

A Facile Method for Dye and Heavy Metal Elimination by pH Sensitive Acid Activated Montmorillonite/Polyethersulfone Nanocomposite Membrane

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Abstract Modified clay/polyethersulfone (PES) mixed matrix membranes (MMMs) were prepared by acid activated montmorillonite (AA-MMT) with different concentrations and used to eliminate dyes and remove heavy metals from aqueous solution. The morphology and physicochemical properties of prepared clay nanoparticles and MMMs were characterized using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, Brunauer-Emmett-Teller (BET) analysis, atomic force microscopy (AFM), contact angle measurement and fouling studies. The filtration study showed that removal of dyes and heavy metals was strongly dependent on pH so that dyes with positive and negative charges showed different separation efficiency in acidic and alkaline conditions. The modified membranes possessed better heavy metal removal in acidic and alkaline pHs. When the rejection of heavy metals was measured in an alkaline environment, it was observed that the rejection had a great increase compared to the neutral values for Zn^{2+} and Ni^{2+} ions, while rejection of Cu^{2+} and Cd^{2+} did not undergo significant changes. So it can be concluded that modified membranes show good selectivity for elimination of Zn^{2+} and Ni^{2+} ions with respect to other cations.

Keywords Nanocomposite membranes; Acid activated montmorillonite; Heavy metal/dye elimination

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INTRODUCTION

In recent years, due to a variety of contaminants that may enter to the environment, great efforts have been focused on removing these pollutants. Pollution of water sources owing to human activities often causes entry of various toxic compounds such as organic compounds, dyes, heavy metals, pesticides *etc.* into water. These compounds are usually water soluble and separation processes have always been faced with complexity^[1]. One of the ways that used in environmental protection, medicine application and especially in water purification is based on membrane processes which are mainly due to lower cost and treatment facilities^[2–4].

Some important areas such as drinking water treatment, wastewater dealing, brackish and seawater desalination are highly dependent on membrane technology. Application of polymeric membranes for water treatment is still limited because of a number of problems like the trade-off relationship between permeability and retention and low fouling resistance^[5]. Among the developed polymer-based membranes, polyethersulfone (PES) has good characteristics of film forming property, chemical and mechanical resistance and miscibility with hydrophilic additives, which made it an

appropriate choice for many membrane-based applications^[6]. However, the intrinsic hydrophobicity causes fouling phenomenon under membrane separation circumstances^[7].

Nanocomposite membranes with mixed matrix are a new category of membranes (mixed matrix membranes, MMMs) which are fabricated by mixing polymeric materials with nanoparticles. These nanocomposites are considered as promising materials to meet the aforementioned challenges^[8,9]. The advanced mixed matrix nanocomposite membranes can have some developed structural and physicochemical properties such as porosity, hydrophilicity, charge density, thermal and mechanical stability and showing inimitable functionalities^[10]. Inorganic nanomaterials like halloysite nanotubes (HNTs), carbon nanotubes, Al_2O_3 and graphene derivatives have been used for the preparation of MMMs which are utilized in various fields^[11,12].

As a promising future of nanostructured material, clay has attracted much attention as an additive to enhance the properties of polymer membranes^[13]. High surface area and relatively low cost of clay particles are the main advantages for utilizing these nanofillers in polymer matrices to enhance the physicochemical properties of fabricated nanocomposites^[14]. Na-MMT is widely used as a nanofiller in the fabrication of polymer nanocomposites. Montmorillonite structure contains phyllosilicate groups that have an octahedral sheet located between two tetrahedral sheets which form a plate-shaped

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structure and its average layer thickness is about 1 nm.

However, clay minerals have limited dispersion due to their strong tendency to aggregate which can lead to a decline in permeability and antifouling performances of membranes. The performance of membranes can be enhanced by modification of clay derivatives. Moreover, interaction behavior between membrane and foulant can be affected by functionalization, which introduces many functional groups and surface charge on MMT sheets and membranes. Clay nanostructures can be dispersed in three possible forms in polymer matrices: the phase-separated, intercalated and exfoliated forms. Intercalation can be defined as the entrance of molecular guests into the finite space between the clay interlayers. Cationic surfactants or polymer chains are some examples of guest compounds that can interlayer the intercalated structure by their molecular layers. When guest molecules enter into the clay, they consequently weaken layer interaction and the clay plates become expanded^[15].

Functionalization of clays with acid treatment causes disaggregation, leaching of the mineral impurities and the dissolution of the external layers. Also, the H^+ is replaced by some exchangeable cations such as Al^{3+} and Mg^{2+} that are adsorbed on the clay surface, leading to an increase in both surface area and pore diameter^[16]. The surface areas of acid modified clay particles increase dramatically due to the decomposition of lamellar structure of MMT^[17]. During decomposition, octahedral aluminum ions are released from the clay structure, causing the formation of additional $Al-OH$ and $Si-OH$ hanging bonds which do not have a significant effect on the original structure of clay^[18]. Due to the presence of hydroxyl groups, these activated clay minerals could be applied for adsorption of some environmentally hazardous contaminants such as $Pb(II)$, $Ni(II)$, $Cu(II)$ ions^[19]. Clay minerals activated with acid could also be used to remove printing and dyeing wastes in wastewater treatment^[20].

In this paper, the fabrication of novel membrane nanocomposite by incorporating acid activated clay (AA-MMT) is reported. To the best of our knowledge, AA-MMT has not been used to fabricate nanocomposite membranes. The synthesized AA-clay nanomaterial was blended in the PES matrix membrane by phase inversion method. The existence of hydrophilic moiety on clay nanoparticle surface can enhance surface hydrophilicity, surface charge properties and as a consequence, membrane antifouling can be improved. The structural properties of the membranes were investigated by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) analysis, and water contact angle test. The impact of AA-MMT content on membrane morphology, hydrophilicity, flux and antifouling performance was also studied. Bovine serum albumin (BSA) was used to analyze the fouling resistance of the membranes. The salt rejection, heavy metal and dye removal of membranes were also evaluated.

EXPERIMENTAL

Materials and Reagents

The montmorillonite K10 clay (MMT) with surface area of $200\text{ m}^2/\text{g}$ used here was purchased from Aldrich (cat. 281522). Polyethersulfone (PES, $M_w = 6.0 \times 10^4$) was supplied by

BASF. Poly(ethylene glycol) (PEG) was prepared by Merck. Bovine serum albumin (BSA, $M_w = 6.7 \times 10^4$) was purchased from Sigma-Aldrich. Sodium chloride, sodium sulfate and magnesium chloride were purchased from Merck. Phosphoric acid was also purchased from Merck.

Synthesis of AA-MMT

First 0.5 g of MMT was refluxed in a mixture of 5 g of H_3PO_4 and 5 mL of toluene for 5 h. Then the product was filtered and dried in an oven at $100\text{--}120^\circ\text{C}$.

Preparation of Membranes

Membranes were prepared by phase inversion method using PES and PEG as polymer and pore forming agent materials, *N*-methylpyrrolidone (NMP) as solvent, AA-MMT as additives, and distilled water as nonsolvent coagulation bath. First, modified MMT (1 wt%, 3 wt%, 5 wt% and 7 wt% based on the weight of PES) was added into NMP solvent (0.5 g). The mixture was then added into the prepared solution of PES and PEG in NMP solvent (Table 1). Casting mixture which contained amounts of AA-MMT and aforementioned components was then stirred for at least 24 h at 60°C . The resultant mixture was casted with $250\text{ }\mu\text{m}$ thickness using a knife blade on a clean glass plate. Then, the casted film on glass plate was immersed into a water bath slowly at 25°C . Finally, the prepared membranes were washed with distilled water repeatedly and stored in distilled water prior to use.

Table 1 Casting mixture compositions in preparation of PES/AA-MMT membranes

Entry	Casting mixture			
	Modified-clay content (wt%)	PES content (g)	PEG content (g)	NMP content (g)
1	0	2	1	7.00
2	1	2	1	6.98
3	3	2	1	6.94
4	5	2	1	6.90
5	7	2	1	6.86

Characterization

To characterize the surface composition of the membranes (ATR-FTIR) spectroscopy was used (Bruker IFS-66/S FTIR). Field emission scanning electron microscopy (FE-SEM) was used to study the cross-section and surface of membranes (Hitachi (S4160)). In order to do this, the membranes were cut into small pieces, and then these pieces were immersed in liquid nitrogen for 10–15 s to freeze them. The frozen membranes were broken to numerous parts and kept in air for drying. The dried samples were sputtered with gold to make them conductive electrically. The UV-Visible spectra of different solutions were monitored on a UV-Vis spectrophotometer (CARRY100 Bio 5). The energy-dispersive X-ray (EDX) spectra of MMT and AA-MMT were recorded with TSCAN Electron Microscope operating at 200 kV using copper target ($k = 1.5406\text{ }\text{\AA}$). Atomic force microscopy (AFM) study was carried out by FemtoScan, Russia. The heavy metal concentrations were determined by atomic absorption spectrophotometer with a hollow cathode lamp using an air-acetylene flame (Shimadzu AA-670). Brunauer-Emmett-Teller (BET) analysis was used to survey pore diameter, surface area and pore volume for prepared membranes by

Belsorp Mini instrument. XRD analysis was carried out using X'Pert PRO MPD PANalytical Complan instrument.

Membrane Performance Evaluation

Pure water flux (PWF) and hydraulic resistance

A self-fabricated lab scale filtration unit was made to measure the pure water flux of all the prepared membranes. The membranes were maintained in water for 24 h before carrying out the experiment. The circular membrane sample of 3.6 cm in diameter was placed inside the sample holder. Then the pure water flux was measured at 0.75 and 0.9 MPa respectively by collecting the filtrated water. For each membrane, average values obtained from three examinations were reported. The pure water flux was calculated using the following equation:

$$J_w = \frac{Q}{A\Delta t}$$

where pure water flux (J_w) is expressed in unit $\text{kg}/(\text{m}^2\cdot\text{h})$ and Q is the quantity of water collected over the initial 5 min of time (Δt) using a membrane area of A (m^2).

$$J_w = \frac{\Delta P}{R_m}$$

Membrane hydraulic resistance (R_m) was evaluated by measuring pure water flux at various transmembrane pressures such as 0.5, 0.7 and 0.9 MPa after compaction. The resistance of the membrane was evaluated from the slope of the transmembrane pressure difference (ΔP) versus water flux (J_w) using the following equation.

Salt, heavy metal and dye rejection

Rejection percentage of salt, heavy metal or dye was calculated using the following equation:

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100$$

where c_p and c_f are the concentrations (salt, heavy metal or dye) in permeate and the feed, respectively. The concentration of salts in solution was measured by conductometry. Three salts including NaCl, MgSO_4 and Na_2SO_4 were used (salt concentration in the feed was 0.01 mol/L and the applying pressure was 0.5 MPa). Dye rejection tests were performed by methylene blue (MB) and methyl orange (MO) solutions with initial concentration of 0.0005 mol/L. The concentration of dye in permeate was determined by UV spectrophotometer. The heavy metal rejection was determined using aqueous solution of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (1000 ppm). The concentration of ions in permeate was determined by atomic absorption spectrometry method.

To investigate the antifouling properties of membranes, a bovine serum albumin (BSA) solution in phosphate buffer solution (PBS, 100 ppm, 50 mmol/L, pH = 7) was used. All membranes were compacted for 20 min at 0.9 MPa pressure. Then the pressure was reduced to 0.5 MPa and pure water flux of the membrane, J_{w1} ($\text{kg}/(\text{m}^2\cdot\text{h})$), was determined over a period of 1 min. After completion of the pure water flux measurement, BSA was poured inside the permeation cell to be filtered through the membrane for 30 min. Then the

membrane was flushed with pure water for 15 min and pure water flux J_{w2} ($\text{kg}/(\text{m}^2\cdot\text{h})$) was measured again. For each membrane, the pure water flux (J_{w1}) and flux during BSA rejection (J_{w2}) were measured twice. Finally, for determination of antifouling property flux recovery ratio (FRR) was evaluated as follow:

$$\text{FRR}(\%) = \frac{J_{w2}}{J_{w1}} \times 100$$

The maximum absorbance of BSA was observed at 280 nm in UV-spectrophotometry and the concentration of this compound in feed and permeate solution was measured at this wavelength. The samples were kept for 10 min in a Bradford reagent prior to measuring their concentrations and the percent of BSA rejection was calculated by the following equation:

$$\text{SR}(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100$$

where c_p (mg/mL) and c_f (mg/mL) are the concentrations of BSA in permeate and the feed, respectively.

Finally, in order to examine biofouling resistance of the membranes, the modified and bare membrane samples were subjected to the static protein absorption test. For this purpose samples were first ultrasonically treated (100 W, 40 kHz) in phosphate buffer solution (PBS, pH = 7.0, 0.1 mol/L) for 5 min, and then incubated in BSA phosphate buffer solution (1.0 mg/mL) at 25 °C for 24 h. Afterwards, samples were rinsed three times using PBS, and then treated in PBS under ultrasonic irradiation for 2 min to remove the adsorbed protein from the surface. The absorbed protein amounts by the membranes were determined by UV spectroscopy.

RESULTS AND DISCUSSION

Characterization of Modified Clay

FTIR and EDX analysis

The Fourier transform infrared (FTIR) spectroscopy was used to characterize the AA-MMT functional groups. Figure 1 shows the FTIR spectra of Na-MMT and AA-MMT. The characteristic bands of MMT observed at 915, 840, and 524 cm^{-1} were attributed to Al—O—Al, Al—OH—Mg and Al—OH—O—Si vibrations, respectively. For AA-MMT sample, a weak peak at 2971 cm^{-1} appeared which was contributed by P—OH group and it indicated AA-MMT formation.

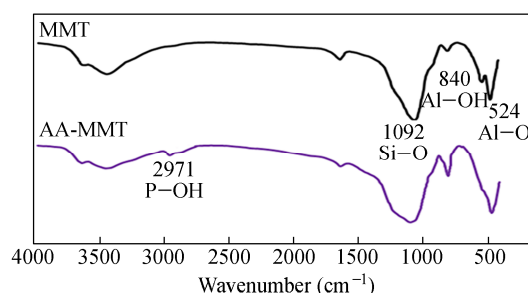


Fig. 1 FTIR spectra of MMT and AA-MMT

EDX analysis was used for further confirmation (Fig. 2). In accordance with the results of FTIR, EDX results showed clearly that phosphorus atom was present on the surface of the acid activated montmorillonite while for pure MMT peaks appeared were related to O, Na, Al and Si atoms.

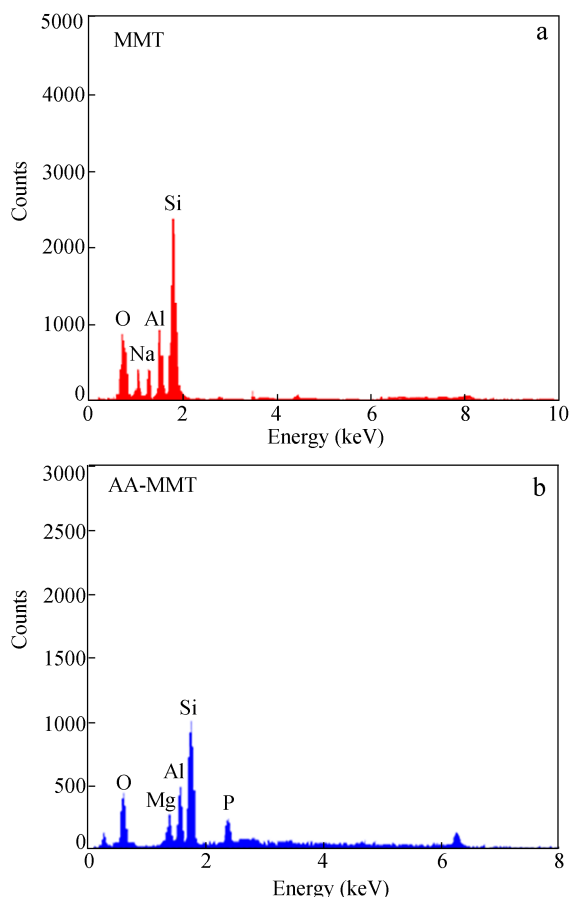


Fig. 2 EDX analysis of (a) MMT and (b) AA-MMT

XRD analysis

X-ray diffraction patterns of the raw Na-MMT, before and after treatment by phosphoric acid are shown in Fig. 3. The peaks (001, 003 and 020) indexed in the X-ray diffraction patterns belong to Na-MMT, according to the literature [16]. Although there was no significant difference between the XRD pattern of Na-MMT and that of AA-MMT, the decrease in intensity for basal (001) peaks indicates the alteration of the layered structure with acid activation. The other clay related peaks showed little shift of 2θ values to 19.84° (003), 20.90° (020) and conservation of two-dimensional lattice was proved by other peaks^[21].

On the other hand, d -spacing of clay layers was obtained by Bragg's law. According to diffraction peak at $2\theta = 8^\circ$ in XRD pattern graph, d -spacing between layers is about 1.10 nm, whereas after acid treatment this characteristic peak slightly shifted to smaller 2θ ($2\theta = 7^\circ$) which demonstrates an increase in d -spacing amount (1.26 nm). Moreover, the decrease in the peak intensity suggests that crystallinity decreased in montmorillonite layers which might be related to the replacement of acid molecules between the layers.

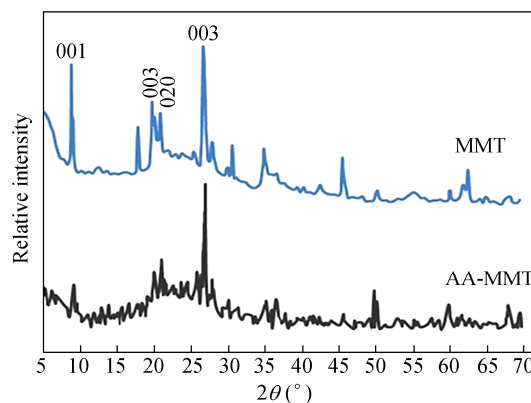


Fig. 3 X-ray diffraction patterns of the raw MMT before and after activation with phosphoric acid

Membrane Characterization and Performance

All the membranes were prepared by phase inversion method using PES as the polymer, PEG as pore forming agent, and AA-MMTs (1 wt%, 3 wt%, 5 wt% and 7 wt%) as additives. Due to the presence of functional groups, AA-MMTs can efficiently be incorporated in polymer casting solution and these are expected to provide adequate functional groups and surface hydrophilicity to the membranes. Also, the flat MMT sheets might be helpful to the high rejection of solute molecules. To evaluate membrane performance, the effect of additive amounts on membrane morphology, hydrophilicity, flux, antifouling, salt rejection and dye and heavy metal rejection performance was investigated.

Membrane Morphology

The cross-sectional and surface SEM images of MMMs with different AA-MMT contents are presented in Fig. 4. There was not much difference in the surface of the prepared membranes and only small particles could be observed on the surface of modified membranes which may be related to AA-MMT, but as shown in Fig. 4, the prepared nanocomposite membranes had different macro-void microstructure from neat PES membrane. The AA-MMT concentration also influenced the morphologies of the nanocomposite membranes. More sponge-like macro-voids were observed in the membranes with a higher AA-MMT amount. As a result of the presence of highly hydrophilic groups on AA-MMT, rapid exchange of solvent with non-solvent generally occurs during the phase inversion process^[22]. AA-MMT is solid and hydrophilic. Therefore, by increasing additive concentration, thermodynamic instability in the casting solution and the inflow rate of water increase which leads to expansion of macro-voids. However, clay can act as a surfactant and decreases the water and membrane dope interface tension which affects the exchange rate of solvent and non-solvent and precipitation kinetics during phase inversion and alters the membrane morphology, consequently^[23]. In addition, modified-clay absorbs more water inside the membrane during phase inversion which increases membrane porosity. On the other hand, as can be seen in the cross-sectional images, no accumulation of AA-MMT particles was observed, which indicated the proper dispersion of nanoparticles in the membrane matrix.

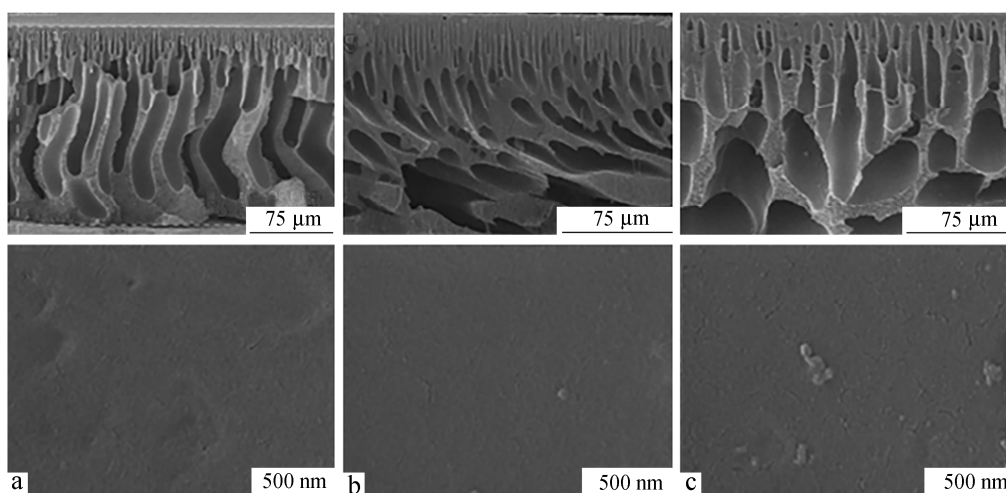


Fig. 4 Cross-section SEM images of the MMT/PES membranes: (a) neat PES, (b) AA-MMT-3%, (c) AA-MMT-7%

Atomic Force Microscopic Analysis of the Modified Membranes

The surface roughness of polysulfone membranes was characterized by AFM analysis. Figure 5 shows the results of AFM analysis, and Table 2 reveals the root mean square roughness (R_q) and roughness average (R_a) values. Results showed that the average roughness of membrane increased with additive loading. It can be justified by migration of AA-MMT toward the surface and so more roughness was created.

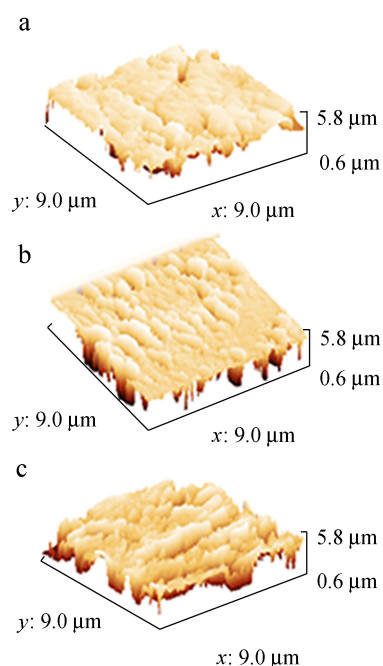


Fig. 5 AFM images of (a) neat PES, (b) AA-MMT-3% and (c) AA-MMT-7% membranes

Table 2 Roughness values for membranes

Membrane	Neat PES	AA-MMT-3%	AA-MMT-7%
R_a (μm)	0.077	0.284	0.312
R_q (μm)	0.106	0.386	0.454

Surface Area to Volume Ratio

Table 3 lists the BET surface area, pore diameter and pore volume of the AA-MMT modified membranes. From these results, as expected, a higher surface area for the mixed matrix membrane was obtained; in particular, the BET surface area was equal to 48.69 and 49.52 kg/m^2 for the PES/AA-MMT-3% and PES/AA-MMT-7%, respectively. The incorporation of AA-MMT in the polymer matrix modifies the pore volume of the polymeric membrane too. The results indicated that changing additive percentage from 3% to 7% had a minor effect on the pore size distribution of the membranes and a slight increase could be observed by increasing loading percentage.

Table 3 BET surface area to volume ratio

Sample	BET specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
PES	31.76	0.03	5.34
PES/AA-MMT-3%	48.69	0.06	5.55
PES/AA-MMT-7%	49.52	0.07	5.76

Pure Water Flux of the Membranes

In Fig. 6, the permeate fluxes of prepared membranes under different trans-membrane pressures (0.5, 0.7 and 1.0 MPa) are represented. As expected, the permeate fluxes increased obviously by increasing the applied pressure for all the membranes. The effect of additive concentration on the permeability of MMMs is also shown in Fig. 6. The water flux

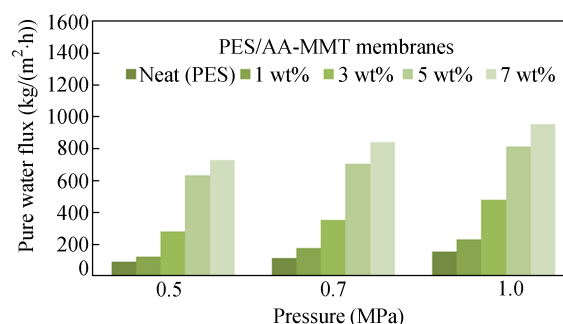


Fig. 6 Pure water flux of neat PES and modified membranes

for nanocomposite membranes was remarkably higher than that for unmodified PES membrane. Modified clay increases the surface hydrophilicity of membranes and also creates larger and more sponge-like macro-voids in the resultant membrane. Improvement in the pure water flux of hybrid membranes is also due to (i) the high water holding capacity of the membrane and the rapid transport of water from one side to another and (ii) the interfacial gaps between layered additive and the matrix for some extra water channels^[22]. On the other hand, by increasing AA-MMT concentration the surface roughness increased due to agglomeration. In general, rough surface area increases pure water flux as a result of increased effective surface area^[24].

Hydraulic Resistance Studies

Hydraulic resistance reflects the tolerance of MMMs towards hydraulic pressure. The lower hydraulic resistance value means better membrane performance under high pressure. As shown in Fig. 7 the hydraulic resistance of all mixed-matrix membranes was lower than that of neat PES. Also R_m decreased by increasing AA-MMT concentration, because a higher percentage of additive improved membrane mechanical strength. During compression, polymeric chains are expected to re-organize which alternates the membrane structure stability^[25]. This is more considerable at lower additive loading. For high AA-MMT additive contents, the chain movements decreased which resisted pore deformation of the membrane and decreased R_m .

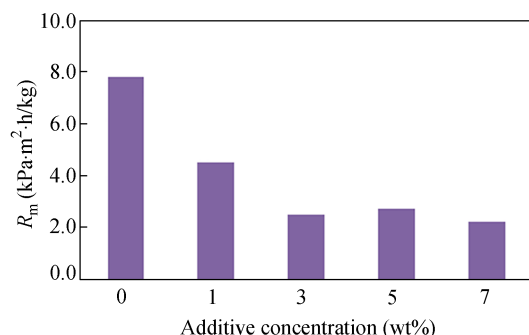


Fig. 7 Hydraulic resistance of prepared membranes

Hydrophilic/Hydrophobic Nature of the Membranes

Contact angle reflects the hydrophilic/hydrophobic nature of membrane surface and strongly influences the absorption and transmission of permeate molecules. Contact angle values of AA-MMT/PES membranes are diagrammed in Fig. 8. Compared to the contact angle of neat PES membranes, hybrid membranes displayed lower contact angles due to the presence of hydrophilic functional groups of AA-MMT. The contact angle values reduced significantly from 72.4° to 50.0° when increasing AA-MMT additive percentage from 1.0 wt% to 7.0 wt%. This may be due to the accumulation of the hydrophilic clay nano-sheets on the membrane surface in high amounts of the nanoplates^[26]. The AA-MMT additive can also increase the roughness of membrane surface which enhances the directional force for droplet spreading through multiple gradients effect^[27].

To study the effect of additive content on fouling problem in prepared membranes, the dynamic fouling analysis (flux

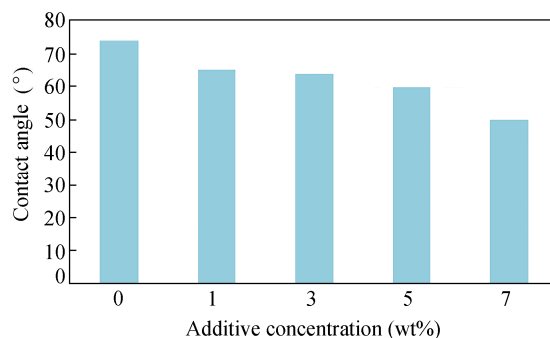


Fig. 8 Water contact angle of the prepared membranes

recovery ratio, FRR) and static fouling (BSA adsorption) were evaluated according to the previously mentioned equation. To this end, 1000 ppm solution of BSA protein was used to accomplish static fouling experiments in pH of 7.4 at a 24 h contact time.

Figure 9 shows the results of BSA adsorption on the membrane surface. As shown, the neat PES membrane had a higher amount of BSA absorption than those of the mixed membranes. Furthermore, increasing AA-MMT percentage from 1 wt% to 3 wt% lowered BSA absorption since more additive concentration can increase the hydrophilicity of the membrane as shown by contact angle studies. The tight hydration layer on the nanocomposite membranes caused a considerable reduction in the adsorbed BSA amount. But further increasing created a rougher surface which in turn led to higher BSA adsorption. The results of FRR or dynamic fouling for the membrane prepared with and without AA-MMT are also shown in Fig. 9. Better flux recovery in modified membranes demonstrated that protein fouling on the membrane was more reversible because of higher hydrophilicity of modified membrane. The highest bio-fouling resistance evaluated by FRR was observed for

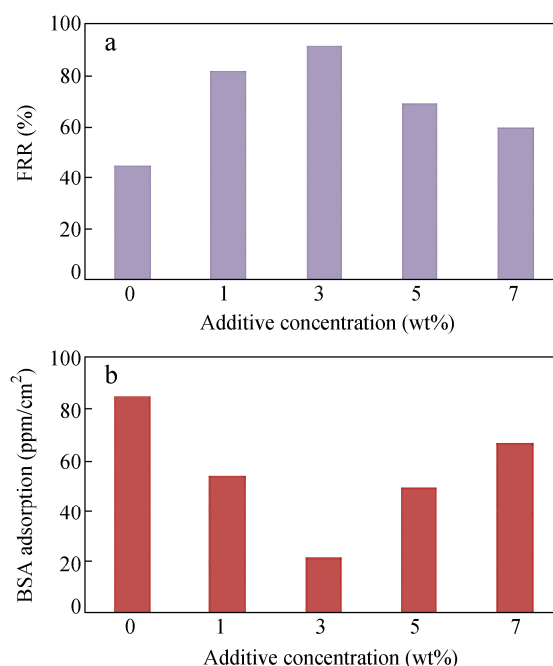


Fig. 9 (a) Water flux recovery ratio (FRR) and (b) BSA adsorption membranes with the different concentrations of additive

AA-MMT-3% sample. Increasing additive percentage increases surface hydrophilicity and meanwhile causes higher surface roughness for nanocomposite membranes. Therefore, increasing additive percentage (higher than 3%) created a rougher surface which resulted in declined FRR.

Salt Rejection

Prepared nanocomposite membrane's salt rejection performance is shown in Fig. 10. The rejection performance of all modified membranes was better than that of neat PES membrane. The salt rejection for all samples was in the order of $\text{NaCl} < \text{Na}_2\text{SO}_4 < \text{MgSO}_4$. Efficient factors on a membrane's salt rejection are: size exclusion (steric effects), Donnan exclusion (electrical repulsion), concentration polarization and mobility which are determined by diffusion coefficient and effective size of ions^[28]. Higher rejection obtained with MgSO_4 compared to NaCl and Na_2SO_4 was ascribed to steric effects^[29, 30]. Increasing modified clay additive concentration from 1 wt% to 3 wt% improved salt rejection. In particular, this increase was accompanied by an important enhancement of water permeability as mentioned previously. The combination of higher porosity and a reduction in the effective pore size of the membrane are the reasons for improvement in permeability and rejection^[31]. Other reports also suggested that both water flux and rejection were improved by additive embedding^[32].

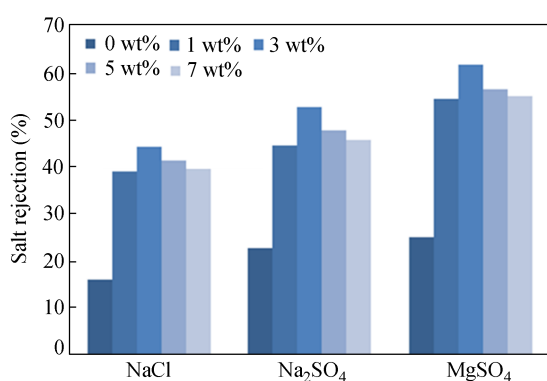


Fig. 10 Salt rejection performance of the prepared membranes with different additive concentrations

Dye Removal and the Effect of Feed Solution pH

The effect of pH on the pure water flux and salt rejection was studied for prepared membranes. The obtained results showed that the performance of membranes improved slightly may be due to the increase of membrane's hydrophilicity which caused more diffusion of water molecules as well as better interactions with ions.

Furthermore, it was already reported that pH variation influenced the ionic dye removal^[33]. Here the performance tests were conducted for investigation of pH effect on the removal of MB and MO which possessed positive and negative charges, respectively. Three pH values of acidic (pH = 3.5), neutral (pH = 7.0) and basic (pH = 10) were selected for comparing the fabricated membrane's performance in the elimination of considered dyes. The results of dye removal are demonstrated in Fig. 11 for PES/AA-MMT series. The prepared membranes showed

better dye removal in the basic pH for MO and acidic pH for MB. However, the nanocomposite membranes exhibited significantly higher dye removal than pure PES. When the nano-clay content was increased, the dye removal percentage also increased in both dyes even in neutral pH. This well exhibits the notable role of nano-clay particles in dye adsorption. The reasons for poor dye removal at neutral pH must be interpreted by electrostatic effects between clay/PES composite and dye molecules.

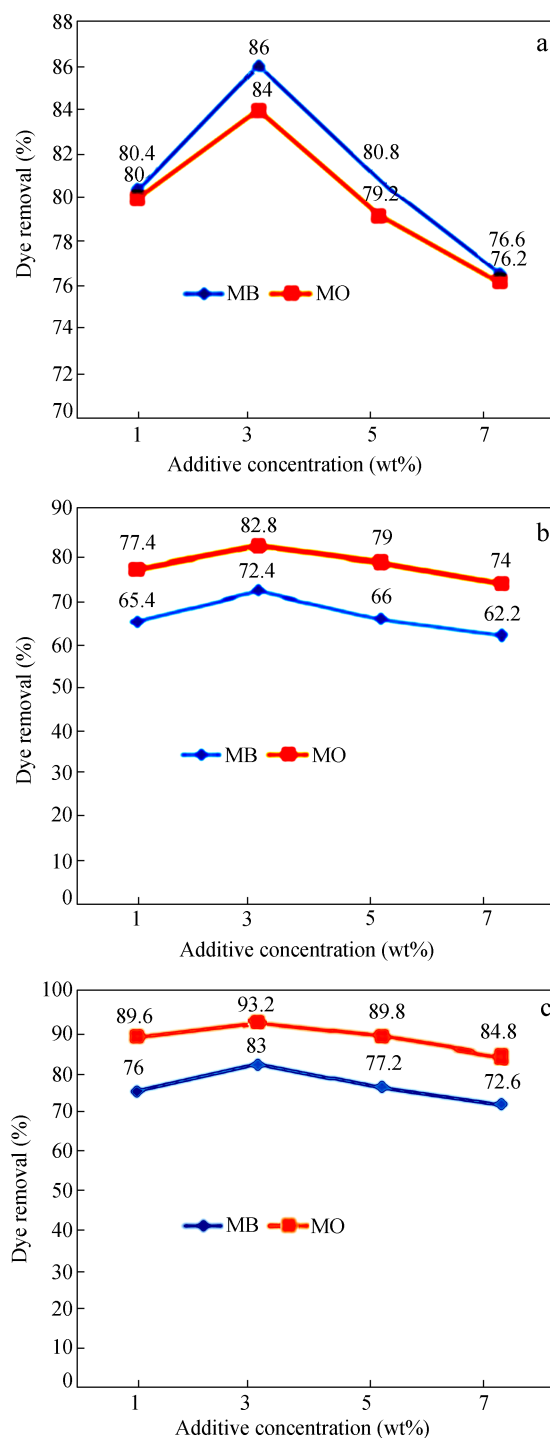


Fig. 11 Effect of feed pH on dye removal of membranes containing AA-MMT: (a) pH = 3.5, (b) pH = 7, (c) pH = 10

Heavy Metal Removal and the Effect of pH

Heavy ion separation with membranes was carried out by size exclusion and electrical interactions between ions in the feed aqueous solution and the membranes. Figure 12 shows the obtained heavy metal rejection values of Cd(II), Cu(II), Ni(II), and Zn(II) ions for AA-MMT modified membranes. In neutral pH (pH = 7), the rejection percentage for heavy metals did not show an ordered trend but it seemed to relatively follow this order: $\text{Cd}^{2+} < \text{Cu}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+}$. This is not proportional to the hydrated ionic radius as Ni^{2+} (4.04 Å) < Cu^{2+} (4.19 Å) < Cd^{2+} (4.26 Å) < Zn^{2+} (4.3 Å). In other words, size exclusion had a trivial effect on the ion rejection and it was controlled mainly by electrostatic interactions (repulsion or attraction). Like salt rejection results, the highest ion removal was observed for mixed matrix membrane containing 3 wt% AA-MMT except for copper ions, for which the membrane with 5 wt% additive showed better

elimination. Some other factors in addition to pore size especially electrostatic interactions are also effective in heavy metal removal, so it can be concluded that a balance between pore size, surface roughness, surface charge and type of interactions is the reason for this trend.

As it can be seen in Fig. 12 in acidic condition (pH = 3.5) heavy metal rejection with the previous trend improved slightly. But by comparing the rejection amounts in neutral and acidic conditions, it can be observed that the rejection of Zn^{2+} and Ni^{2+} were affected mainly by pH and additive percentage in modified membranes. When the rejection of heavy metals was measured in an alkaline environment, it was observed that the rejection had a significant increase compared to the neutral values for Zn^{2+} and Ni^{2+} ions, while rejection of Cu^{2+} and Cd^{2+} did not show significant changes. Thus, it can be concluded that modified membranes with AA-MMT showed partial selectivity for the elimination of Zn^{2+} and Ni^{2+} ions with respect to other cations.

CONCLUSIONS

Acid activated clay was prepared *via* treatment of MMT with phosphoric acid. Mixed matrix nanocomposite membranes were prepared *via* classical phase inversion method by dispersing AA-MMT additive (1 wt%–7 wt%) in the PES casting solution. The SEM analyses showed that the addition of AA-MMT changed the microstructure of the PES membranes. Hydrophilicity, water flux, and antifouling properties were improved by hybrid membranes. Addition of AA-MMT also improved the rejection of salts and removal of dyes more efficiently than those of neat PES membrane. The trade-off between permeability and rejection of PES membranes was reduced by the incorporation of AA-clay. So it can be drawn that these additives could remain in PES membrane for a long period of time. Additionally, the present work provides a facile method for dye and heavy metal elimination by pH sensitive acid activated montmorillonite/polyethersulfone nanocomposite membrane which acts selectively in the separation of some ions.

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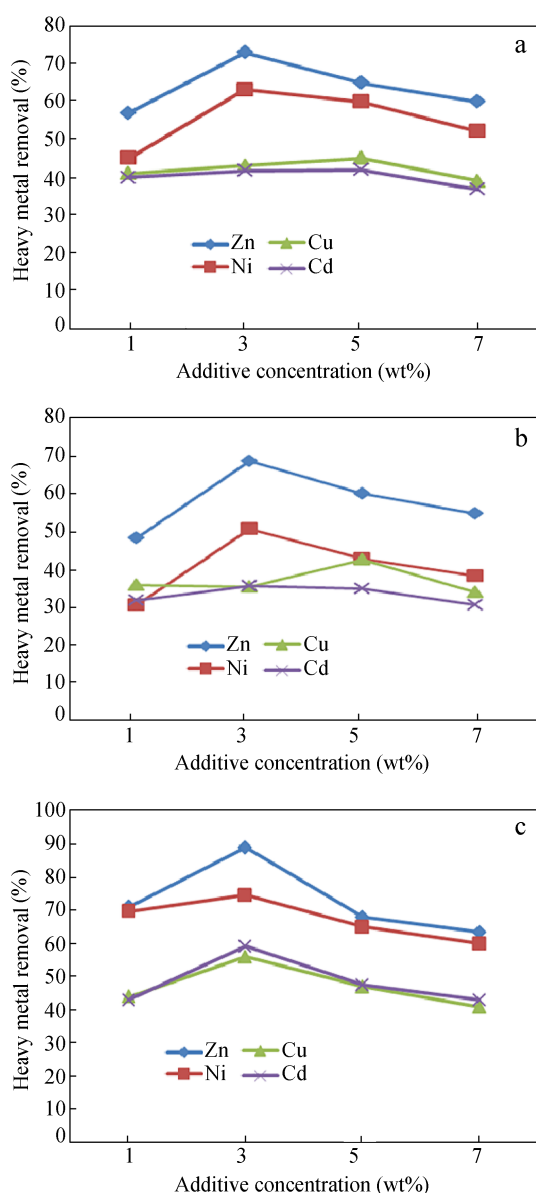


Fig. 12 Separation of heavy metals under different pH conditions: (a) pH = 3.5, (b) pH = 7, (c) pH = 10

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