

Fabrication of layer-by-layer ion exchange membrane by applying PDA-POSS nanocomposite onto a heterogeneous cationic substrate for water treatment

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Abstract

Double-layer Cation Exchange Membranes (DLCEMs) have been prepared by surface polymerization of dopamine-co-POSS nanoparticles on a PVC-based heterogeneous cation exchange membrane. FTIR and FESEM images proved relatively uniform forming of intended DLCEMs. The FESEM images illustrated almost integrity dispensation of nanoparticles through the surface layer. Results represented that developing a nanocomposite layer resulted in surface hydrophilicity enhancement. The obtained data for Cu²⁺ and Cr²⁺ removal percentage for the prepared membranes represents a higher capacity for DLCEMs to remove heavy metals compared to the pristine cationic membranes. Also, membranes showed higher Cr²⁺ removal capacity rather than Cu²⁺. The membrane surface modification by introducing PDA nanocomposite also caused to improving sodium permeability and flux. Furthermore, the transport number and permselectivity of the prepared CEMs generally follow an increasing procedure nearly. It should be noticed that the incorporation of POSS nanoparticles into the surface layer resulted in electrical resistance reduction obviously.

Keywords: Electrodialysis, Double layer Membrane, Electrochemical Characterization, Water Treatment

1. Introduction

In recent years Ion Exchange Membranes (IEMs) have been utilized extensively in electrodialysis systems for desalination, industrial effluent treatment possessing heavy metals, food processing and supplying basic chemical products [1-4]. So, many studies have been performed lately and a number of renovation methods have been introduced to membrane-based separation research to achieve separation systems with higher efficiency, sufficient mechanical strength and more cost-effectiveness. In this case, some modification techniques have been proposed to be used such as polymer blending [5,6], incorporating organic/inorganic additives [7, 8], using a vast variety of ionic functional groups [9,10] and utilizing a thin surface modifier [11, 12]. As time is going on, many novel functional ion exchange membranes (IEMs) prepared with nanofillers have illustrated optimistically functional application points of view among all various fields in research studies and also in industries [13, 14]. Most recently Doublelayeratin Exchange Membranes Membranes (DLCEMs) have received substantially attraction and have been investigated in many electrodialysis (ED) studies [15]. In ED which is considered as an electrochemical separation process, cation and anion exchange membranes are applied to transfer ions selectively from one compartment to another under an electrochemical potential gradient [16, 17]. Many outstanding advantages of ED compared with Reverse Osmosis (RO) and NanoFiltration (NF) such as high water recovery, thermal, chemical and mechanical stability, acceptable separate properties and also effective behavioural characteristics to remove harmful ions from feed water, may justify widely application of the ED technique for the treatment of more brackish water [18-21]. In spite of some advantages discussed above, fouling of IEMs can be the main difficulty in the ED separation procedure, since the membrane body is usually considered to be a hydrophobic polymer due to the plasticization tendency of hydrophilic one in aqueous environments. Although hydrophobic polymers are likely to adsorb foulants, these materials can be surface modified to improve their hydrophilicity by a few techniques such as plasma treatment [22] or chemical oxidation and grafting [23]. Up to now, a surface modification with polydopamine (PDA) has attracted considerable interest to increase the membrane's antifouling potential [24, 25]. As a matter of fact, in an alkaline aqueous solution, Dopamine can be oxidized and its polymerization may occur to create a crosslinked PDA. PDA is a hydrophilic bio-inspired polymer that can deposit onto any solid surface. Vasselbehagh et al, reported that the antifouling potential can improve with the increase in surface charge density and hydrophilicity in their IEMs coated by PDA [26].

So far, the surface modification of hydrophobic porous MMMs by adhesive poly(dopamine) has been studied only occasionally.

In the present study, the polymerization of dopamine and different loadings of POSS nanoparticles in the casting solution are investigated to prepare PVC-PDA-DLCEM and PVC-PDA-POSS-DLCEMs. Cage-like structure, organic-inorganic compatibility and different functional and reactive groups of POSS nanoparticles make them act as polymer cross-linkers and improve physicochemical characteristics [27].

2. Experimental

2.1. Materials

Actually, all solvents and reagents were commercially available and applied as received. Polyvinylchloride (PVC, S-7054, density: 490 g/l, viscosity number: 105 cm³/g) supplied by BIPC, Bandar Imam, Iran was applied as a polymer binder. Tetrahydrofuran (THF, Mw: 72.11, density: 0.89 g/cm³) was utilized as the solvent. Dopamine hydrochloride was purchased from Sigma-Aldrich. Glutaraldehyde (GA) (25% by weight water-soluble) is provided by Sigma Aldrich. Polyhedral oligomeric silsesquioxane (POSS) nanoparticles were synthesized and used in accordance with previous work as published earlier [28].

2.2. Preparation of surface-modified CEMs (PVC-PDA-DLCEMs)

In this study, the cation exchange membranes (CEMs) which were applied as the substrate have been prepared via the casting solution process. To attain this goal, the polymer used as the main body (PVC) was dissolved in THF solvent in a glass reactor with the ratio of (1: 20) (W/V) equipped with a mechanical stirrer model: VelpScientifica Multi 6 stirrer) for more than 5 h. For the next step, grigrainsin particles (ion exchanger Amberlyst1 15, strongly acidic cation exchanger, H⁺ form more than 1.7 meq/g dry, density: 0.6 gr/cm³, particle size (0.355–1.18 mm), ≥90% Merck) in a certain amount ((Resin particle: Polymer inder) (w/w), (1:1)) was added to the polymeric solution. Utilizing an ultrasonic instrument (Parsonic, S11, S/N PN-88159, Iran, 28 KHz, and 150W), the mixture was sonicated for 90 min for breaking up the particles aggregates. The obtained solution was then casted on nonwoven fitting fabric and have been left at room temperature (~ 25 °C) to be dried. In this stage, dopamine hydrochloride and different loading ratios of POSS nanoparticles as filler additives were dissolved in 30 ml deionized (DI) water and sonicated for 2h to fabricate the DLCEMs. As represented, the casting solution compositions of prepared membranes were characterized in table 1. The circular pieces of PVC-CEMs were prewetted by deionized (DI) water 1 h, and immediately transferred and immersed into the prepared solution @ pH 10 for dopamine polymerization on the membrane surface. Moreover, a few drops GA as a cross-linking agent was poured into the solution. The reaction continued for 3 hours at 90 °C. ultimately, the obtained surface-modified DLCEMs were rinsed with DI water to remove the alkaline substance on the surface.

Table 1. Prepared CEM samples composition

Membrane Sample number (CEM _x)	Membrane sample	Dopamine (W/W)	POSS (W/W)
CEM ₁	PVC-CEM	0.00/100	0.00/100
CEM ₂	PVC- PDA-DLCEM	7.00/100	0.00/100
CEM ₃	PVC – PDA – POSS – DLCEM ₁	7.00/100	0.10/100
CEM ₄	PVC – PDA – POSS – DLCEM ₂	7.00/100	0.30/100
CEM ₅	PVC – PDA – POSS – DLCEM ₃	7.00/100	0.70/100

2.3. Characterization

Field Emission Scanning Electron Microscopy (FESEM, Razi-foundation, model MIRA3TESCAN-XMU) was utilized to capture the surface morphology of the prepared CEM. Also to gain more information about the prepared membrane's chemical structure, dried samples were evaluated by a single beam Fourier transform infrared spectrometer (FTIR, Galaxy series 5000) in the range from 4000 to 200 cm⁻¹. Moreover to provide information about surface hydrophilicity or hydrophobicity and photocatalytic effects of the prepared membranes contact angle (CA) was measured by using deionized water at ambient temperature.

2.3.1. Heavy Metal Ions Removal

To investigate the prepared membrane's performance in heavy metal ion removal, an electro dialysis test cell which consists of three parts has been applied. Cu^{2+} and Cr^{2+} cations have been studied in the present work. The middle part of the electro dialysis cell functioned with an aqueous solution of CuSO_4 and CrSO_4 . The treated solution was collected after 30 min for measuring the separation performance of the system and finally analyzed by atomic emission spectroscopy. The residual cations concentration has been utilized to estimate the separation percentage. It should be noted that the pH of the feed was adjusted neutral condition.

2.3.2. Electrochemical measurements

2.3.2.1. Permeability and flux

To measure the ionic flux, two NaCl solution samples (0.1 M/0.01 M) were placed on each side of a test cell (Fig. 1) with platinum electrodes. Across the cell, a DC electrical potential was applied. During the experiment, both parts were stirred energetically to reduce the effects of boundary layers. So the cations can pass through the membrane towards the cathodic section. Ionic flux through the membrane was measured by considering the pH changes in the compartments [30].

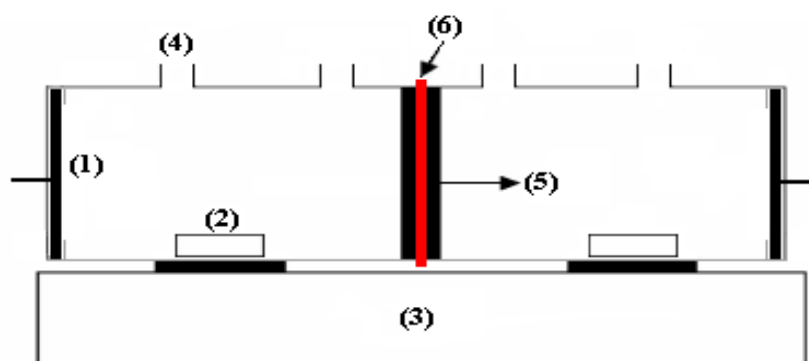


Fig. 1. Schematic diagram of ED test cell: (1) Pt electrode, (2) magnetic bar, (3) stirrer, (4) orifice, (5) rubber ring, (6) membrane.

2.3.2.2. Transport number and permselectivity

The current fraction carried by a special ion is considered as ion transport number, characterized as follows [31,32]:

$$t_i = \frac{z_i j_i}{\sum_i z_i j_i} \quad (2)$$

to measure the mean dynamic transport number (MDT) equation 8 can be utilized. The permselectivity has been analyzed based on the counter ions migrations through the membrane and is characterized as below:

$$P_s = \frac{t_i^m - t_0}{1 - t_0} \quad (3)$$

Where t_0 is defined as the transport number of counter ions [32-34].

2.3.3. Electrical resistance

At first, prepared CEMs were incorporated into a cell with an electrolyte solution to reach the first electrical resistance (R_1). The second electrical resistance (R_2) was measured by making use of the apparatus without a membrane. Ultimately, membrane electrical resistance can be specified utilizing the following equations:

$$R_m = R_1 - R_2 \quad (4)$$

$$r = R_m A \quad (5)$$

Where r is a real resistance and A is the CEM surface area.

3. Results and discussion

3.1. Prepared CEMs Characterization

3.1.1. Morphological study

Fig. 2 displays the FTIR spectra of POSS, pure PVC and PVC-PDA-POSS-DLCEM. The FTIR spectrum was performed to attain a better evaluation of bond formation. Obtained results represented bonds at $3000\text{-}3500\text{ cm}^{-1}$ associated with the $-\text{OH}$, $-\text{NH}$ groups in prepared DLCEMs due to the presence of polydopamine and functionalize-POSS nanoparticles on the membrane surface. The cage structure of Si-O-Si groups in POSS are clear in the bonds at around 1100 cm^{-1} . Actually, a peak can be seen in the 1493 cm^{-1} , 1600 cm^{-1} and 1250 cm^{-1} which are regarded to aromatic C-C stretching vibrations, N-H bending vibrations, and aromatic amine C-N stretching vibrations, respectively which represents the existence of the aromatic rings in dopamine [35, 36] and also the peak at 1198.17 cm^{-1} is attributed to the partial inter-chain interactions between C-Cl bonds (in PVC) and

C–N bonds (in dopamine) [37]. The CH₂ and CF₂ groups in PVC are recognized clearly in 1330–1429 cm⁻¹ and 1096–1250 cm⁻¹, respectively [38,39].

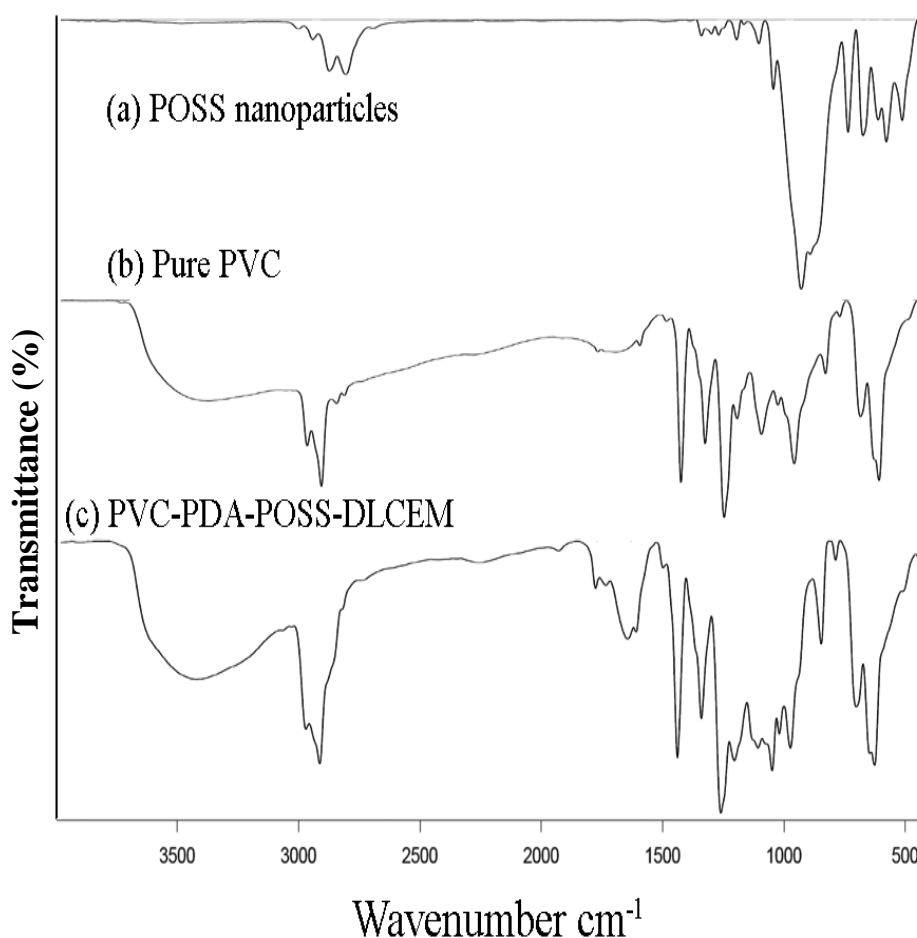


Fig. 2. FTIR spectra of (a) POSS nanoparticles, (b) pure PVC, (c) PVC-PDA-POSS- DLCEM.

Figs. 3 and 4 which indicate FESEM images of prepared CEMs identified nearly structural homogeneity and integrity of studied DLCEMs samples as a result of surface modification with PDA and also the incorporation of POSS as additives. As it can be observed the resin particles and also POSS additives are fairly uniform dispersed on the membrane's surface. With utilizing PDA and also with incorporating nanoparticles into membrane casting solution (Figs. 3b and 4c) which resulted in M_2 and M_3 samples, cavities and voids have been developed due to sudden emersion of additives and finally, with an increase in nanoparticles loading ratio up to 0.7 wt% (M_5), making use of high concentration of POSS additives in membrane structure made more uniformity at a few points and in some cases it can partly progress nanoparticles agglomeration (Fig. 3d).

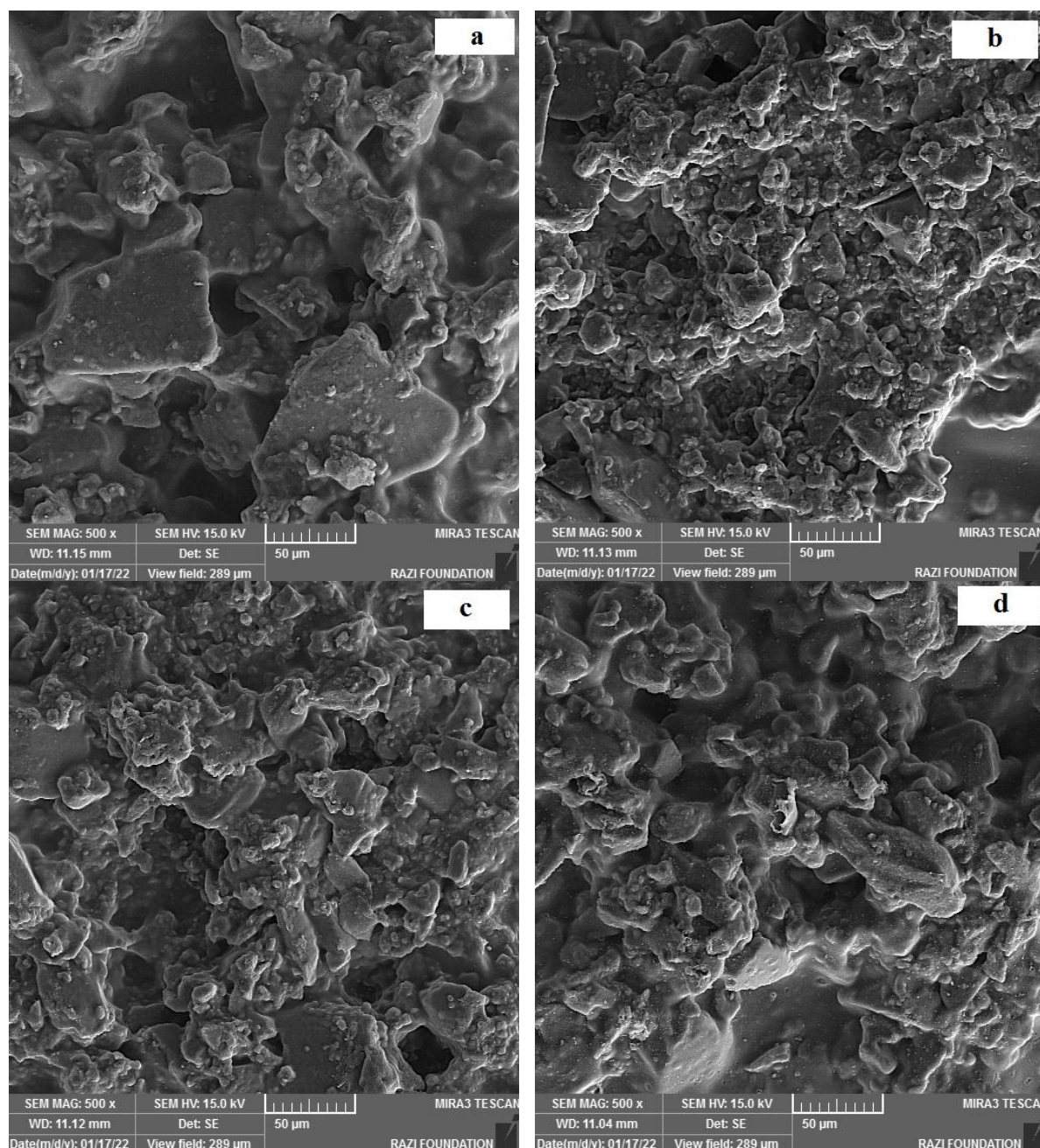


Fig. 3. FESEM images of prepared CEMs samples with a 500x magnification for (a) CEM₁ (b) CEM₂ (c) CEM₃ and (d) CEM₅.

As illustrated in Fig. 4 the roughness of the membrane surface has been increased partly with membrane surface modification with dopamine (Fig. 4b), although in many studies suitable antifouling potential and also more hydrophilicity characteristics of PDA have been proved. Also, it is recognized that rough surfaces may represent lower antifouling properties rather than smooth ones [40].

So, it is worth mentioning here that the most optimal loading ratio of dopamine has been considered in this study via the competition between the antifouling potential improvement resulting from the increase in membrane surface hydrophilicity and the decrease in antifouling potential due to the increase in membrane surface roughness.

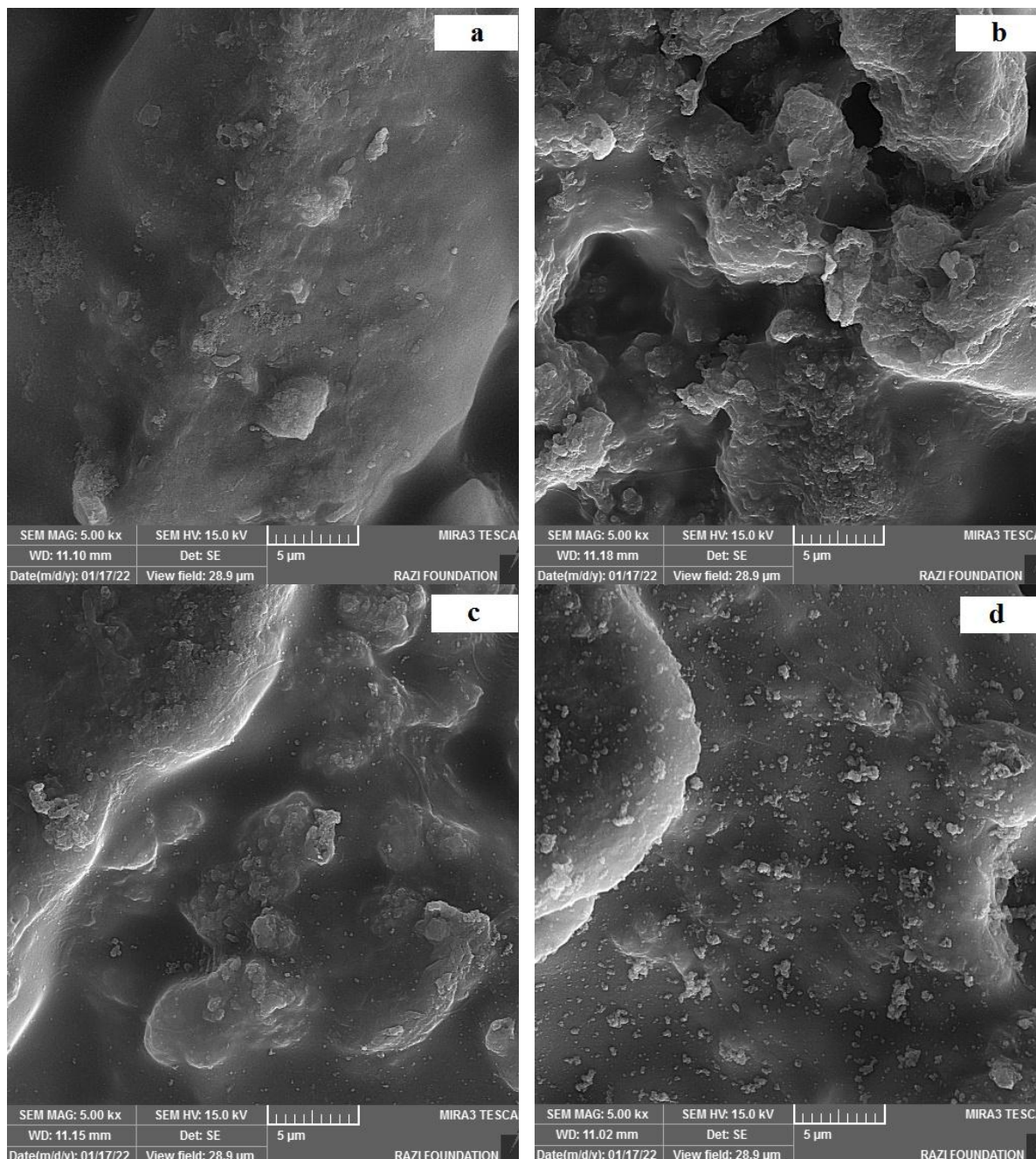


Fig. 4. FESEM image of prepared CEMs samples with a 5000x magnification for (a) CEM₁ (b) CEM₂ (c) CEM₃ and (d) CEM₅.

3.1.2. Water uptake

Fig. 5 obviously illustrates water content percentage improvement by the incorporation of both PDA and POSS into the membrane structure. Higher hydrophilic nature of PDA and also utilizing POSS nanoparticles in membrane casting solution have resulted in a clear enhancement trend that can cover the hydrophobicity nature of the substrate membrane surface [26]. Also, it can be derived that the heterogeneity increasing of the membrane structure and developing cavities and voids which has been regarded as the sudden appearance of POSS nanoparticles, should have been effective in representing such behaviour as indicated in figure 3. As can be seen in figure 5, with a further increase in POSS nanoparticles up to 0.7 wt%, the water uptake amount in the prepared CEMs has still been representing a rising manner. This situation may mean that with an increase in the loading ratios of POSS particles in the membrane matrix, higher uniformity and spreading and lower agglomeration of nanoparticles can be expected as it is clear in Fig. 4d [41].

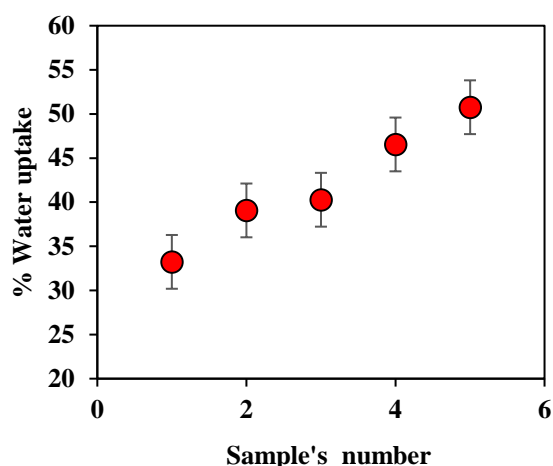


Fig. 5. water uptake of prepared CEMs.

3.1.3. Metal ion removal

The obtained data for Cu^{2+} and Cr^{2+} removal rates of prepared membranes are illustrated in Table 2. The improved behaviour for modified membranes can be attributed to higher water content and better hydrophilicity characteristic of PDA resulting from the presence of $-\text{NH}$ and $-\text{OH}$ groups, more adsorptive sites and also higher porosity of prepared CEMs (created by POSS incorporation into the membrane matrix) that all enhance the removal rate for the heavy metal ion. Also, the electrostatic exclusion of ions produced by the negative charges on the membrane surface can be considered as a justification for higher heavy metal removal [42,43]. Furthermore, it should be mentioned that with more increase in POSS loading ratio up to 0.3 wt% in membrane casting solution, the CEMs samples removal capacity of Cu^{2+} and Cr^{2+} experiences a decreasing trend as it is clear in Table 2. This certain type of behaviour can be related to the agglomeration of the nanoparticles which may lead to lower porosity and also lower adsorption sites [44, 45]. Moreover, higher valence ions represent more repulsion from the membrane surface. The ion removal increases by increasing the valence of co-ion. Since the heavy metal removal improves with an increase in hydrated radius and charge of anions, Generally, a high hydrated radius and lower ionic radius lead to lower diffusion of ions into the nanofibers and membrane surface. As a matter of fact, the ion removal capacity improves with an increase in the valence of co-ion and hydrated radius because of more repulsion of ions with higher valence. Also, a high hydrated radius alongside with lower ionic radius leads to lower diffusion of ions into the nanoparticles and membrane surface. Therefore, Cr^{2+} with a higher hydrated radius and lower ionic radius than Cu^{2+} has displayed higher removal capacity than Cu^{2+} which can be caused by the steric hindrance effects and the ions tough pass across nanoparticles [42, 46].

Table 2. The Cu^{2+} and Cr^{2+} removal rate for prepared membranes

Membrane (M_x)	Membrane sample	Cu^{2+} removal rate	Cr^{2+} removal rate
M_1	PVC-CEM	17.04	27.46
M_2	PVC- PDA-DLCEM	23.43	30.82
M_3	PVC – PDA – POSS – DLCEM ₁	25.09	28.29
M_4	PVC – PDA – POSS – DLCEM ₂	14.61	11.83
M_5	PVC – PDA – POSS – DLCEM ₃	16.98	23.71

3.1.4. Desalination measurement

3.1.4.1. Permeability and flux

Changing procedures of flux and permeability for prepared CEMs are displayed in Fig. 6. Membrane surface modification with PDA may enhance both ionic permeability and flux which can be attributed to the hydrophilicity properties of PDA and controlled interspaces between accumulated PDA and nano aggregates [31]. On the other hand, a suitable amount of water uptake, and also the ionic pathways formation in the prepared membrane structure may have resulted in both permeability and flux enhancement due to an increase in POSS loading ratio in the casting solution up to 0.1 wt%. However, with further increase in nanoparticles concentration from 0.1 to 0.7 wt%, the ionic permeability and flux generally began a decreasing manner. This particular type of action may be regarded as narrow channel formation which can control ions passing through the membrane matrix and exactly for the studied DLCEMs can restrict the ion transportation as it is clear in figure 6. Also, nanoparticle agglomeration at some points with more concentration of POSS in the casting solution which helps to decrease membrane charge density, can be considered as a justification for this decreasing behaviour [47].

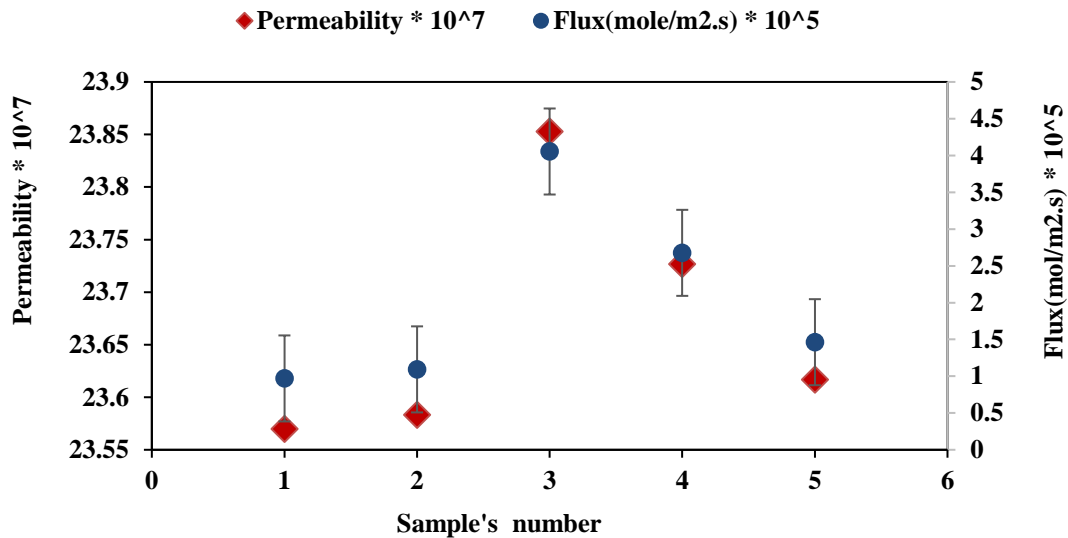


Fig. 6. Sodium permeability and flux for prepared CEMs.

3.1.4.2. The permselectivity

The perm-selectivity of the prepared membranes is indicated in Table 3. It can be concluded that the results totally represented an increasing or constant procedure except for M_4 . This improvement can be recognized more clearly by utilizing PDA as a surface modifier and also at higher concentrations of POSS nanoparticles up to 0.7 wt%. This is attributed to the adsorption properties of PDA due to the presence of $-NH$ and $-OH$ groups and more adsorptive sites of nanoparticles which cause to increase in surface charge density and membrane potential [47]. On the other hand, the pore filling in the prepared CEMs restricts the channels used to pass the ions and creates a compact membrane structure, with improved Donnan exclusion. Ultimately the controlling procedure of the ionic agent groups and resin particles can overcome ion passing which may cause increases in transport number and permselectivity. It should be noticed that the nearly considerably lower amount of transport number and permselectivity for M_4 compared to other prepared CEMs can be justified with water content enhancement which may decrease the transport number and permselectivity. In such similar situations, higher amounts of water content may facilitate ion passing through the channels [29].

Table 3. The permselectivity for the prepared membranes

Membrane Sample (M_x)	Permselectivity
M_1	$>94 \pm 7$
M_2	$>89 \pm 6$
M_3	$>88 \pm 5$
M_4	$>80 \pm 8$
M_5	$>83 \pm 7$

3.1.5. Electrical resistance (ER)

Table 4 indicates the areal electrical resistance of the studied CEMs samples. As it is significantly obvious in the figure, membrane surface modification with PDA has to increase in the areal electrical resistance. Incorporation of POSS in to membrane casting solution has been resulted in ER reduction (M_3). In this condition, possibility of ion transportation may increase and because of that membrane electrical resistance may decrease. With more increase in POSS nanoparticles concentration in the membrane structure up to 0.7 wt%, membrane electrical resistance increases clearly in comparison with unmodified membrane sample which can be regarded as restriction of the ions transportation through the membrane matrix. It can be concluded that voids may be surrounded more by nanoparticles and as a result, ionic pathways decrease [47]. Therefore in a similar situation, ER increases with more increase in nanoparticles concentration in the modifier layer.

Table 4. The real electrical resistance of prepared CEMs: unmodified and modified membranes

Membrane Sample (M_x)	Resistance ($\Omega.cm^2$)
M_1	17.78±3.5
M_2	23.45±4.1
M_3	19.14±3.6
M_4	20.20±2.8
M_5	21.89±3.1

4. Conclusion

It was found that the surface hydrophilicity of the prepared CEMs was increased in the appearance of PDA alongside with incorporation of POSS nanoparticles. Novel DLCEMs can represent higher sodium flux in comparison with unmodified membrane. Also, modified membranes showed appropriate water content, higher permeability and flux and more reasonable permselectivity. In some cases, surface modified membrane with PDA and incorporation of POSS nanoparticle additives can improve the removal ability of heavy metal ion from water. In general, PVC-PDA-DLCEMs in A lower loading ratios of POSS nanoparticles are more functional in desalination and heavy metal removal.

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