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A novel low-fouling zeolite-polysulfone nanocomposite membrane for advanced water treatment

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ABSTRACT

A novel zeolite-polysulfone composite ultrafiltration membrane was synthesized. 50–1500 mg/L zeolite nanopowder was added in 15% (w/v) polysulfone solution in N,N-Dimethylformamide solvent. The membrane was formed by phase inversion process. It was found that the membrane became more hydrophilic in nature as manifested by 134.3% increase in pure water permeability at 50 psig pressure of 700 mg/L zeolite nanopowder composite as compared to polysulfone membrane. It was also proven by decline in contact angle from 91.08° to 59.89° for the same. The membrane selectivity performance was also improved as exhibited by albumin rejection from 86.39% to 95.31% for the nanocomposite formed with 700 mg/L zeolite nanopowder. Fouling and flux decline were monitored with 5000 mg/L albumin concentration at 50 psig pressure and it was found that the flux decline at the end of 8th hour was 22.41% for 700 mg/L zeolite nanocomposite as compared to 39.8% for virgin polysulfone membrane. However, on increasing nanomaterial loading to 1500 mg/L in the composite, the pure water permeability declined about 19%, contact angle increased from 59.89° to 81.55°, albumin rejection decreased from 95.31% to 80.55% as compared to the nanocomposite with 700 mg/L nanomaterial loading. SEM and AFM images were taken of the virgin polysulfone and the nanocomposite. It was found that at higher concentration, e.g., 1500 mg/L the nanomaterial agglomerates and thus the incentives of using nanomaterial is attenuated at higher concentration. It was found that 700 mg/L zeolite nanomaterial loading was optimum for advanced water treatment applications as the selectivity of membrane for protein separation and the pure water permeability are the highest. Thus, zeolite nanocomposite can work as a low-fouling, high flux membrane for ultrafiltration applications.

Keywords: Anti-fouling; Hydrophilic; Membrane; Nanocomposite; Polysulfone; Zeolite

1. Introduction

In recent years, Nanocomposite Ultra-filtration membranes have got wide popularity and attention in research community because of their higher performance in terms of water-flux rejection of desired material and also lower fouling on account of increased hydrophilicity. Reports have shown that membranes constructed using carbon nanotubes [1–3] and zeolite [4–6] as nanomaterials have opened up enormous possibilities. Many researchers have tried to make ultrafiltration nanocomposite membranes. The revolutionary energy saving is possible by membrane technology as compared to thermal option and with increased separation capability membrane technology has become more attractive [7]. Zeolite and carbon nanotubes have been employed in mixed membrane films for gas separations, pervaporation and Ion-exchange functionalities [8–12]. Carbon nanotube membranes have a good potential for water desalination and advanced water treatment [13]. Incorporating amino functionalized multi-walled carbon nanotubes (NH_2-MWCNTs) in membrane improved membrane surface hydrophilicity and formed low-fouling membranes for bio-reactor applications [14]. Removal of organic carbon was achieved by nanocomposite tubular ultrafiltration membrane of Al_2O_3- PVDF by phase inversion method [15]. Higher hydrophilicity and better

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anti-fouling properties were demonstrated by polyether sulfone nanocomposite membranes with mesoporous silica particles as inorganic filler [16]. Blending of TiO_2 nanoparticles within polymeric membranes has improved the fouling performance. However, agglomeration of nanoparticles is the major obstacle for generating a uniform surface. Researchers achieved a better dispersion of nanoparticles in the membrane after both chemical and mechanical modifications of particles [17]. Hydroxyl functionalized multi-walled carbon nanotubes were blended with polyacrylonitrile to prepare the ultrafiltration membrane. The nanocomposite membrane showed an improved resistance against compaction as compared to the neat membrane [18].

Zeolites are micro-porous alumino-silicate minerals with wide applications in adsorption and catalysis. They are also used in water treatment as ion-exchange beds. Because of their peculiar structure, it is interesting to make its composite with polymer. Earlier, a Polysulfone–zeolite nanocomposite membrane was made and applied for air separation application. Air separation measurements of the nanocomposite membranes showed enhanced performance in O_2/N_2 selectivity and O_2 permeability [19]. Zeolite-polysulfone nanocomposite membrane has also been used for sorption of heavy metals such as lead and nickel [20]. Effect of NaA zeolite particles addition on poly (phthalazinone ether sulfone ketone) composite ultrafiltration (UF) membrane performance was studied [21]. Researchers reported that by incorporating zeolite 4A in polysulfone membrane, microchannel dimension, the particle size and zeta potential changes to break the trade-off between permeability and selectivity [22].

This paper demonstrates for the first time that highly permeable, low-fouling and highly selective ultrafiltration membrane can be developed by incorporating zeolite nano-powder in polysulfone matrix. Moreover, it shows the effect of change in zeolite concentration in polysulfone matrix to achieve the optimum concentration of zeolite for highest permeability and selectivity. Fouling resistance of such membranes has also been evaluated. The membranes were duly characterized to understand the effect of incorporating nanomaterial in the membrane.

2. Experimental

2.1. Materials

Polysulfone (PSF) pellets and N,N-dimethylformamide (analytical reagent grade) for preparing the casting solution of ultrafiltration membrane were supplied by Spetrochem Pvt, Ltd, Mumbai (India). Zeolite nanoparticles (average particle size <80 nm) were purchased from High Purity Laboratory Chemicals (HPLC), Mumbai (India). Non-woven fabric for the membrane support was purchased from Awa Paper Mfg. Co. Ltd. Japan. RO water was used as the gelation bath for the solidification of membrane.

2.2. Membrane preparation

Zeolite nanocomposite PSF membrane was fabricated by classical phase inversion method. Polysulfone pellets were dried in oven for 2 h at 80°C temperature and added in N,N-dimethylformamide solvent to prepare 15% (w/v) solution. The mixture was stirred at 400 rpm at 80°C till the complete dissolution of the polysulfone pellets, rendering a light yellow homogeneous solution. Zeolite was carefully measured and heated in Oven at 60°C for 2 h to remove moisture. Zeolite was then added into the polysulfone solution in closed conical flask to prevent entry of moisture or undesired material into the solution. The mixture was then stirred at 400 rpm and 60°C for 4 h. After ensuring the complete homogeneity of the prepared solution, it was further kept in an ultra-sonication bath (50 Hz, 230 V) for 45 min to achieve uniform dispersion of zeolite throughout the solution. The solution was then spread evenly on the non-woven fabric with a definite casting gap to make the zeolite nanocomposite polysulfone membrane of thickness 130 µm in a membrane casting machine with the linear speed 2 m/min. The various dosages of zeolite are as mentioned in Table 1.

2.3. Membrane performance

The casted membrane was dipped into deionized water for 48 h before experimentation. Experiments were carried out for 20 min at 50 psig pressure for pure water permeability testing after pressurizing the membrane for 20 min at same pressure in the same feed water as per the standard procedure as optimal for ultrafiltration membrane. Experiments for protein rejection with Albumin solution of 500 mg/L were carried out for 20 min at 50 psig pressure. Fouling study of each membrane was done using 5000 mg/L Albumin solution for 8 h at 50 psig pressure.

2.4. Membrane characterization

Membrane characterization was done using scanning electron micrographs to study the surface morphology. Top surface of the casted membrane was carefully pilled off from the non-woven fabric and it was fractured using liquid nitrogen to take cross section image of membrane as per standard procedure [23]. Moreover, surface features were evaluated by atomic force micrographs. Attenuated total reflectance infrared spectroscopy (ATR FTIR) was done to understand the chemical structure. The phase and crystallinity of zeolite nano-powder and the composite membrane can be investigated with X-ray diffraction (XRD) [24]. X-ray diffraction study was done. Contact angle analysis was done for measuring surface hydrophilicity.

Table 1
Membranes with different dosages of zeolite

Zeolite (mg)	Membrane
Nil	Polysulfone
5	50 mg/L zeolite nanocomposite
20	200 mg/L zeolite nanocomposite
50	500 mg/L zeolite nanocomposite
70	700 mg/L zeolite nanocomposite
100	1000 mg/L zeolite nanocomposite
150	1500 mg/L zeolite nanocomposite

3. Result and discussion

3.1. Pure water permeance and contact angle of membrane

Results indicated that the pure water permeability increased with increase in zeolite dosage up to a certain point and later showed a continuous decline. At higher concentration of zeolite nanomaterial, agglomeration of nanomaterial blocks the passage of water through membrane decreasing the pure water permeability. AFM images confirmed it as shown in Fig. 4c. The SEM images further support the evidence of agglomeration of nanoparticles as seen in cross section of 1500 mg/L zeolite nanocomposite membrane (Fig. 3e, f). The flux for various dosages of zeolite is mentioned in Fig. 1. It can be observed that 700 mg/L gives optimum flux beyond which there is a marked decline in flux.

Contact angles of the various membranes were measured using the drop shape analyzer (DSA 100) provided by Krüss Optronic Germany by sessile drop method. The contact angles demonstrate the hydrophilicity of membrane, i.e., lower the contact angle, higher the hydrophilicity of the membrane. Contact angles for various membranes are mentioned in Fig. 2. The trend of contact angle is similar to the water-flux, with constant decline in contact angle till 59.89° at 700 mg/L zeolite loading, beyond which there is a gradual increase in contact angle.

3.2. Albumin rejection

Albumin rejection experiments were carried out on the zeolite nanocomposite membranes with 500 mg/L concentration of albumin at 50 psig pressure after stabilizing the membrane for 20 min. The concentration of albumin was measured using UV-VIS absorption spectrophotometer (UV-2700 Shimadzu) at 284 nm wavelength. The results are noted in Table 2. 95.31% rejection of albumin was obtained with 700 mg/L zeolite nanocomposite as compared to 86.39% rejection with neat polysulfone membrane thus, 9.35% increase was noted in the 700 mg/L zeolite nanocomposite membrane as compared to the neat polysulfone membrane. With increase in concentration further to 1500 mg/L, the albumin rejection declines to 80.55%.

Table 2
Albumin rejection of polysulfone and nanocomposite membrane

Membrane	Albumin rejection
Polysulfone	86.39%
700 mg/L zeolite nanocomposite membrane	95.31%
1500 mg/L zeolite nanocomposite membrane	80.55%

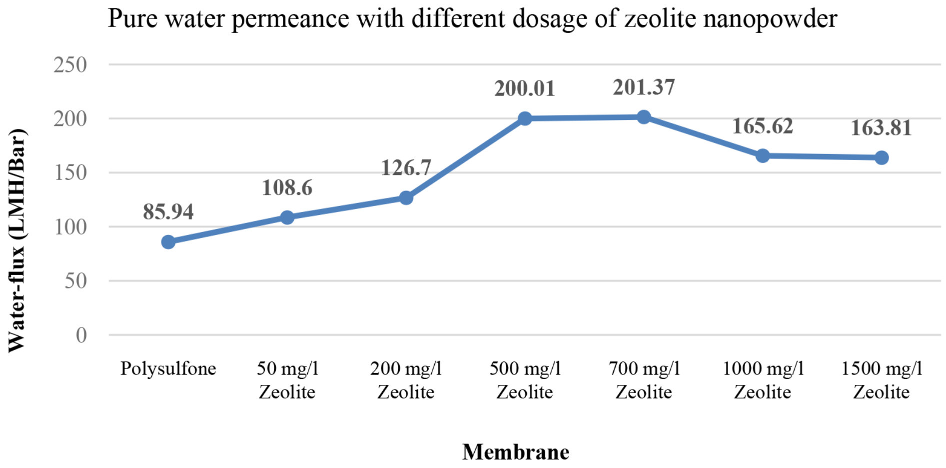

Fig. 1. Pure water flux with different dosage of zeolite nanopowder.

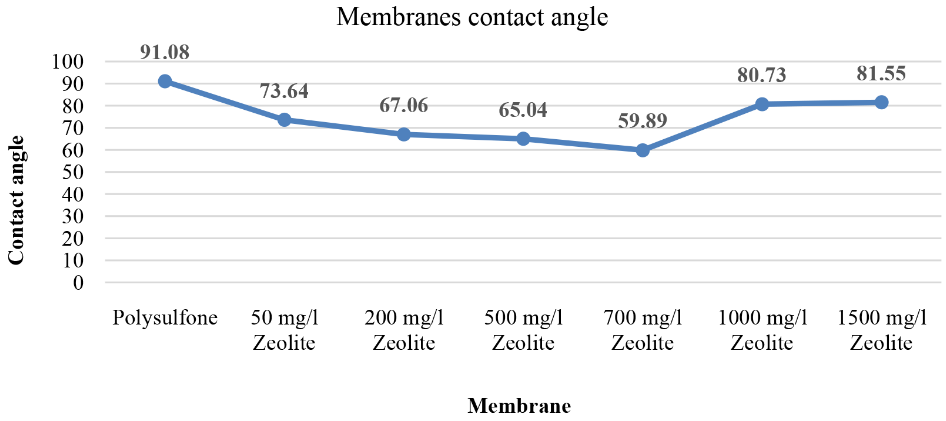

Fig. 2. Membrane contact angle with different dosage of zeolite nanopowder.

Table 3
Membrane fouling

Sr. No.	Membrane	1st h volume collected (mL)	8st h volume collected (mL)	% Flux decline
1	Polysulfone	98	59	39.79%
2	50 mg/L zeolite nanocomposite membrane	104	76	26.92%
3	200 mg/L zeolite nanocomposite membrane	107	83	22.42%
4	500 mg/L zeolite nanocomposite membrane	113	88	22.12%
5	700 mg/L zeolite nanocomposite membrane	116	91	21.55%
6	1000 mg/l zeolite nanocomposite membrane	132	98	25.75%
7	1500 mg/l zeolite nanocomposite membrane	138	94	31.88%

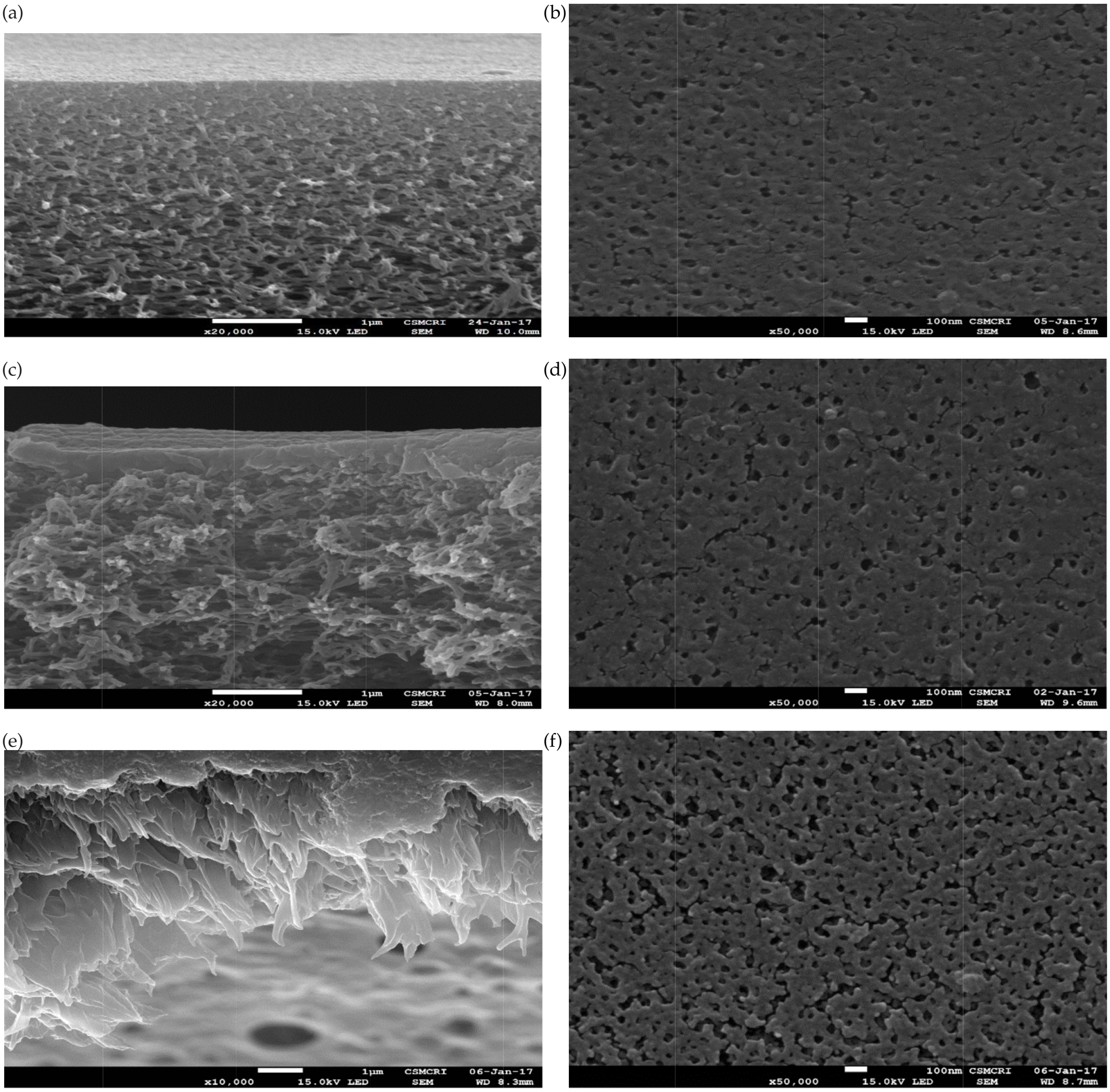

Fig. 3. SEM images (a) cross section of polysulfone (b) polysulfone membrane (c) cross section of 700 mg/L zeolite nanocomposite (d) 700 mg/L zeolite nanocomposite (e) cross section of 1500 mg/L zeolite nanocomposite (f) 1500 mg/L zeolite nanocomposite.

3.3. Fouling

Resistance to fouling was monitored by measuring corresponding decline in flux with a 5000 mg/L albumin solution at 50 psig pressure for 8 h. Table 3 shows the water flux during first and 8th hour and percentage decline in water-flux at the end of 8th h. It was found that the flux decline at the end of 8th h was 21.55% for 700 mg/L zeolite nanocomposite as compared to 39.79% for virgin polysulfone membrane. As this nanocomposite membrane has the least contact angle and highest pure water permeance, its propensity to foul is the least amongst all other membranes.

3.4. Scanning electron micrographs

The morphology and porosity of zeolite nanocomposite membrane was studied using Field emission scanning electron microscope (JSM-7100F Scanning Electron Microscope, Jeol, Japan).The SEM images of membranes are shown in Fig. 3. Top surface of the casted membrane was carefully pilled off from the non-woven fabric and it was fractured using liquid nitrogen to take cross section image of membrane [23].

Presence of zeolite nanoparticles can be observed in Fig. 3c where, the cross-section of membrane with 700 mg/L zeolite nanomaterial has been taken. The cross-section of virgin polysulfone membrane is devoid of white zeolite particles. Also, the presence of zeolite nanoparticles is confirmed from energy dispersive X-ray by presence of sodium, aluminium and silicon as shown in Table 4. With presence of zeolite nanoparticles, the pore-density increases, which results in increased water-flux.

3.5. Atomic force microscope images

The Topography and surface roughness properties of the membrane were measured using atomic force microscope (NTEGRA Aura, NT-MDT Instruments, Russia). The images of virgin polysulfone, 700 mg/L zeolite nanocomposite and 1500 mg/L zeolite nanocomposite membranes are shown in Fig. 4. Presence of zeolite nanoparticles can be seen in the membrane with 700 mg/L zeolite concentration. Increasing concentration of zeolite nanomaterial resulted in agglomeration as can be seen from AFM image of 1500 mg/L zeolite nanocomposite. Table 5 indicates that the average roughness and surface area ratio increases gradually with the increase in dosage of zeolite. The membrane with the best performance in terms of water-flux, albumin rejection and fouling resistance, i.e., 700 mg/L zeolite nanocomposite had the least surface skewness. This shows that the nanoparticle dispersion in membrane matrix is uniform at this concentration.

Table 4
Energy dispersive X-ray analysis of nanocomposite and polysulfone membrane

Element	Atomic % (700 mg/L zeolite nanocomposite)	Atomic% (polysulfone membrane)
Carbon	81.91	82.49
Oxygen	15.80	14.32
Sodium	0.07	Nil
Aluminium	0.02	Nil
Silicon	0.10	Nil
Sulphur	2.10	3.19
Total	100	100

3.6. Powder X-ray diffraction pattern

We performed powder XRD using Empyrean, PANalytical X-ray diffractometer with cuKα radiation. Fig. 5 shows the XRD pattern of polysulfone membrane, zeolite nanopowder and polysulfone-zeolite nanocomposite. It can be

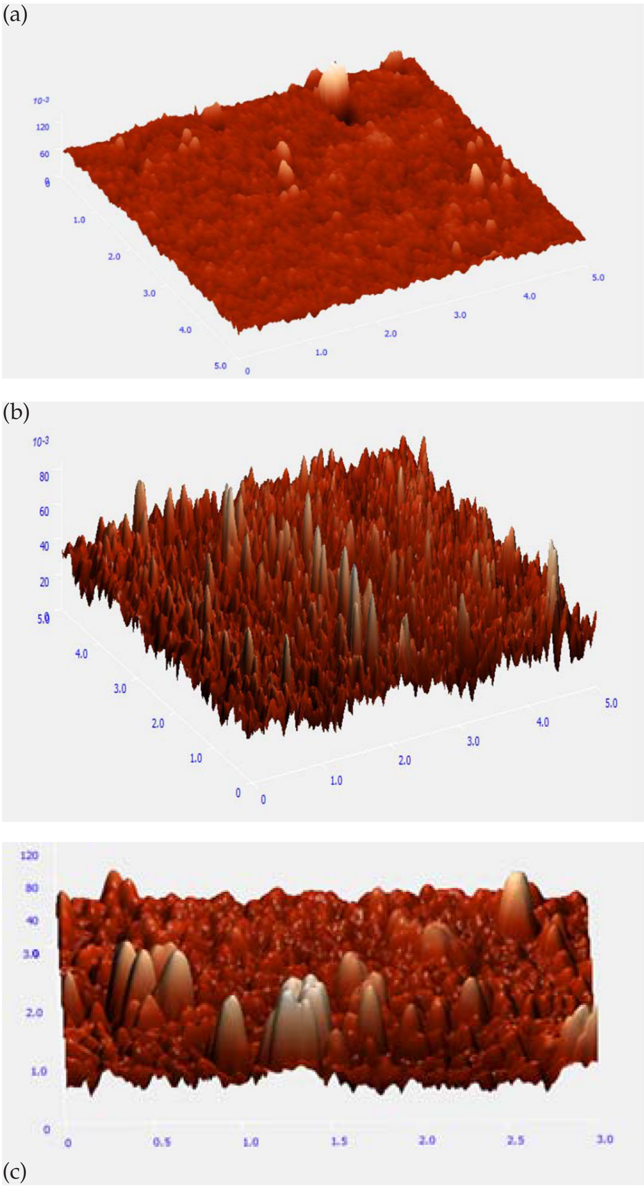

Fig. 4. AFM images (a) polysulfone membrane (b) 700 mg/L zeolite nanocomposite (c) 1500 mg/L zeolite nanocomposite.

Table 5
AFM data of polysulfone and zeolite nanocomposite membranes

	Polysulfone	200 mg/L zeolite	700 mg/L zeolite	1500 mg/L zeolite
Roughness average, Sa (nm)	4.93	5.97	6.28	11.3
Surface skewness, Ssk	1.194	2.701	0.536	1.525
Surface area ratio, Sdr	2.28%	2.37%	3.57%	7.89%

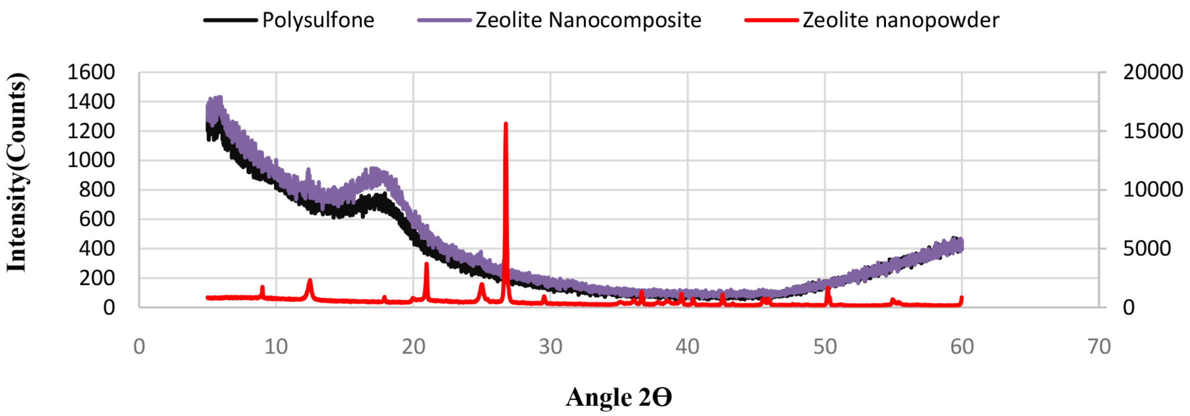

Fig. 5. XRD pattern of polysulfone and zeolite nanocomposite membrane.

seen that the peak intensity at 2θ = 17.123 increases in nanocomposite with a slight increase in crystallinity as a result of zeolite addition in the polymer matrix.

3.7. ATR-FTIR analysis

Attenuated total reflectance Fourier transform Infrared spectroscopy (Spectrum GX FTIR Spectrometer, PerkinElmer, USA) was used to analyze the chemical structure of the polysulfone membrane and zeolite-polysulfone nanocomposite. ATR-FTIR spectrum of polysulfone membrane and 700 mg/L zeolite nanocomposite membrane are shown in Fig. 6. The identifiable peaks are as mentioned in Table 6.

It can be seen that aromatic C=C bond and ether linkages (C–O–C) have been modified as a result of zeolite addition in polysulfone membrane. Sharp change in transmittance indicates the nanocomposite formation.

Thus, the characterization of membrane reveals the chemical, surface morphological and roughness changes and hydrophilic surface formation with addition of nanomaterial into the polysulfone membrane matrix.

4. Conclusion

Nanocomposite zeolite membranes were synthesized by varying the degree of concentration of zeolite in them. The membranes were tested for pure water permeance,

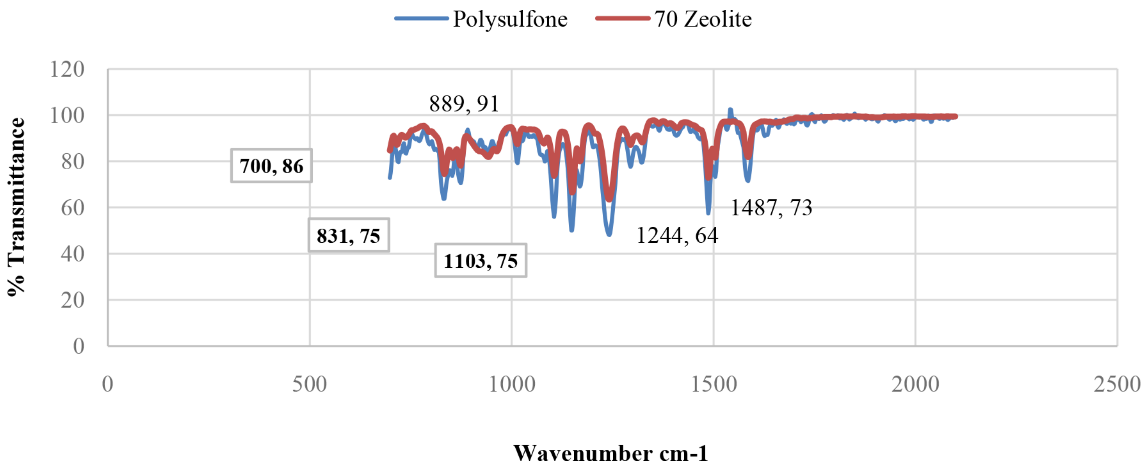

Fig. 6. ATR FTIR spectra of polysulfone membrane and 700 mg/L zeolite nanocomposite membrane.

Table 6
ATR FTIR spectra of 700 mg/L zeolite nanocomposite and identification of peaks

Sr No	% Transmittance	Wavenumber cm^{-1}	Functional group	Type of vibration	Intensity
1	86	700	Aromatic (ring C=C)	Bend	Two bands strong
2	75	831	Aromatic (ring C=C)	Bend	Medium-strong
3	91	889	Alkene (C=C)	Bend	Strong
4	75	1103	Ether (C–O–C)	Stretch	Strong
5	64	1244	Ether (C–O)	Stretch	Strong
6	73	1487	Aromatic ring (C=C)	Stretch	Medium-strong

protein removal and fouling resistance. The nanocomposite with 700 mg/L zeolite nanopowder demonstrated 134.3% increase in pure water permeance as compared to virgin polysulfone membrane. Albumin rejection increased from 86.39% to 95.31% for the nanocomposite formed with 700 mg/L zeolite nanopowder as compared to virgin polysulfone membrane. It was found that the flux decline at the end of 8th hour was 21.55% for 700 mg/L zeolite nanocomposite as compared to 39.79% for virgin polysulfone membrane when exposed to high-fouling solution of 5000 mg/L albumin. The nanocomposite membrane became more hydrophilic in nature as depicted by decline in contact angle from 91.08° to 59.89° for the polysulfone and nanocomposite respectively. The roughness of nanocomposite steadily increased from 4.93 to 11.3 nm with increasing concentration of zeolite nanomaterial. Atomic force micrographs indicated the presence of zeolite nanomaterial. Scanning electron-micrographs revealed that the pore-density of membrane increased for nanocomposite membrane and presence of zeolite was confirmed by energy dispersive X-ray. XRD pattern indicated the increase in crystallinity with zeolite addition and ATR FTIR spectra confirmed the nanocomposite formation with zeolite. Thus, different characterization methods depicted the incorporation of zeolite nanoparticles in the polysulfone membrane can create a favourable structural change resulting in higher flow, better separation and increased resistance to fouling as compared to the virgin polysulfone membrane.

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