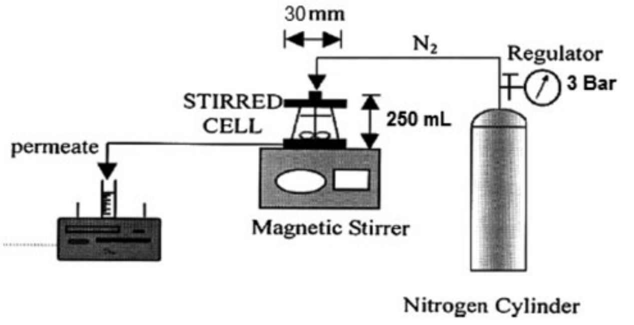

Fig. 2. Schematic design of membrane performance testing method.

membranes are presented in Fig. 3. A Si–O–Si group has peaks in about 1,050 and 1,105 cm^{-1} due to asymmetric and symmetric stretching of Si–O bonds. Moreover, Si–O–Si groups show peaks at 808 cm^{-1}, too. S=O stretching peaks are located at 1,151 and 1,105 cm^{-1} and C–S groups have a peak at 714 cm^{-1}. The benzene ring skeletal vibration peaks of PES are displayed at 1,574, 1,486, and 1,409 cm^{-1}, and C–O–C stretching peaks are present at 1,324 and 1,242 cm^{-1}. Therefore, there is a considerable overlap between the absorbing bands of Si–O–Si and S=O groups, which makes it difficult to distinct the presence of modification agent. In spite of the FTIR limitations due to overlapping bands of surface modifier agent (MPTMS) and PES, a weak peak at about 800 cm^{-1} is observed for MPTM modified samples that indicates the presence of Si groups on the membrane surface.

For careful scrutiny of membrane chemical modification, Raman spectroscopy and elemental analysis (EDS analysis) were utilized. Fig. 4 indicates Raman spectra of MPES/C5/A and unmodified PES membranes. The Raman spectroscopy indicates a peak at 2,574 cm^{-1} which is attributed to the stretching vibration of S–H bonds. The peaks at 629 and 790 cm^{-1}attributed to aliphatic C–S bonds and at 471 cm^{-1}attributed to Si–O–Si bonds, besides a weak peak at 3,072 cm^{-1} attributed to O–H bonds are other signs that indicate MPTMS was considerably adsorbed on the surface of PES membrane. Peaks at 1,073, 1,108, and 1,592 cm^{-1} related to the aromatic C–S bonds and C–C aromatic ring chain vibrations of PES were also observed.

Carbon, oxygen, sulfur, and silica content of unmodified PES and MPTMS-modified PES membranes measured by EDS analysis are shown in Fig. 5. As the results of elemental analysis test show, Si content of modified samples has increased considerably with increasing the MPTMS concentration in dipping bath.

In sol–gel process of silane precursors, hydrolysis and condensation are simultaneous processes. Fig. 6 shows the reaction steps involved in the process (for 3-mercaptopropyletrimethoxy silane R is (–(CH$_2$)$_3$–SH)). In the acidic condition (in this study the acidic pH was about 3.5), hydrolysis reaction of silane molecules (step1 in Fig. 6) is faster than condensation, which causes the number of siloxane groups increase in solution [27]. Moreover, at pH of 3.5, PES is above its isoelectric point (IEP = 3.1) [28], while MPTMS is below its isoelectric point (IEP = 6.6). Consequently, the opposite surface charge of PES and MPTMS makes

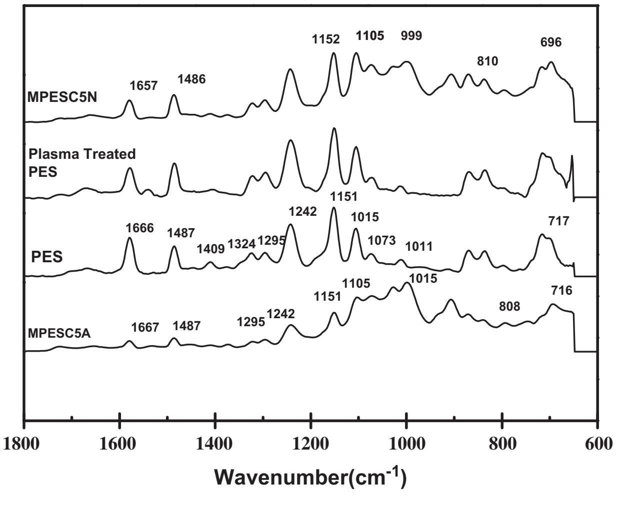

Fig. 3. ATR-FTIR spectra of: unmodified PES membrane, Plasma treated PES membrane, MPES/C5/A and MPES/C5/N modified membranes.

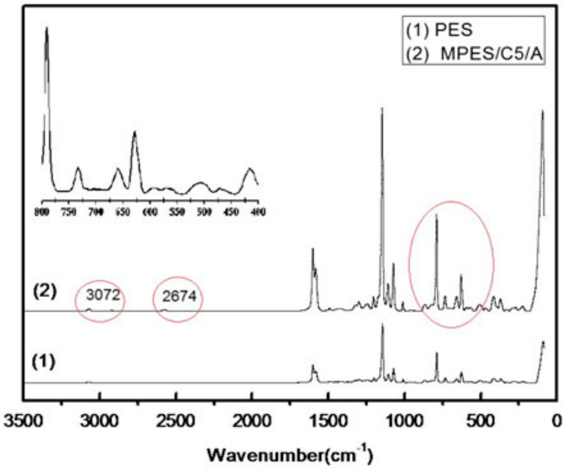

Fig. 4. Raman spectra of the surface of MPTMS modified sample (MPES/C5/A) and unmodified PES membrane.

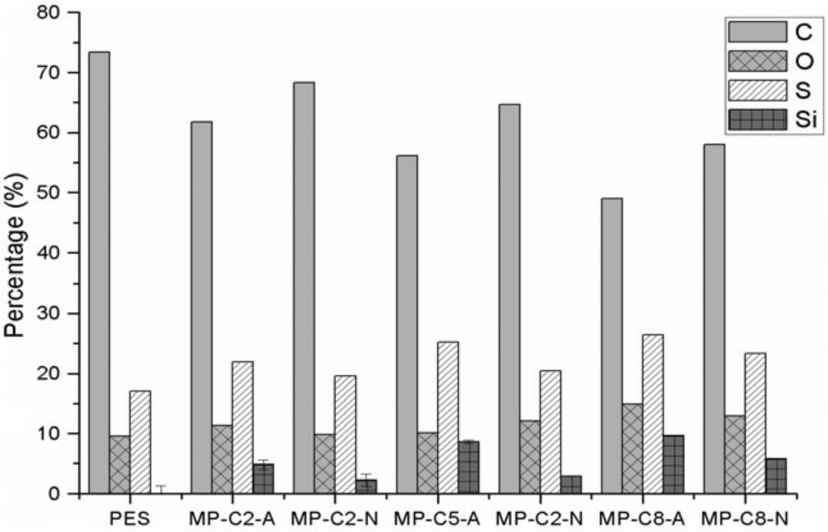

Fig. 5. Elemental analyses-oxygen, carbon, sulfur, and silica content of samples obtained by EDS test.

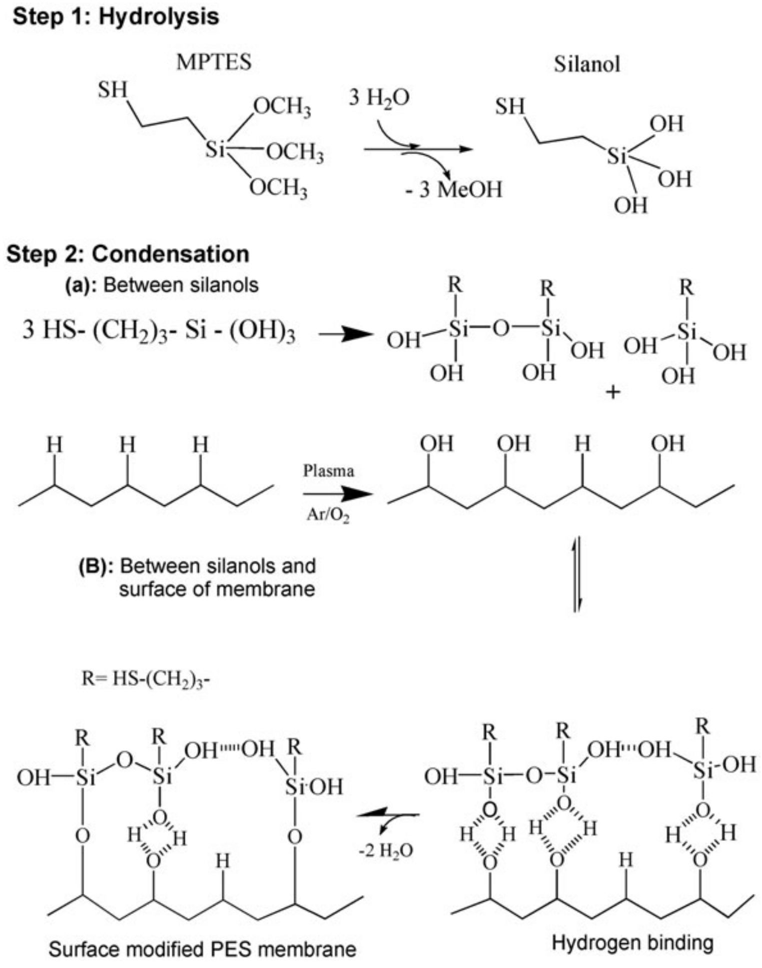

Fig. 6. Steps invovled in silanation of PES.

an attractive force for adsorption of MPTMS molecules on the surface of PES membrane. Elemental analysis shows that the Si content of samples prepared at pH 3.5 were more than that of the samples prepared at pH 6.5, which is consistent with the described reaction principles. Accordingly, the results of elemental analysis indicate that the adsorbed MPTMS on PES membrane in the acidic condition was about two times more than that in the neutral condition. Carbon content of unmodified PES membrane measured by EDS analysis is in good agreement with the results obtained by Shen and coworkers using XPS technique [29].

To study the silane diffusion into PES membrane structure, elemental analysis was applied for membranes cross sections. For this purpose, the cross section of each membrane was approximately divided into three sections, and the elemental analysis was carried out for each section. According to the elemental analysis of cross section of a modified membrane (Table 2), MPTMS could slightly penetrate into the membrane structure, but the silica content of the inner layer was not considerable in comparison with the membrane surface. An increase in the oxygen content can be related to the oxidation of PES during plasma treatment [18,22].

3.2. Morphological studies

Figs. 7 and 8 show the cross-sectional and surface SEM images of the membranes modified with different concentrations of MPTMS in two pH levels. All the prepared membranes exhibited a typical asymmetric structure with a skin layer, and a porous sub-layer including macrovoids elongated from skin to bottom of the membranes. As the cross-sectional images show, the thickness of the membranes was about 60 ± 5 μm and they all had a skin layer of about 1.5 ± 0.3 μm. The chemical modification of surface had no effect on the cross-sectional morphology of the membranes.

In contrast with cross-sectional morphology, a significant change was observed in the surface morphology of the membranes after chemical modification. The SEM micrographs of the membranes surfaces show that after modification, the surface smoothness of the PES membranes was slightly decreased. The surface roughness of the membranes increased with increasing of the MPTMS concentration in solution, due to increased amount of adsorbed MPTMS on the membrane surface. In addition, as described in Section 3.1, with decreasing the pH level of the silane solution the amount of adsorbed MPTMS on the membranes was increased, which also led to a decrease in the surface uniformity of the membranes. Although the cross-sectional morphology of both modified and unmodified PES membranes look alike (Figs. 7 and 8), the surface thin layer of modified membranes was influenced by the modification process.

3.3. Hydrophilicity

The surface contact angles of the unmodified PES membrane and MPTMS-modified PES membranes were measured to understand the effect of surface modification on membrane hydrophilicity. As shown in Table 3, the contact angle of unmodified PES membrane was about 70˚, whereas by plasma treatment of PES membrane the contact angle decreased to 47.7˚ because of PES oxidation during plasma radiation [22]. After modification of plasma-treated PES membranes with MPTMS solutions, the contact angle increased up to 83˚ due to the presence of MPTMS molecules on the PES membrane surface. The increase in contact angle of MPTMS-modified membranes can be attributed to the hydrophobicity of the organic chain of MPTMS, which is mercaptopropyl group (HS-$(CH_2)_3$). Lee and coworkers [11] demonstrated that the organic chain of organo-silane coupling agents affects the surface properties of silane-modified silica particles, and consequently the contact angle and wettability of particles vary with silane functionality [11]. Mansur and coworkers [30] indicated that the contact angle of MPTMS-functionalized nanosilica was above 70˚, which agrees with our data obtained from modified membranes. Therefore, in our experiments, increasing of contact angle is a result of changes in surface chemistry of the membranes and the formation of a silane layer on the membranes surfaces, which

Table 2
Elemental analysis of cross section of MPES/C2/A

Sample MPES/C2/A	C	O	S	Si	C/S
Surface	61.80	11.37	21.99	4.85	2.81
Edge: 5 μm depth (from surface)	68.31	13.83	15.78	2.08	4.33
Middle: 25 μm depth	70.07	14.09	14.23	1.62	4.92
End: 45 μm depth	70.92	14.58	13.72	0.78	5.21

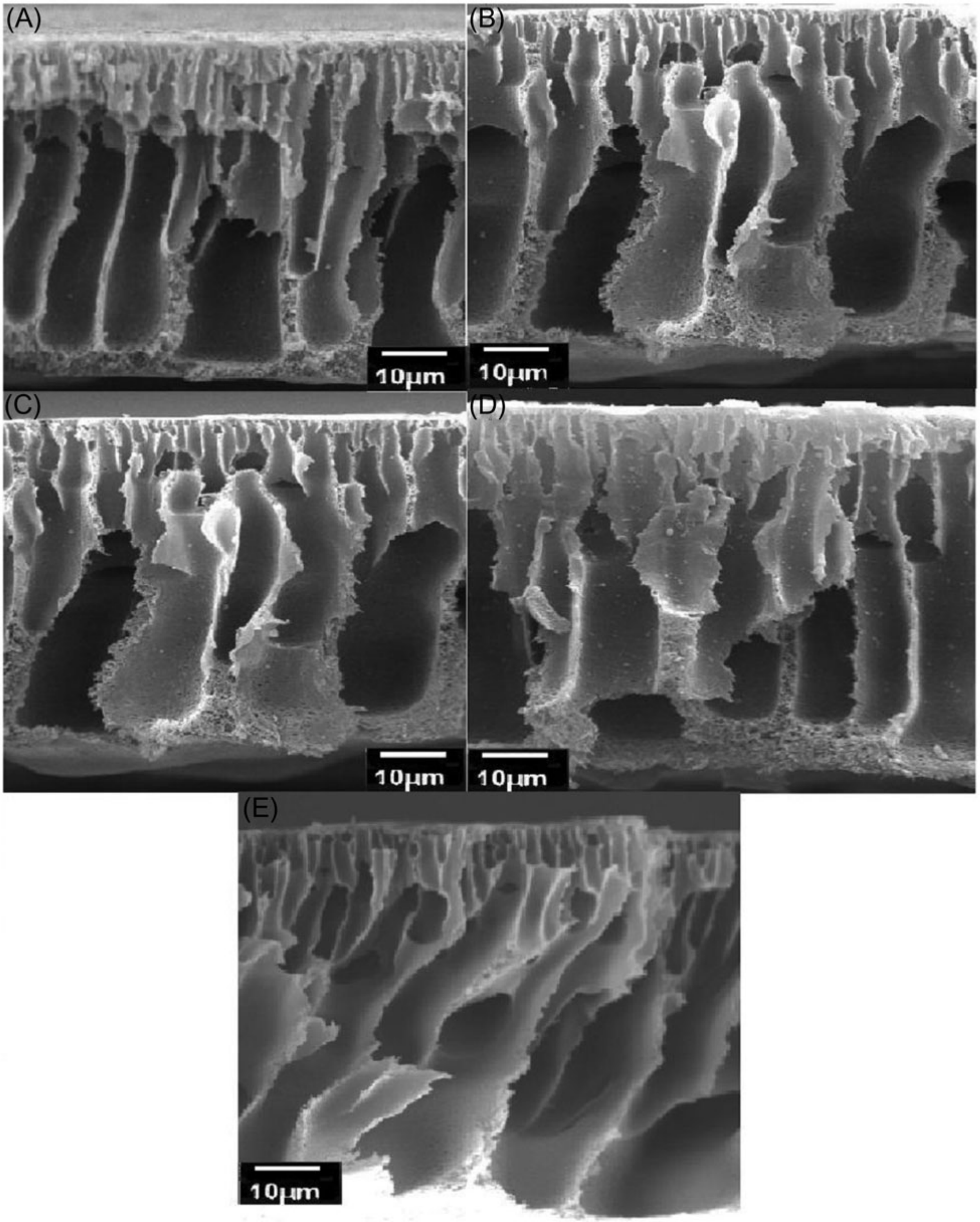

Fig. 7. Cross sectional SEM images of samples: (A) MPES/C5/N, (B) MPES/C8/N, (C) MPES/C5/A, (D) MPES/C8/A, and (E) PES membrane.

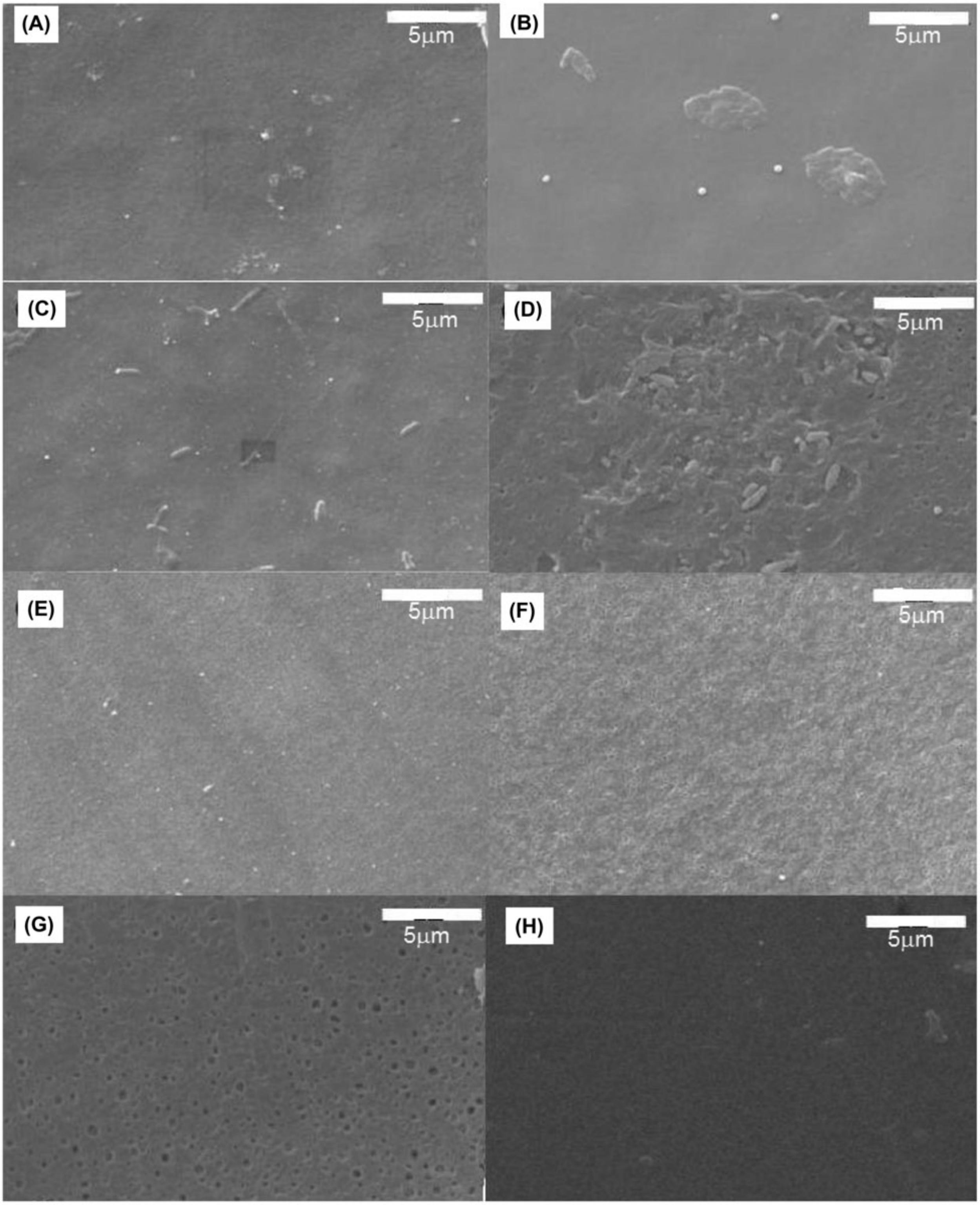

Fig. 8. Surface SEM images of MPTMS modified membranes: (A) MPES/C2/N, (B) MPES/C2/A, (C) MPES/C5/N, (D) MPES/C5/A, (E) MPES/C8/N, (F) MPES/C8/A, (G) back of MPES/C5/A, and (H) unmodified PES membranes.

Table 3
Contact angle, free energy of hydration, and flux of pure water (PWF) from unmodified and MPTMS-modified PES membranes

Samples	PES	MPES/C2/A	MPES/C2/N	MPES/C5/A	MPES/C2/N	MPES/C8/A	MPES/C8/N	Plasma treated PES
Contact angle	70.1	78.3	83.5	72.4	81.0	71.3	79.3	47.7
STDEV	3.1	1.9	2.6	2.5	2.3	3.4	3.2	2.2
$-\Delta G_{sw}$ (mJ/m^2)	97.6	87.56	81.04	94.81	84.19	96.14	86.32	121.80
PWF (kg/m^2 h)	63.6	43.2	54.4	9.3	17.4	3	14.7	112

were indicated in chemical analysis and SEM images of modified membranes as well. The contact angle analysis shows that silanol molecules adsorbed on the surface from hydroxyl side (Si–OH group), and other side of the MPTMS molecule which is a propyl chain was oriented outwards. The hydration free energy ($-\Delta G_{sw}$) is another parameter used to evaluate the modification of hydrophilic character of membranes [25]. The values of the hydration free energy indicate that modified membranes are more hydrophobic than unmodified PES membranes.

3.4. Membrane performance

Fig. 9 shows the flux of pure water (PWF) across the modified and unmodified PES membranes. The PWF of all membranes shows an initial decline and then reaches a steady state after about 60 min. This initial decline is reduced by MPTMS modification of the membranes. Moreover, membrane permeability decreased with silane treatment, from 63.6 kg/m^2 h for unmodified PES membrane to 3 kg/m^2 h for MPES/C8/A membrane. Besides, membrane permeation decreased with increasing of silane concentration, for example, from 43.2 kg/m^2 h for MPES/C2/A to 3 kg/m^2 h for MPES/C8/A. This parameter decreased with pH of MPTMS solutions as well (for example from 17.4 kg/m^2 h for MPES/C5/N to 9.4 kg/m^2 h for MPES/C5/A). These results are consistent with elemental analysis results which indicated that by increasing the concentration and decreasing the pH level of silane solutions, the adsorbed amount of MPTMS on the membranes is increased. Plasma treatment led to an increase in the membranes permeation (112 kg/m^2 h) due to the increase in the membrane hydrophilicity.

The heavy metal rejection measurements were carried out every 30 min for each sample using the ICP device. Then the value of rejection was calculated by Eq. (3). The rejection of Pb^{2+} and Hg^{2+} ions were measured after 30, 60, and 120 min, and the results are shown in Table 4.

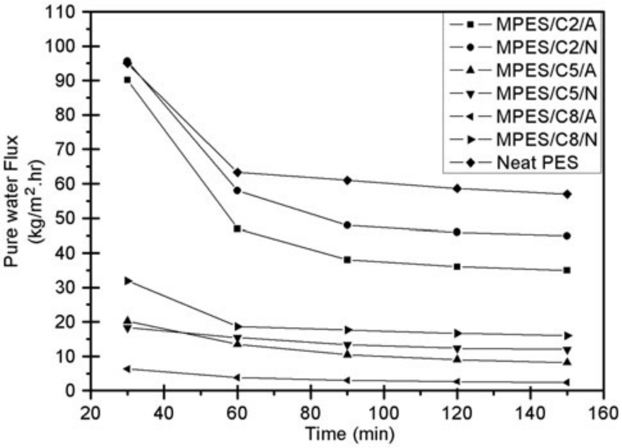

Fig. 9. Pure water flux of unmodified PES membrane and modified membranes during time.

As the rejection results indicate, MPTMS-modified membranes showed high rejection properties during the separation process and in comparison with the unmodified PES membrane, the rejection could be increased by 70% (MPES/C8/A). Comparing the unmodified PES membrane with MPES/C8/A sample shows that by MPTMS modification, the rejection of Hg^{2+} and Pb^{2+} ions was increased from 56.4 to 97.5% and from 55.3 to 89.3%, respectively. As shown in Table 4, all modified membranes kept their rejection properties after 120 min. Furthermore, the decrement of rejection of unmodified PES membrane was about 11%, while it was about 3% for the modified membranes. These results demonstrate that the rejection proprieties of modified membranes can be retained during separation process. The decline in the rejection properties of PES membranes could be explained by surface polarization of membranes during filtration process due to the adsorption of ions on the membrane surfaces. The better rejection properties of the membranes that were prepared in acidic condition can be attributed to more adsorbed silanol groups on the membranes at acidic condition (as the elemental analysis showed in Sections 3.1.).

Table 4
Rejection results of modified and unmodified PES membranes measured at different periods of time (30, 60, and 120 min) for Pb^{2+} and Hg^{2+} ions (concentration of feeding solution of 10 ppm)

Samples	Hg rejection				Pb rejection			
	30 min	60 min	120 min	Ave.	30 min	60 min	120 min	Ave.
MPES/C2/A	86.6	85.4	84.55	85.5	72.2	71.5	69.5	71.1
MPES/C2/N	78.7	77.23	74.21	76.7	62.1	60.4	59.6	60.7
MPES/C5/A	92.5	91.73	90.9	91.7	76.5	75.4	74.9	75.6
MPES/C2/N	83	81.1	80.7	81.6	67.7	66.5	65.7	66.6
MPES/C8/A	98.8	97.2	96.6	97.5	89.9	89.3	88.7	89.3
MPES/C8/N	86.5	84.3	83.8	84.9	75.4	73.7	72.7	73.9
PES	60	56	53.3	56.4	58.6	55.2	52.2	55.3

The rejection of both Hg^{2+} and Pb^{2+} ions by unmodified PES membrane was approximately the same due to the same electric charge of the ions. After modification of membranes with MPTMS, the rejection of both Hg^{2+} and Pb^{2+} ions increased, but this increase was greater for Hg^{2+} ions in comparison with Pb^{2+} ions (for MPES/C8/A membrane it was 97.5 and 89.3% for Hg^{2+} and Pb^{2+} ions, respectively). This difference is because of higher affinity of mercaptan groups for soft metal ions, such as Hg^{2+}, in comparison with hard metal ions, such as Pb^{2+}, according to Pearson theory for hard and soft acids and bases [16]. Besides, a great selectivity for Hg^{2+} ions was observed by rejection measurement of an aqueous solution containing 10 ppm of each of Ni^{2+}, Pb^{2+} and Hg^{2+} ions (MPES/C5/A). The results are illustrated in Fig. 10.

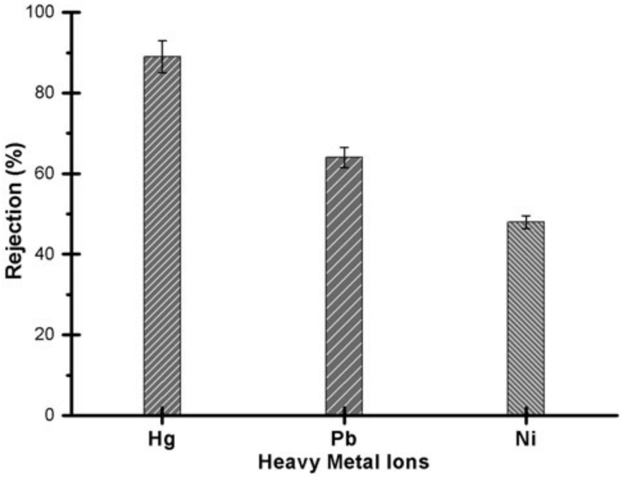

Fig. 10. Membrane selectivity–membrane rejection of metal ions in an aqueous solution containing a mixture of Hg^{2+}, Pb^{2+}, and Ni^{2+} ions.

The separation mechanism of a functional membrane comprises two mechanisms: sieving and/or Donnan exclusion rejection mechanism, and chemically adsorption mechanism by surface functional groups. Adsorption reactions are normally considered as intermolecular interactions between solutes and solid phases (adsorbent), which may be described as a surface complex adsorption process. These complex interactions comprise two reactions between the metal ions and surface functional groups: chemical binding and electrostatic binding. The former leads to specific adsorption (a more selective adsorption), and the latter which is accompanied by the formation of complexes leads to non-specific adsorption [12]. The Mercaptan group due to its ability to form chemical bonding with Hg^{2+} and Pb^{2+} ions has selective adsorption ability.

To investigate the interaction between the membranes and metallic ions, elemental analysis was used for MPES/C2/A and MPES/C5/A membranes. For this purpose, a piece of each membrane 4 cm^2 in area was put into a 10 ppm solution of heavy metal ions (Pb^{2+} and Hg^{2+}) and stirred for 24 h. Subsequently, the elemental analysis was carried out on the samples using the EDS method. The results are displayed in Table 5. According to the elemental analysis results, the amount of absorbed Hg^{2+} ions on the modified membrane compared to absorbed Pb^{2+} and Ni^{2+} ions was significantly high. These results demonstrate that -SH groups have a more affinity for Hg^{2+} ions than for other ions. This result is consistent with the rejection results in the mixture solution.

Fig. 11 shows the rejection of Hg^{2+} ions by MPES/C8/A membrane in different concentrations of feeding solution. As the results indicate, the membrane retained its rejection properties with increasing of Hg^{2+} ion concentration in feeding solution. With increasing of the feeding concentration, the percentage of rejection increased slightly. As described before, rejection mechanism of MPTMS-modified membranes is a combination of Donnan exclusion mechanism and chemical adoption mechanism. By increasing the feeding solution concentration, adsorption capacity of modified membranes increases, which results in an increase in the membrane rejection.

To study the effect of feeding concentration on adsorption properties of modified membranes, adsorption capacity (q_{em}) of an MPTMS-modified membrane (MPES/C5/A) was calculated by using (Eq. (4)).

$$q_{\mathrm{em}} = \frac{\Delta C \times V}{A} \tag{4}$$

where q_{em} is the adsorption capacity of membrane (g/m^2), $\Delta C = (C_0 - C_e)$ in which C_0 and C_e are the initial and final heavy metal concentration of solution, respectively, V is the volume of the solution and A is the membrane surface area.

For this purpose, some pieces of MPES/C5/A membrane 4 cm^2 in area were cut and put in 10 ml of different solutions containing 6, 12, 20, and 40 ppm of Hg^{2+} and Pb^{2+} ions. The solutions were stirred for 24 h. The results are shown in Table 6. It was found that by increasing the concentration of heavy metals in feeding solution, adsorption capacity of the membrane increased. It was also indicated that the adsorption capacity of the membrane for Hg^{2+} ions was more than for Pb^{2+} ions, which confirms the previous results obtained for the selectivity properties of modified membranes. These results corresponded with increasing of rejection of modified membranes with increasing of feeding concentration (Fig. 11).

It can be seen that the adsorption capacity of the modified membrane increased with the increasing of concentration of the feeding solution. To measure the equilibrium adsorption capacity of membranes, a piece 4 cm^2 in area from each membrane was cut and put into a solution containing 500 ppm of heavy metals (Pb^{2+} or Hg^{2+} ions) and stirred for 24 h. Then the samples were washed with a 15% HCl solution for desorption of ions that were adsorbed on the membranes. The ion concentration of each sample was measured by ICP technique. Adsorption capacity of membranes (g/m^2: grams of heavy metal ions per m^2 of membrane) that were calculated by Eq. (4) (ΔC is defined as the concentration of heavy metals in washing solution) are exhibited in Table 7. As the results demonstrate, the adsorption capacity of membranes increased significantly with MPTMS modification of the membranes. In addition, the adsorption capacity of membranes for Hg^{2+} ions was more than that for Pb^{2+} ions which is consistent with the selectivity properties of modified membranes.

The stability of functional groups on modified membranes during filtration process is an important issue. To investigate the MPTMS stability, Si content of MPES/C5/A and MPES/C5/N membranes was

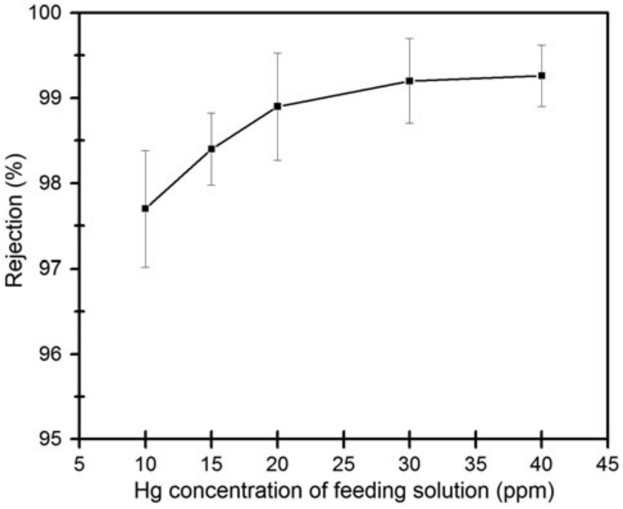

Fig. 11. Rejection of Hg ions by MPES/C8/A membrane in different feed concentrations.

Table 5
EDS test results of samples MPES/C2/A and MPES/C5/A after adsorption test

Sample	C	O	S	Si	Hg	Pb	Ni	Hg/Si	Pb/Si	Ni/Si
MPES/C2/A	61.43	12.06	20.06	4.44	2.06[a]	–	–	0.46	0.00	–
	64.25	11.88	19.77	3.98	–	0.17[b]	–	0.00	0.04	–
MPES/C5/A	55.96	11.22	21.91	7.84	3.19[a]	–	–	0.41	0.00	–
	57.03	12.26	22.09	7.44	–	1.27[b]	–	0.00	0.17	–
	57.47	12.73	19.69	6.74	2.24[c]	0.97[c]	0.16[c]	0.33	0.14	0.02

[a] Feeding solution contained 10 ppm of Hg^{2+} ions.

[b] Feeding solution contained 10 ppm of Pb^{2+} ion.

[c] Feeding solution contained 10 ppm of metal ions including equal amounts of Hg^{2+}, Pb^{2+}, and Ni^{2+}.

Table 6
Adsorption capacity (q_{em}) of MPES/C5/A sample in different feeding solutions

	q_{em} (g/m^2: g of heavy metal ions per m^2 of membrane) Heavy metal concentration of feeding solutions (ppm)			
	6	12	20	40
Hg^{2+}	0.71	0.91	1.45	3.13
Pb^{2+}	0.44	0.63	1.04	2.22

measured after filtration. The surface of the membranes was washed with pure water using the cross flow filtration process with a velocity of 1.5 m/s. The washed membranes were analyzed by elemental analysis. The elemental analysis showed that the Si losing was 5.5% for MPES/C5/A membrane and about 11% for MPES/C5/N membrane (Table 8). For membrane recovery studies, membranes were washed with a feeding inclusive solution of 5% thiourea at pH 2 and then their rejection values were measured with the same procedure. Recovery factors were calculated using Eq. (5).

$$R_f\ (\%) = \left(\frac{R_{wm}}{R_0}\right) \times 100 \tag{5}$$

where R_{wm} is the rejection of the used membrane after washing and R_0 is the initial rejection of the same membrane at same processing time.

The results indicate that the recovery of MPES/C5/A and MPES/C5/N membranes was over 94% and about 87%, respectively. These results show that the MPTMS-modified membranes, especially the samples prepared in an acidic condition, had suitable stability and recovery. Consequently, this method can introduce a new useful method for the preparation of selective membranes for heavy metal ion separation applications.

Efficiency of MPTMS-modified PES membrane was investigated by testing a real industrial wastewater sample containing various heavy metal ions. Wastewater sample was filtered with MPES/C5/A for 120 min. Results (Table 9) indicate that the modified membrane considerably removed heavy metals from wastewater sample, and the modified membrane exhibited high rejection for heavy metal ions specially for Hg^{2+} and

Table 7
Equilibrium adsorption capacity (q_{eq}) of PES and modified PES membranes

		q_{eq} (g/m^2: g of heavy metal ions per m^2 of membrane)					
Samples	PES	MPES/C2/N	MPES/C5/N	MPES/C8/N	MPES/C2/A	MPES/C5/A	MPES/C8/A
Hg^{2+} ions	0.222	3.15	5.18	7.12	3.35	5.55	8.08
Pb^{2+} ions	0.217	2.24	3.83	4.95	2.45	4.22	5.73

Table 8
Elemental analysis result (Si Content) of MPES/C5/A and MPES/C5/N before and after filtration process

Si content %					
MPES/C5/A			MPES/C5/N		
New membrane	Used membrane (After filtration)	Decline %	New membrane	Used membrane (After filtration)	Decline %
9.1	8.7	−5.5	4.5	4	−11

Table 9
Rejection of heavy metal ions from an industrial real sample after 120 min filtration with MPES/C5/A membrane

	Fe^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Hg^{2+}	Ca^{2+}	Fe^{3+}
Ion concentration of real sample (mg/L)	14.2	150.1	96.2	188.1	107.8	227.9	151.4	7.3
Rejection %	75.4	69.3	88.1	91.1	84	95.2	71	66.7

Table 10
A comparison of heavy metal rejection for different modified PES membranes

	Membrane type	Modification method	Modifier	Ion	Rejection %	Refs.
1	Flat sheet	Surface grafting	MPTMS	Hg	97	This work
				Pb	87	
2	Flat sheet	Surface immobilization	Thiol functional nanosilica	Hg	91	[31]
				Pb	81	
3	Flat sheet	Grafting	Poly(amidoamine)	Cd	87	[32]
4	Flat sheet	Blending	PEG-coated cobalt-doped iron oxide	Cu	95	[33]
5	Flat sheet	Blending	Carbonaceous material	Cu	80	[34]
6	Hallow fiber	Grafting	Polybenzimidazole	Cd	95	[35]
				Pb	93	
				Mg	96	
7	Hallow fiber	Grafting	Polybenzimidazole	Mg	87	[36]

Pb^{2+} in the presence of other metal ions. Comparative representations for rejection property of different modified PES membranes are illustrated in Table 10. Based on the results, a successful modification on the surface of PES membrane has been done in this study. Pb^{2+} rejection with MPTMS-modified membrane is close to which of polybenzimidazole grafted PES hollow fiber reported by Zhu et al. [35]. As a result, MPTMS modification is a simple and efficient method for modifying the surface of PES membranes in order to remove heavy metals from wastewaters.

4. Conclusion

A new method was introduced for surface modification of PES membranes for the separation of heavy metal ions from aqueous solutions directly. The PES membranes were prepared using phase inversion technique, and plasma treated before being functionalized with MPTMS molecules. To functionalize the membranes, they were immersed in silane solutions with different concentrations and pH levels. The results showed that concentration and pH of silane solutions had a significant effect on membrane properties. Our results confirmed that adsorbed silane molecules on the membranes surfaces had acceptable stability which caused the modified membranes to exhibit abiding performance during filtration process. It was observed that PES membranes modified with MPTMS coupling agent, could directly remove toxic heavy metals such as Hg^{2+} and Pb^{2+} ions by filtration process in one step. The modified membranes showed a lower flux and higher rejection properties than unmodified PES membrane. As the results indicate, the separation mechanism of MPTMS-modified membranes was a combination of filtration and chemical adsorption due to chemical affinity of mercaptan groups for heavy metal ions. The modified membranes had high adsorption capacity and kept their separation properties at high solute concentration. With increasing the concentration of heavy metals in the feed, the adsorption capacity of membranes increased. Due to high chemical affinity between –SH groups and Hg ions, MPTMS-modified membranes showed high rejection of this ion (up to 99%). The MPTMS-modified membranes had higher selectivity for Hg ions in comparison with Pb and Ni ions.

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Nomenclature

A	—	effective area of the membrane (m^2)
ATR	—	attenuated total reflection
CA	—	contact angle (deg)
C_{Feed}	—	concentration of heavy metal ion in the feed solution (mg/L)
C_{Permeate}	—	concentration of heavy metal ion in the permeation solution (mg/L)
C_0	—	initial concentration of heavy metal ions (mg/L)
C_e	—	heavy metal concentration at equilibrium (mg/L)
DI-Water	—	deionized water
DMAc	—	N,N-dimethylacetamide
EDS	—	energy dispersive X-ray spectroscopy
EtOH	—	ethanol
FTIR	—	Fourier transform infrared spectroscopy
ICP	—	inductively coupled plasma mass spectroscopy
J_w	—	permeation flux of membrane ($kg/m^2/h$)

m — mass of permeated water (kg)
MPTMS — 3-mercaptopropyltrimethoxy silane
MPES/C2/N — surface-modified polyethersulfone membrane by using a solution containing 2 wt% of MPTMS in natural pH
MPES/C2/A — surface-modified polyethersulfone membrane by using a solution containing 2 wt% of MPTMS in acidic pH
PDDA — polydiallyldimethylammonium chloride
PES — polyethersulfone
PVA — polyvinylalcohol
PVP — polyvinyl pyrrolidone
PWF — pure water flux ($kg/m^2/h$)
Q — volume of the permeate water per unit time (m^3/s)
R — rejection of heavy metal ions (%)
R_f — recovery factor
R_0 — initial rejection of membrane
R_{wm} — rejection of used membrane after washing
SEM — scanning electron microscopy
TMP — transmembrane pressure (MPa)
Δt — permeation time (h)
V — solution volume (l)
XPS — X-ray photoelectron spectroscopy
$-\Delta G_{sw}$ — free energies of hydration (mJ/m^2)
ΔC — diffraction of ion concentration in solution before and after adsorption
γ_w^{TOT} — total surface tension of the water (mJ/m^2)

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