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Comparing the effect of adding supported conductive polymers and quaternium agent on the physio-chemical properties of polysulfone membranes

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Abstract: In this research, three nanocomposites including HMS and MCM coated by conductive polymers and a quaternized MOF were used as additive of polysulfone membrane to improve physio-chemical properties of the mixed matrix membranes. It was found that the quaternized ammonium agent immobilized on UiO-66-NH_2 increased pure water flux and porosity of the membrane more than polyaniline and polypyrrole coated on MCM-41 and HMS, respectively. It was also observed that the migration of hydrophilic nanocomposites towards the aqueous phase during phase inversion of the casting solution increased the porosity and permeability of the membrane. The results showed that the quaternized MOF exhibited the highest value of the surface potential resulting higher hydrophilicity and permeability of polysulfone membrane and faster diffusion of water molecules.

Keywords: Polysulfone, conductive polymer, Quaternium agent, membrane, nanocomposite

Introduction

Polymer membranes are widely used for water treatment, food industries, pharmaceutical and medical industries due to the simple mechanism of separation, high flexibility, low space for installation and relatively low costs compared to the inorganic membranes [1-3]. Most of them are made by several polymers such as cellulose acetate, polypropylene, Teflon, polyamide, polyeimide, polysulfone and polyethersulfone. Although these polymers demonstrate good properties during manufacture of the membranes, their permeability and selectivity are not satisfactory [4-6]. It can be improved by coating the polymer by a thin film composite (TFC) or adding composite fillers to the membrane structure, called the mixed matrix membranes (MMM's). In fact, the final properties of MMM is strongly dependent on the nature of the adding composite fillers to the membrane structure, called the mixed matrix membranes (MMM's). In fact, the final properties of MMM is strongly dependent on the nature of the interactions between the filler and polymer [7].

Nanocomposite materials have received much attention due to their ability to increase membrane permeability and selectivity [8]. These additives form porous structure, increase membrane hydrophilicity and create a sponge structure in the membrane. Different composite materials base on zeolite, carbon molecular sieve, silica, carbon nanotubes, aluminum oxide, iron oxide and manganese are used to improve the membranes [9, 10]. However, it is interesting to compare their effects on the physical and chemical properties of polysulfone membranes and find a relationship

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*Corresponding author Email: mrtoosi@gmail.com between molecular parameters of the nanocomposite and mechanical properties of the membrane. In this work, three nanocomposites have been synthesized and applied as the additive of polysulfone membrane. The effect of nanocomposite on the membrane permeability and porosity was investigated and explained based on the nature of the surface interactions between the additives and polymer chains.

Results and discussion

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Figure 1 show the porosity of the synthesized membranes. It is observed that the existence of nanocomposite in the membrane structure increases the porosity in polysulfone membranes. It is observed that while the porosity is 55% for the non-blended membrane, the porosity increases to 68, 61, and 71% for the samples blended with 0.1% wt. of MCM@PAN, HMS@PPyr, and MOF@DMDAC, respectively. It is also observed that porosity and PWF increase by the nanocomposite percentage. For example, the porosity of M_1, M_2, and M_3 increases to 71, 73, and 79%, respectively.

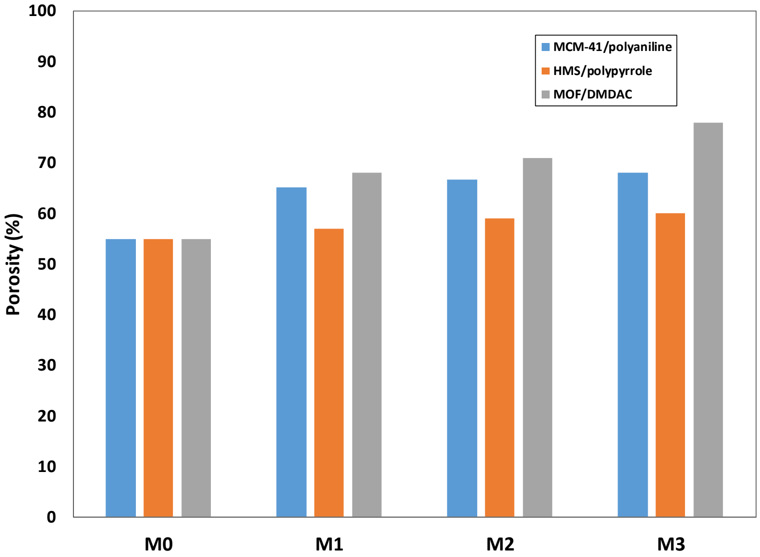

Figure 1: porosity of mixed matrix polysulfone membranes (TMP = 2 bar)

Figure 2 shows that the values of pure water flux (PWF) for the membranes blended with MOF@DMDAC are higher than the other nanocomposites. Values of PWF for these types of MMM are 90, 148, and 261 kg/hm^2), respectively.

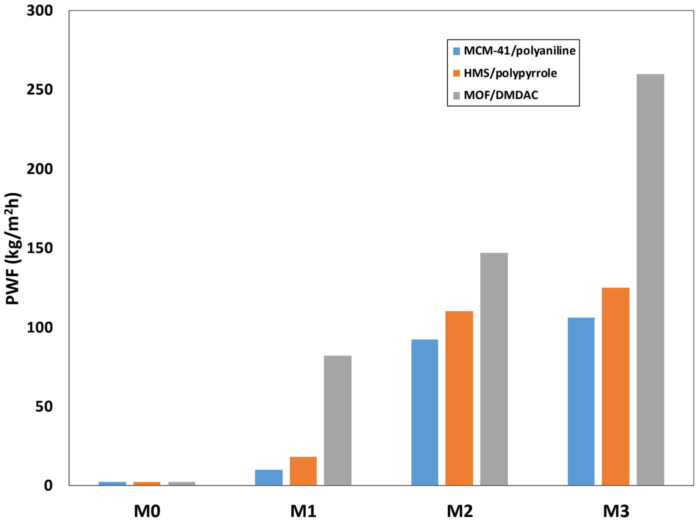

Figure 2: pure water flux (PWF) of mixed matrix polysulfone membranes

Table 1 shows results of contact angle and surface roughness obtained by camera analyzer and AFM micrograph, respectively. It is seen that the nanocomposite increases the hydrophilicity of membrane surface. This factor enhances the rate of diffusion of water molecules through the membrane. In addition, existence of the nanocomposite in the membrane structure increases the roughness parameters including R_a and R_z. It has been found that increase of surface roughness increases the area of the membrane surface resulting faster rate of diffusion of water [11].

Table 1: Contact angle and roughness parameters for polysulfone membranes with different nanocomposite

nanocomposite (1.2%wt.)	CA (^{o})	R_a (nm)	R_z (nm)
MCM-41/PAN	62[a]	25.1[a]	297.7[a]
HMS/PPyr	68	19.7	243.1
UIO-66/DMDAC	60	31.5	338.0

[a] From [12]

Figure 3 shows the results of zeta potential obtained from dynamic light scattering (DLS) measurements. It is seen that the values of zeta potential of MCM@PAN, HMS@PPyr, and MOF@DMDAC at neutral pH are -10.6, -14.5, and 28.8 mV, respectively. It can be concluded that the membrane mixed with MOF@DMDAC exhibits higher surface potential resulting higher hydrophilicity and permeability. Higher surface area and pore volume of 3D channels in MOF in comparison of mesoporous materials provides more active sites to functionalize with quaternium agent [13].

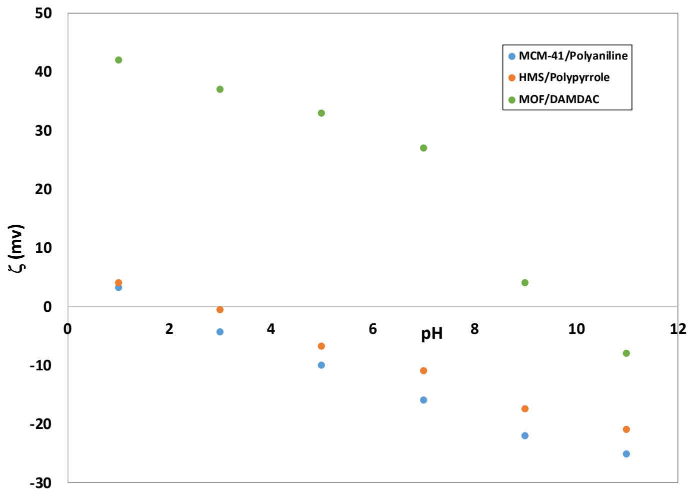

Figure 3: surface zeta potential of the prepared nanocomposites in different pH

Conclusion

Post-synthesized UiO-66-NH_2 and functionalized with quaternium agent exhibited more efficiency for increasing the hydrophilicity, porosity and permeability of the polysulfone membranes. It was observed that zeta potential of quaternized UiO-66-NH_2 nanocomposite showed zeta potential higher than MCM-41 and HMS particles coated by polyaniline and polypyrrole, respectively. Increase of surface potential in nanocomposite particles led to a decrease of thermodynamic stability of casting solution during the phase inversion process. It can be concluded that the rate of diffusion and migration of the particles between the solvent (NMP) and non-solvent (water) phases increases and more porous structure of polysulfone membranes enhance permeability of the water molecules.

Experimental

Materials and methods

Materials used to prepare nanocomposites including tetra ethyl silicate (TEOS) as a silica source, CTAB as template, sulfuric acid, Hydroxy Propyl Cellulose (HPC) as surfactant, 2-Amino benzene dicarboxylic (H_2BDC), zirconium chloride, DMF, N-Methyl-2-pyrrolidone (NMP), potassium iodate, and aniline were purchased from Merck (>99%). Polysulfone (PSF) as the basic polymer was provided from Ultrason® trademark made by BASF.

Synthesis of the nanocomposits

Hydrothermal method was used for the MCM-41 synthesis using a teflon lined autoclave by hydrolysis of TEOS in the presence of ethanol and CTAB. To coat the mesopores with aniline, 100 cc of sulfuric acid (1M), 1.14 g of potassium iodate, and 1 g of HPC were mixed and stirred 15 min. 0.67 g of MCM-41 and 0.67 g of aniline were then added and stirred at room temperature for 5 hours. The sample was centrifuged, dried at 50 ° C for 24 hours, and named as MCM@PAN. HMS was produced using the method described by Pinavaya [14]. Similar to the previous section, the nanocomposite was made using the previous regents and pyrrole instead of aniline, named as HMS@PPyr. Solvothermal method was used to produce Uio-66-NH_2. Post-synthesis of MOF was performed through the Schiff base reaction between amine group of UiO-66-NH_2 and the hydroxyl group in the salicylaldehyde [15]. Finally, preparation of quaternized MOF was followed by the procedure reported in ref. [16]. 5.842 mol of (3-chloropropyl) trimethoxysilane and 3.599 mol of N, N -dimethyl dodecyl amine was mixed at 85 ◦C for 48 h in order to formation of dimethyl dodecyl[3-(trimethoxysilyl)propyl] ammonium chloride (DMDAC) as the quaternary ammonium agent. The mixture was then kept at 100 ◦C for 48 h under reflux condition, filtered and washed by toluene.

Synthesis of the membranes

Phase inversion method was used to prepare mixed matrix membrane by means of the casting solution. Firstly, PSf was dissolved in NMP at 60 ^oC and then stirred 18 h. A certain amount of nanocomposite was dispersed in 10 cc NMP and then added to the polymer solution. After 8 h, casting solution was held in room temperature for 1 day and sonicated for removing the micro-bubbles. Membrane films were provided by means of a home-made film applicator. The membrane films were immersed in a water bath and kept 24 h for the removal of NMP. In this way, three membrane containing 0.3%, 0.6%, and 1.2% of nanocomposite was blended by polysulfone, named as M_1, M_2, and M_3, respectively

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