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RESEARCH ARTICLE

Mixed matrix membranes incorporated with sonication-assisted ZIF-8 nanofillers for hazardous wastewater treatment

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Abstract

Mixed matrix membranes (MMMs) provide a unique pathway to treat hazardous industrial effluents. MMMs containing zeolitic imidazolate framework-8 (ZIF-8) as filler in polydimethoxysilane (PDMS) matrix were synthesized. ZIF-8 was prepared using a modified recipe and characterized by different techniques to evaluate its morphology, thermal stability, surface area, pore volume, and other characteristics. The performance of membranes was evaluated for their application in industrial dye-stuff wastewater treatment and solvent-resistant nanofiltration. The results demonstrated that increase in the percentage of ZIF-8 loading in PDMS led to simultaneous increase in the solvent permeability as well as solute rejection from wastewater. The permeability of MMMs increased up to 32% as compared with neat PDMS membrane. The organic dye rejection was achieved more than 87% with MMMs incorporated with 20% loading of nanofillers. Rejection of MMMs was 22% higher than that of unfilled PDMS membrane due to the effect of reduced polymer swelling and size exclusion of the nanofillers. Membrane swelling tests with toluene and isopropanol demonstrated that nanofiller amount has inverse relation with membrane swelling, which implied that nanofillers were in good interaction with polymer and allowed defect free membranes with higher solute rejections and reduced membrane swelling.

Keywords Hazardous wastewater, mixed matrix membrane · ZIF-8 nanofillers · Solvent-resistant nanofiltration · Membrane swelling

Introduction

Mixed matrix membranes (MMMs) are attractive for industrial wastewater treatment because colloidal and suspended organic compounds can be removed efficiently with high permeance performance. Solvent-resistant nanofiltration (SRNF) process is one of the advancements in the field of MMMs. SRNF membranes are used for the separation of solutes through solvent streams. Small molecules of solutes with molecular weight ranges from 200 to 1000 Da are retained by SRNF membranes while solvent molecules are passed through them (Vandezande et al. 2008). It is a relatively new research area and has gained a lot of interests. Due to the recent research and advancement in the field, SRNF has the opportunity to become a promising alternate to the conventional separation methods for organic solvents and industrial wastewater applications (Cheng et al. 2014). In comparison with conventional separation methods such as distillation, crystallization, and chromatography, SRNF is an energy-efficient process, which not only operates at mild conditions but also is much cleaner process (Basu et al. 2009).

Many polymeric and inorganic materials have been used for the preparation of SRNF membranes (Guillen et al. 2011). Polymeric SRNF membranes are preferred because of commercial availability of a number of polymers, low cost, easy fabrication, and upscaling methods to transform the lab-made membrane to commercial modules (spiral wound, hollow

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fiber etc.). Along with these advantages, few limitations are also experienced: polymeric membranes are less stable thermally and chemically as compared with inorganic membranes. Moreover, polymeric membranes usually swell on exposure to organic solvents, leading to decrease in their separation performance (Hermans et al. 2015). MMMs combine the advantageous properties of both the polymeric and inorganic materials thereby producing synergistic results. In MMMs, different porous molecular materials (fillers for membrane) are dispersed in the polymeric matrix (Penkova et al. 2018). Commonly used fillers for MMMs are zeolites, carbon molecular sieves, carbon nanotubes, chitosan, graphene oxide, silica etc. (Goh et al. 2011; Holder et al. 2017; Selakjani et al. 2018; Sun et al. 2016).

Recently, metal organic frameworks (MOFs) gained significant attentions as nanofillers in MMMs. MOFs actually are porous crystalline material, composed of metal ions and organic ligands (Sabouni et al. 2014). They have high surface area and good thermal stability and show strong interaction with polymer in the matrix (Chae et al. 2004; Eddaoudi et al. 2000; Li et al. 1999) (Chen et al. 2019). MOFs have found their application in a number of different industrial processes. For example, MOFs are used as storage media, carrier materials for drug delivery, and catalysts and adsorbents for different kinds of separation processes (Kumar et al. 2018; Mueller et al. 2006; Toosi et al. 2018; Wen et al. 2018; Wu et al. 2018). MOFs are also being used in membranes for pervaporation separation of organics (Si et al. 2019b), solvents recovery from aqueous solutions through the diffusion process (Si et al. 2019a), purification of drinking water (Sun et al. 2018), water desalination (Zhai et al. 2019), and enhancement of antifouling properties of membranes (Mohammadnezhad et al. 2019). The incorporation of MOFs in MMMs has resulted in remarkable results in solving the limitations of polymers (Yang et al. 2019), removing the hazardous material from wastewater (Gnanasekaran et al. 2019), removal of dyes from industrial effluents (Meng et al. 2019), and gas separation (Cheng et al. 2019; Sánchez-Laínez et al. 2019).

Zeolitic imidazolate frameworks (ZIFs) are the subclass of MOFs composed of transition metals, i.e., Zn or Co, which are tetrahedrally connected to different organic imidazolate linkers. Zeolitic topologies can be achieved by systematic alteration of the linker. Because of their potential applications in separations, ZIFs have attracted the attention of researchers in recent years (Banerjee et al. 2008; Fairen-Jimenez et al. 2011; i Xamena et al. 2008; Phan et al. 2010; Wang et al. 2008). Approximately 105 ZIF materials with different properties and structures have been reported so far (Phan et al. 2010). ZIF-8 was selected as nanofillers in this study because it has abundant active surface sites and large surface area along with high chemical and thermal stability (Wu et al. 2014; Zhang et al. 2013), with numerous applications such as gas storage agent (CO_2, CH_4, etc.), strainer for organic chemicals (benzotriazoles, organic vapors, etc.), and as a catalyst (Jiang et al. 2013; Van de Voorde et al. 2014; Zhang et al. 2014).

In this study, ZIFs were selected as nanofiller material. MMMs were synthesized by the incorporation of ZIF-8 as nanofillers containing zinc ions as coordination centers and linked with 2-methylimidazole and their performance in hazardous wastewater and SRNF applications was evaluated. MMMs were fabricated using P84 polyimide as the support material and polydimethoxysilane (PDMS) as the separating layer. P84 was selected as support material because of its outstanding properties such as heat resistant, mechanical stability, and most important is its chemical resistance as required for industrial applications (Vandezande et al. 2008). Polyimide is widely used in SRNF applications where a wide range of organic solvents are treated (See-Toh et al. 2007; Soroko and Livingston 2009; Toh et al. 2007; Vanherck et al. 2008; Xiao et al. 2005). However, PDMS is an elastomer, which is chemically and thermally stable, but like other elastomers, it also has swelling tendency in organic solvents (Gevers et al. 2005). It is expected that addition of nanofillers in PDMS would enhance the stability as well as filler's interaction with the polymer to improve the cross linking density and reduce the degree of swelling (Kraus 1963). The synthesized ZIF-8 nanofillers and MMMs were characterized by different techniques along with permeation, and rejection performance of Congo red dye compound from isopropanol (IPA) was performed. Swelling tests were also conducted to evaluate the effect of nanofiller addition on membrane stability against different organic solvents (toluene and IPA).

Materials and methods

Reagents

P84 polyimide powder was purchased from HP polymer (Austria). Toluene (99.5%) and methanol (99.8%) were purchased from VWR international (UK). 4-Methyl-2-pentanone (MIBK) (98.5%) and isopropanol (IPA) (99%) were purchased from BDH laboratory supplies (England) and Sigma-Aldrich, respectively. *N*-Methylpyrrolidinone (NMP) (97%) and tetrahydrofuran (THF) (99.5%) were purchased from Merck Schuchardt OHG (Germany). PDMS prepolymer and cross linker (RTV 615 A and B) were acquired from Techsil (UK). 2-Methylimidazole (99%) and zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (98%) were obtained from Acros Organics and Fischer Chemicals respectively.

Synthesis of ZIF-8 nanofiller

ZIF-8 was synthesized according to the reported procedure using a modified approach of subsequent stirring and sonication to obtain nano-sized particles (Cravillon et al. 2009). The

0.5 g (1.68 mmol) zinc nitrate hexahydrate and 2.2 g (26.83 mmol) 2-methylimidazole were added in 100 ml of pure methanol. The mixture was stirred and sonicated for a period of 24 h. The white precipitates obtained, after centrifugation at 3500 rpm, were washed with methanol for 3 times to remove impurities. Finally, the drying of sample was carried out overnight at 120 °C.

Membrane synthesis

All the membranes prepared in this study were composite membranes. A P84 porous support layer was first prepared by phase inversion technique, and subsequently coated with PDMS layer using dip-coating technique. For the preparation of P84 support layer, the polymer dope solution was prepared by dissolving 15 wt.% of P84 powder in a mixture of NMP and THF in a composition of 3:1. The dope solution was deposited on a non-woven polypropylene support (Novatex 2471). After an evaporation period of 30 s, the cast film was immersed in a coagulation batch containing water and ethanol. In order to keep the pores intact and prevent them from collapsing, the films were post-treated by immersing first in IPA (3 h) and then in a mixture of MIBK, toluene, and oil in a 40:40:20 (v/v) compositions for 3 days.

The top player comprising of PDMS was prepared by the solution of 15 wt.% PDMS (RTV 615 A (monomer) and 615 B (crosslinker) in a ratio 10:1) solution in solvent mixture comprising of 80:20 composition of toluene and hexane. Coating solutions with different filler loading (5, 10, 15, and 20 wt.%) were prepared by adding the fillers in a PDMS solution, which was then stirred and sonicated simultaneously for 15 min each (2 times), to ensure a better dispersion of the particles. The prepared solution was then coated on the P84 support, an inclined plate at 60°. This step was repeated two times to ensure homogenous coating. Finally, the crosslinking and polymerization was completed in an oven at 110 °C for 24 h.

Characterization of ZIF-8 nanofillers and MMMs

X-ray diffraction (XRD) patterns of nanofiller were recorded by Expert^3 PAN Analytical using Cu Kα radiation. SEM images of prepared samples of membrane and fillers were taken by TESCAN Vega LMU–Variable pressure Scanning Electron Microscope. BET (Brunauer-Emmett-Teller) results of ZIF-8 were acquired by Tristar II 3020. X-ray photoelectron spectroscopy (XPS) of nanofiller was performed on an ESCALab250 electron spectrometer from Thermo Scientific Corporation with monochromatic 150 W Al Kα radiations. Fourier-transform infrared spectroscopy (FTIR) was used to record spectra of nanofiller by Thermo-Nicolet 6700 P FTIR Spectrometer (USA). To verify the thermal stability of ZIF-8, thermogravimetric analysis (TGA) was carried out by SDT Q600 TGA/DSC, TA Instrument. Elmer Lambda-25 UV-Vis spectrophotometry (VWR Pennsylvania) was used to measure absorbance of Congo red dye solution at 500-nm wavelength.

Membrane swelling analysis

MMMs with different loadings of ZIF-8 filler (0, 5, 10, 15, 20 wt.%) were tested to analyze stability of membranes against swelling. Small pieces of membranes were weighed before immersing in solvents and then poured into close containers having toluene and IPA. The membranes were allowed to swell at room temperature for 48 h. After swelling, membranes were wiped with tissue paper and weighed as soon as possible. The swelling of membrane was calculated by using Eq. 1.

$$\textbf{Swelling}\ (\textbf{ml/g}) = \frac{W_s - W_d}{\rho \times W_d} \tag{1}$$

where ρ is the density of the solvent (g/ml), W_s is the weight of the swollen membrane (g), and W_d is the weight of the dry slab (g).

Permeance and solute rejection performance

shows filtration experimental set-up to test permeance and rejection performance of fabricated MMMs. The filtration experiments were carried out using a stainless steel dead-end filtration cell (Sterlitech, USA) with 0.00146-m^2 active membrane area. The feed solution was poured into the cell and pressurized with nitrogen to the desired pressure. Permeate was collected under atmospheric pressure. The feed solution was stirred by a Teflon-lined magnetic stirrer at 700 rpm. All the experiments were carried out with a feed solution containing Congo red dye and IPA. The selected concentration of solute was 17.5 μmol/l. The pressure was kept at 10 bar, and experiments were conducted at room temperature. Permeance was calculated by using Eq. 2.

$$\textbf{Permeance} = \frac{V}{A \times t \times p} \tag{2}$$

where V is the permeate volume, A is the membrane surface area (m^2), t is the permeation time (h), and p is the pressure (bar).

The rejection of Congo red dye from IPA (organic solvent) with membranes of different loadings was calculated by using Eq. 3.

$$R\ (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{3}$$

where C_f and C_p are the solute concentrations in the feed and permeate respectively.

Results and discussion

Characterization of ZIF-8 nanofillers and MMMs

Figure 2 shows XRD pattern of synthesized ZIF-8 particles. The overall XRD pattern of ZIF-8 particles matches well with the reported literature (Cravillon et al. 2009). The sharp peaks at 7.3°, 10.2°, 12.9°, and 18° in the diffractogram indicate the crystalline nature of ZIF-8. SEM analysis of ZIF-8 particles was carried out to observe the morphology of the prepared material. Figure 3 shows that obtained particle size ranges from 50 to 80 nm supporting their nano-configuration. It is envisaged that ultra-sonication approach during the synthesis of ZIF-8 particles resulted in particles with smaller sizes. The small-sized particles are expected to improve dispersion in polymer matrix Figs. 1, 2 and 3.

BET surface area and pore volume of ZIF-8 particles were 1258.84 m^2/g and 0.609 cm^3/g, respectively, which are consistent with the literature (Dai et al. 2019). The higher BET surface area of ZIF-8 could be due to the highest micropore volume indicating that the ZIF-8 samples have a crystalline structure, consistent with the XRD results. This high pore volume and high surface area of nanofillers are expected to improve the permeation flux of synthesized MMMs.

FTIR spectrum of the synthesized ZIF-8 (Fig. 4a) showed peaks that were well-match with the previous literature (Li et al. 2014). The peaks appearing at 690 cm^{-1} and 756 cm^{-1} were associated with aromatic sp^2 C–H bending. The peaks between 900 and 1350 cm^{-1} attributed to in-plane bending of the entire imidazole ring. The peaks at 1382 and 1456 cm^{-1} correspond to the entire ring stretching. The broad peak between 3135 and 2850 cm^{-1} was associated with C–H stretching vibrational modes of the imidazole ring (Kaur et al. 2017).

XPS results of ZIF-8 are presented in Fig. 4b, which is consistent with the reported study (Dai et al. 2019). ZIF-8 has zinc ions that act as coordination center and are attached with benzimidazole. The XPS spectra distinctly indicate the presence of four major peaks of elements namely carbon (C 1s), nitrogen (N1s), oxygen (O1s), and zinc (Zn 2p) with different binding energies and electronic states. Carbon has sharp peak at 284.8 eV while nitrogen, oxygen, and zinc can be identified by their respective peaks at 398.70 eV, 531.60 eV, and 1021.30 eV respectively. Thus, the results reaffirm the successful synthesis of ZIF-8 nanofiller.

The TGA curve of ZIF-8 is presented in Fig. 5 (Cravillon et al. 2009). The results show that the prepared ZIF-8 particles are thermally stable and can be used in thermally harsh applications. The weight loss up to 200 °C is associated with the removal of some guest molecules and some of the unreacted molecules in the sample. Moreover, the weight loss at elevated temperature explains the release of organic linker molecules.

Figure 6 presents the cross-sectional SEM images of the MMMs. The membranes show dense top layer containing ZIF-8 particles with porous sub-layer. A number of solvent mixture compositions (hexane:toluene) were used to study the dispersion of filler in PDMS matrix. The difference in polarity of the solvents was crucial in determining the filler dispersion. An 80:20 composition of toluene-hexane resulted in optimum dispersion even at the highest filler loadings.

Membrane swelling analysis

Figure 7 presents the results of swelling studies using IPA and toluene solvents. Neat PDMS membrane, being an elastomer, shows good interaction with organic solvents, so resulted in higher swelling index as compared with MMMs. In MMMs, as the filler loading was increased from 5 to 20 wt.%, the degree of swelling decreased up to 12% and 11% in IPA and toluene solvents respectively. This decreased swelling is attributed to the increased rigidity at the interface due to better

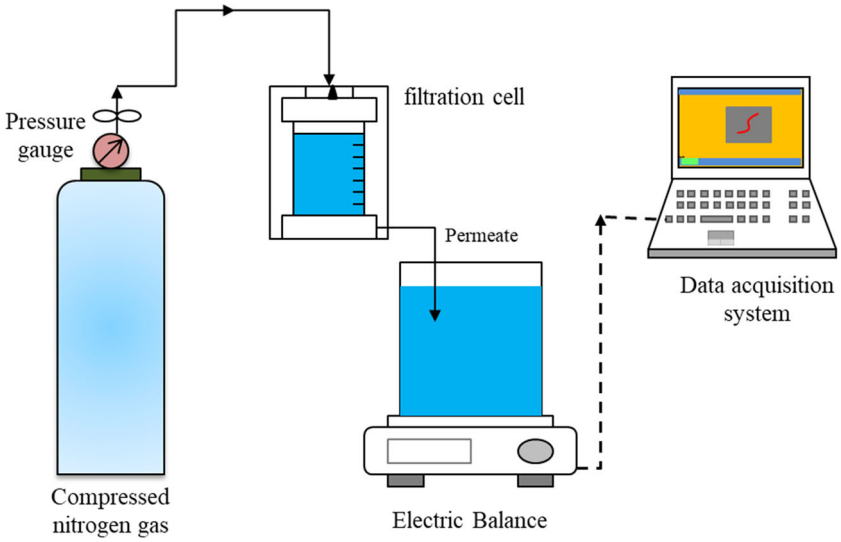

Fig. 1 Filtration experimental set-up to test permeance and rejection performance of synthesized MMMs treating dye-stuff industrial wastewater

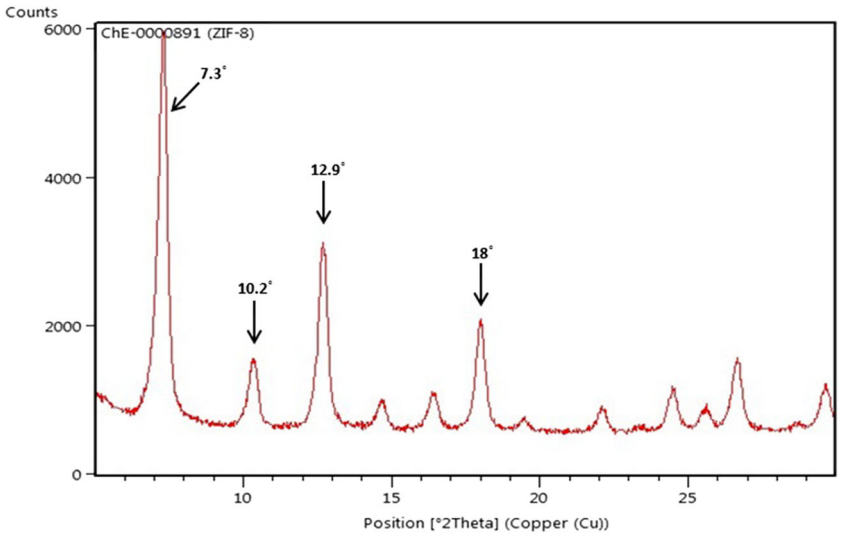

Fig. 2 XRD diffractogram of ZIF-8 nanofillers

polymer filler interaction. As the filler loading increases in the polymer matrix, it resulted into more porous membranes due to the uniform dispersion of nanofillers as shown in SEM images. When a porous membrane swells, the pores become narrower. The membrane becomes "less open," which would result in higher rejections (Geens et al. 2004).

Permeance and solute rejection performance

Dye-stuff industrial wastewater containing Congo red dye was used to test the separation performance of the MMMs. This dye has molecular mass of 696.66 g/mol and shows λ_{max} at 500 nm in UV-Vis spectroscopy. All the experiments were conducted at 10 bar and room temperature. In order to ensure reproducibility and reliability of measurements, at least three membrane coupons were cut and tested for each experiment. Moreover, at least three measurements were taken for each experiment and an average of the obtained values was used in further analysis. Any deviation was presented in the form of error bars in the relevant figures.

The permeance of neat PDMS and MMMs is calculated using Eq. 2, and results are presented in Fig. 8. The results illustrated that neat PDMS membrane showed the lowest permeance of about 3.15 l/m^2/h/bar. This was due to the dense PDMS layer, and the transport passage offered in this case was mainly through the free volume of polymer. By the addition of filler from 5 to 20 wt.%, the permeance was increased from 3.7 to 4.2 l/m^2/h/bar. This increased permeance of MMMs up to 32% as compared with neat PDMS membrane is due to the uniform dispersion of porous filler in the polymer matrix as

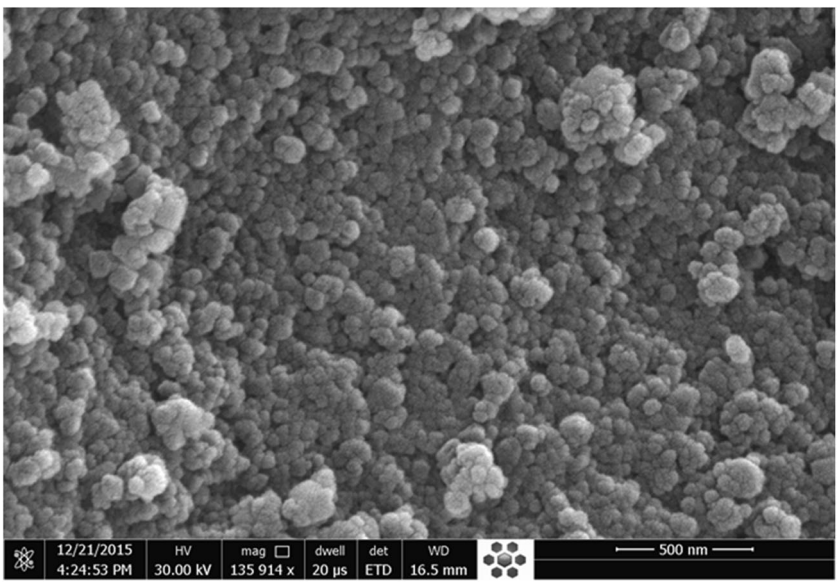

Fig. 3 SEM image of synthesized ZIF-8 nanofiller

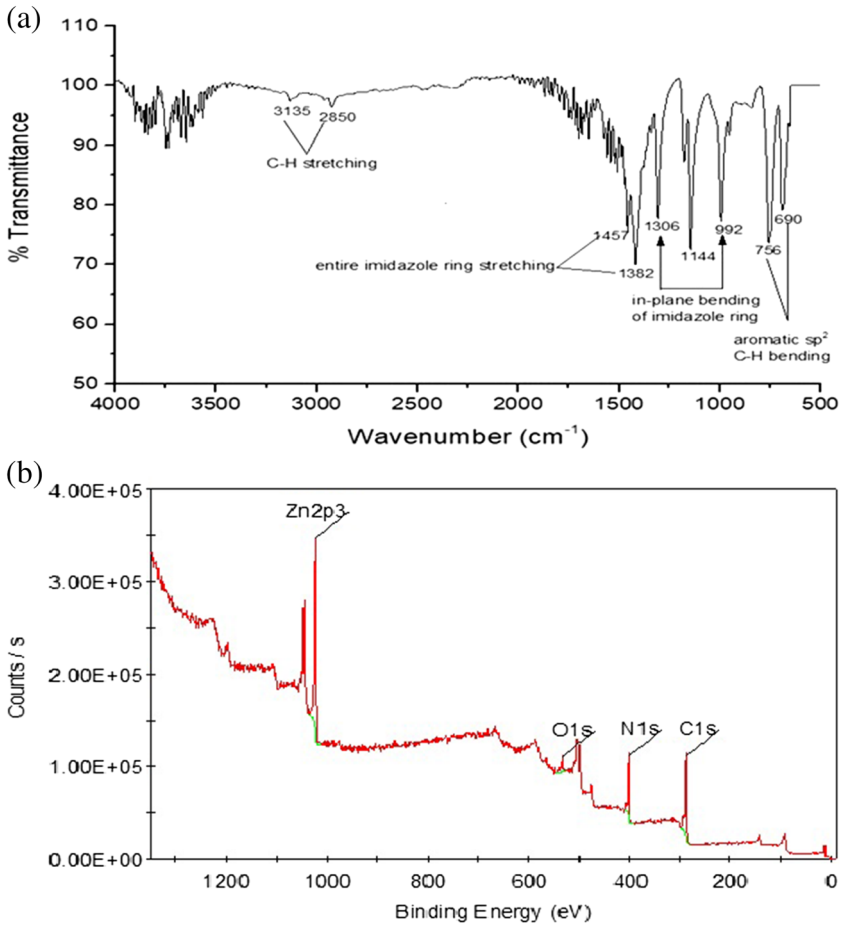

Fig. 4 **a** FTIR spectra of ZIF-8 nanofillers; **b** XPS Spectra of ZIF-8 nanofillers (2 scans, 54.4 s, 400 μm, CAE 200.0, 1.00 eV)

shown in SEM images (Fig. 6), which provided the new pathways for solvent penetration and its transport by increasing the overall porosity of membranes. But this increase in porosity only facilitated the solvent to pass and rejected the solute molecules due to the molecular sieving effect.

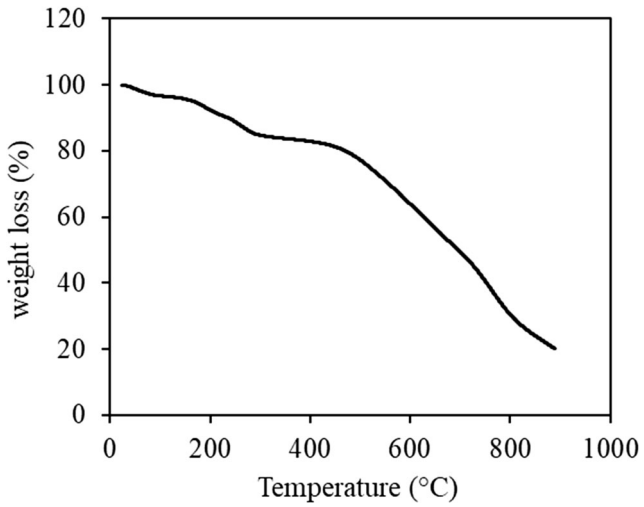

Fig. 5 TGA curve for ZIF-8 nanofillers

The rejection of membranes was measured using Eq. 3, and the results are shown in Fig. 9. Neat PDMS membrane showed rejection of about 65%. As the filler concentration was increased from 5 to 20 wt.%, the rejection of dye increased up to 87%. Rejection of MMMs was 22% higher than that of unfilled PDMS membrane. This increased rejection can be due to two factors; first, the reduced swelling of membranes leads to the narrowing of pores as discussed above and, second, due to the unique pore structure of ZIF-8 filler. The pore size of ZIF-8 is so small that it allows only solvent molecules to pass through them but solute molecules are retained, leading to increased rejection values. The transport of solvent molecules through membranes could be explained by solution diffusion through dense polymeric part of matrix or through the pores of filler. However, the transport of dye molecules (indication of poor separation) was only possible through the free volume of polymeric part of membranes and due to the small pores of filler, dye molecules were not allowed to pass through them. At higher percentages of fillers, the adsorption of dye molecules on the filler surface and sieving effect had played a key role in separation performance; thus, higher retention values were observed.

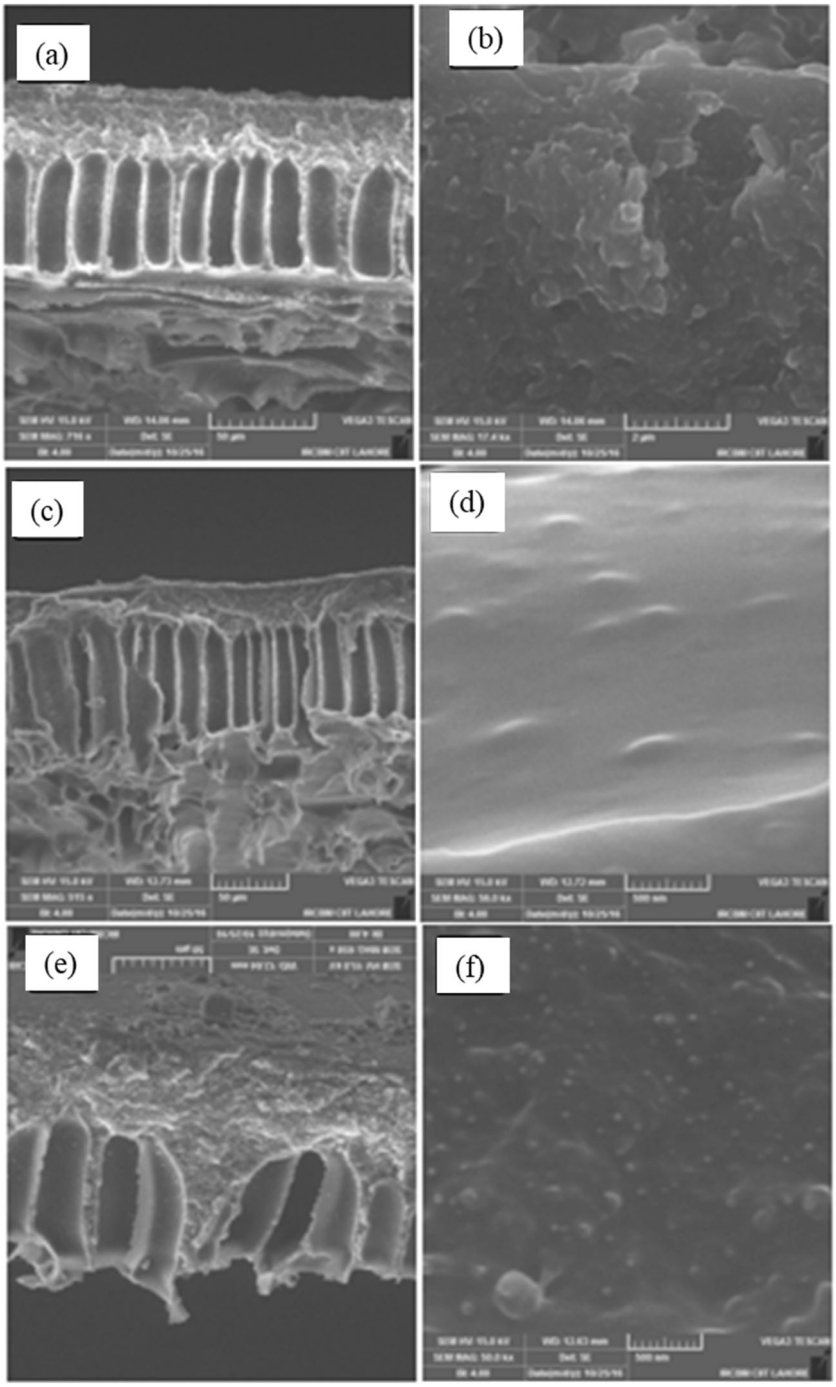

Fig. 6 Cross-sectional and surface SEM images of MMMs with different loadings of ZIF-8 nanofillers **a** and **b** 10 wt.%, **c** and **d** 15 wt.%, **e** and **f** 20 wt.%

In this study, 20 wt.% filler loaded membrane showed 87% rejection, which was 25.49% higher than the previous comparative study with ZIF-8 particles (Basu et al. 2009). The possible reason for the improved results might be the modification in synthesis procedures of ZIF-8 particles leading to nano-sized particles, i.e., 50 to 80 nm. Moreover, the optimization of ratio of solvents (20% hexane and 80% toluene) during synthesis of PDMS solution provided excellent dispersion of ZIF-8 particles in PDMS layers. All these factors contribute in improving interaction between the filler and matrix resulting in higher separation performance.

In order to evaluate the commercial potential, the membranes were exposed to feed solution for 10 h and permeate and retention was calculated after every 1 h. The results are illustrated in Fig. 10 (a–c), which shows that in the period of 10 h, neat PDMS, 10 wt.% and 20 wt.% membranes showed the reduction in retention of about 2%, 1.8%, and 1.7% respectively, which fall in the range of experimental error. And

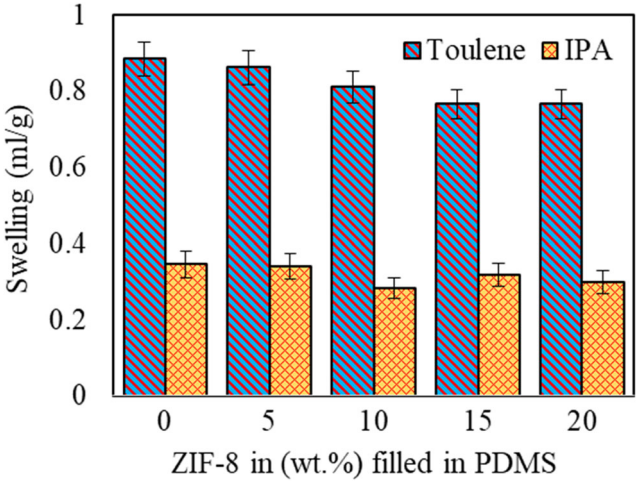

Fig. 7 The effect of MOF filled PDMS membranes with different MOF loadings on swelling behavior of the membranes with toluene and IPA (25 °C). Three membrane coupons were cut and tested for each experiment. Moreover, three measurements were taken for each experiment and an average of the obtained values was used in further analysis

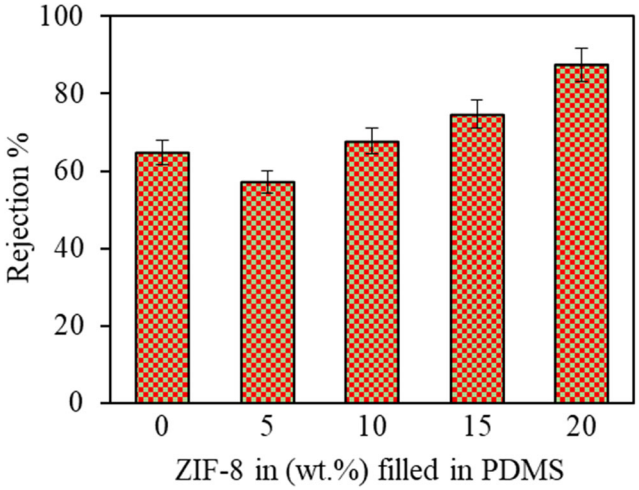

Fig. 9 Rejection of dye by PDMS membranes incorporated with different loadings of ZIF-8 nanofillers. The operating conditions were 10 bar and 25 °C. Three membrane coupons were cut and tested for each experiment. Moreover, three measurements were taken for each experiment and an average of the obtained values was used in further analysis.

in the same period of 10 h, neat PDMS, 10 wt.% and 20 wt.% membranes showed the permeance reduction of 9%, 11.5%, and 14.3% respectively. This slight decrease in permeance is attributed to membrane compaction over time although the membrane compaction was conducted in accordance with standard operating manual of supplier before taking the actual measurements. The filler content in the membrane has direct relation with permeance, but with the passage of time, the deposition of solute molecules on membrane could cause clogging of filler pores; therefore, the maximum permeance decrease was observed in 20 wt.% loading membrane.

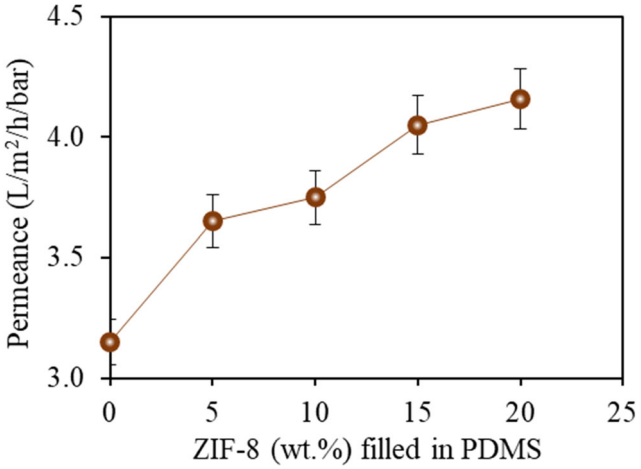

Fig. 8 Permeance of PDMS membranes with different loadings of ZIF-8 nanofillers. The operating conditions were 10 bar and 25 °C. Three membrane coupons were cut and tested for each experiment. Moreover, three measurements were taken for each experiment and an average of the obtained values was used in further analysis

Practical implications of this study

The textile effluent typically composed of different types of dyes, detergents, solvents, and salts depending on the particular textile process such as scouring, bleaching, dyeing, printing, and finishing (Lau and Ismail 2009). In this study, the effects of major components (solvent and solute) of textile effluent were studied by making the model solutions rather than using the real industrial effluent because, otherwise, it was difficult to understand the behavior of different solutes present in the same solution towards the performance of membranes. In order to relate the performance of membranes in lab scale environment with the real situation, the swelling test of membranes and their commercial potential was also analyzed. As membranes have the benefits of high separation efficiency, easy automation, and compactness of design and require relatively low energy consumption process, membranes are viable to use in the textile industries. But in the long run, these membranes face the issue of reversible and irreversible fouling caused by the attachment of foulants on the membrane surface and their accumulation inside the pores of membranes. Such fouling results into the number of inefficiencies in membrane performance such as decreased permeation flux, reduced membrane life, change in selectivity and rejection, and high operational energy and maintenance (Zhang et al. 2008). So, for the long-run implementation of this work; the antifouling performance of membranes can be evaluated by measuring flux recovery ratio (FRR), relative flux reduction (RFR), and degree of reversible and irreversible fouling. Due to the promising results of this study, it is recommended in future to analyze the effect of other components present in the wastewater and the performance of membranes can be analyzed by treating with real textile waste water.

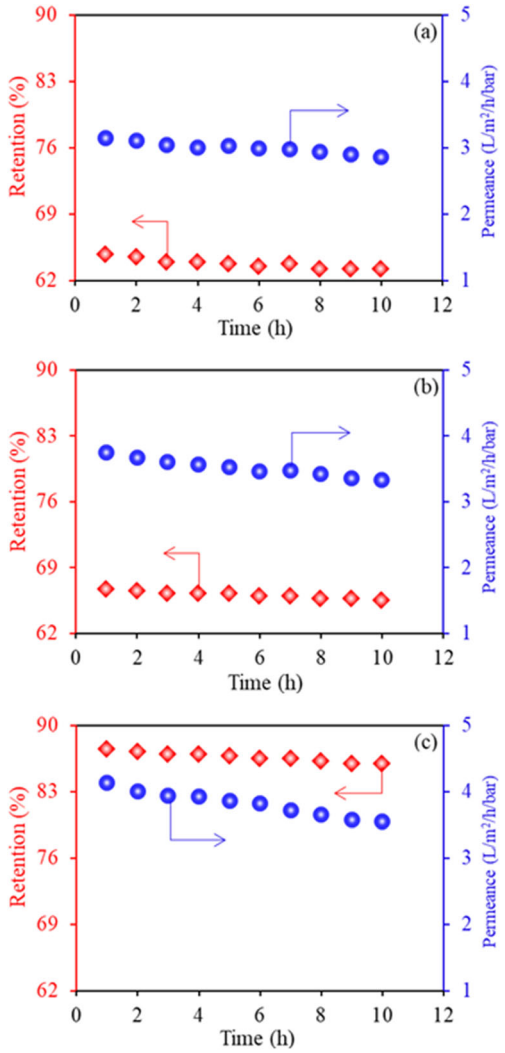

Fig. 10 The extended permeance and solute rejection performance of mixed matrix membranes incorporated with different loadings of ZIF-8 nanofillers **a** 0%, **b** 10%, and **c** 20%. The operating conditions were 10 bar and 25 °C. Three membrane coupons were cut and tested for each experiment. Moreover, three measurements were taken for each experiment and an average of the obtained values was used in further analysis

Conclusion

ZIF-8 was selected as filler for fabricating MMMs to enhance the performance of SRNF membrane. The high surface area of ZIF-8 and their incorporation in the matrix showed very good adsorption and sieving mechanism, leading to higher retention of dye molecules at higher loadings of filler. The synthesized membranes showed good stability for longer period of time even under dead end flow. The membranes showed a simultaneous increase in solvent flux and dye retention. The incorporation of filler not only increased the separation but also decreased the swelling of membrane as tested in IPA and toluene solvents.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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