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Modification of surface characteristics of functionalized multi-walled carbon nanotubes containing mixed matrix membrane using click chemistry

Priyanka Mistry[a], Km Nikita[a], V.K. Aswal[b], S. Kumar[b], C.N. Murthy[a,*]

[a]*Macromolecular Materials Laboratory, Applied Chemistry Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India, 390001, emails: chivukula_mn@yahoo.com (C.N. Murthy), pm35315@gmail.com (P. Mistry), nikitatiwari.m34@gmail.com (Km Nikita)*

[b]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, India, emails: vkaswal@barc.gov.in (V.K. Aswal), sugam@barc.gov.in (S. Kumar)*

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ABSTRACT

This work probes the polysulfone/azide-functionalized multi-walled carbon nanotubes mixed matrix membrane where the azide groups were converted into triazole rings. This modification was confirmed from X-ray photoelectron spectroscopy studies. Post modification, unlike the polyethersulfone based mixed matrix membranes, these membranes show improved heavy metal rejection. Membrane morphology by atomic force microscopy and scanning electron microscopy images shows membrane bulk morphology does not change after the modification. Also, the modified membrane showed better antifouling property with high flux recovery ratio and lower irreversible fouling as compared to the polyethersulfone-based membrane. This modified membrane shows smaller pore size as compared to modified polyethersulfone mixed matrix membrane due to their different morphology. Surface energy provides additional information such as the wetting and adhesion characteristics of the membranes. These results indicate that the pristine membrane morphology has profound influence on the final morphology of mixed matrix membrane it becoming more hydrophilic and permeable post modification. Surface modified membrane via click reaction gives nearly 99% rejection for Cu(II), 90% rejection for Pb(II) and 95% rejection for Cr(VI), which is higher than the unmodified and pristine polysulfone membranes.

Keywords: Polysulfone; Functionalized carbon nanotubes; Click reaction; Surface modification; Antifouling; Heavy metal rejection

1. Introduction

Surface modification on prepared membrane imparts new properties like improved separation characteristics, energy, and chemical efficiency varying from the unmodified membrane. The modification allows chemical resistance such as swelling resistance, fouling or solvent resistance, control pore size, and removal of membrane irregularities with improved flux or selectivity.

The main purpose for surface modification is to improve permeability and antifouling property by increasing the hydrophilicity of the membrane surface. It also enhances the chemical stability and provides surface charge for the rejection of certain type of ions through the membrane [1,2]. Modification of the membrane can be accomplished by various approaches like blending of polymers, adding fillers [3–7], which is implemented before the membrane preparation. However, there are other techniques used for the membrane surface modification after the membrane preparation, like plasma treatment [8–12], UV irradiation [13–15], coating from gas [16–18] or wet phase [19,20] and grafting which involves the covalent bond formation during the modification [21–23].

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* Corresponding author.

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Polyethersulfone and polysulfone are the most common polymers used for the preparation of nanofiltration membranes, have good mechanical strength, thermal and chemical stability. Membranes become more hydrophilic after some modification as above-mentioned by introducing more hydrophilic functional groups on the surface of the membrane. Bulk modification is also a new approach for the modification of the membrane. Instead of the membrane surface it modifies the polymer structure, which provide better antifouling property and makes it more hydrophilic. Commercial membranes are prepared after the sulfonation of the polymer having the good membrane stability [24], for example, f-CNT/SPES (functionalized carbon nanotubes /sulfonated polyether sulfone) mixed matrix membrane shows better antifouling property as well as good tensile strength. The membrane become more hydrophilic and negative charge on the surface of the membrane increases due to the sulfonate functional group. This membrane shows better metal rejection also [25].

Among the above-mentioned modification techniques, chemical modification is also used, like controlled radical polymerization, redox initiated grafting and click chemistry [26]. Reversible addition fragmentation chain transfer polymerization was used for the grafting of porous anodic aluminum oxide-silica on the poly(methacrylamidomethyl) pyridine (PMAMP) membrane, this quaternized PMAMP-grafted composite membrane has high binding energies, good flexibility and adsorption capacity [27]. Similarly, photoinduced electron transfer-reversible addition fragmentation chain transfer (PET-RAFT) was used to introduce brush like carboxybetaine methacrylate (CBMA) on polyvinyl alcohol hydrogel membrane for biocompatible surface, which gives good adhesion properties by increasing the grafting on the surface of the membrane. This method has advantages like low cost and low toxicity [28]. Atom transfer radical polymerization and RAFT polymerization techniques have been used for the modification of the membrane which creates zwitterionic monomers on the membrane surface. By using the SI-eATRP method polymer brushes were grafted onto PES (polyether sulfone) membrane and it was shown that the modified membrane has better hydrophilic and anticoagulant properties than the pristine PES membrane [29]. Aqueous atom transfer radical polymerization on the porous polyvinylidene difluoride (PVDF) membrane surface at room temperature has been reported. This modified membrane shows improved hydrophilicity and reduced pore size distribution [30,31]. Zwitterionic polymers were also bonded on the cellulose membrane via *in-situ* ATRP, after that modified cellulose membrane gives good resistance towards proteins and platelet adhesion [32]. By merging click chemistry with reversible addition–fragmentation chain transfer radical polymerization, an innovative three-step technique for grafting polyacrylamide to the polypropylene macroporous membrane was developed. This modification gives hydrophilic surface on the membrane and improved protein rejection because of the functional group on the surface [33]. Similarly, in a two-step process, zwitterionic sulfobetaine groups were grafted onto the surface of a polysulfone (PSU) membrane with 2-azidoethyl methacrylate and N,N-diethyl-N-propargyl-N-(3-sulfopropyl) ammonium (DEPAS) via surface-initiated ATRP and click reaction, after this modification polysulfone membrane becomes more resistance to bovine serum albumin and shows better adhesion property [34]. Click chemistry involves the copper catalyzed azide-alkyne cycloaddition reaction resulting in the formation of 1,2,3-triazoles. This cycloaddition reaction is exothermic in nature and performs well in most protic and aprotic solvents, including water [35–37]. It has been reported that pristine polysulfone membrane surface modified by click reaction shows more hydrophilicity than unmodified polysulfone membrane [38]. We have previously shown that surface modification of polyethersulfone/azide-CNT mixed matrix membrane via click reaction after modification gives good hydrophilic surface and improved antifouling property [39].

Here, in this work, a polysulfone mixed membrane incorporated with azide-functionalized carbon nanotubes modified via click reaction is investigated, where azide functional groups on the surface of the membrane undergo cycloaddition click reaction with 1-pentyne in the presence of copper bromide and form a 1,2,3-triazole ring on the surface. As previously reported, modification of a polyethersulfone/azide-functionalized membrane results in improved heavy metal rejection, hydrophilicity, and antifouling properties. A similar approach was used in this work, however, with a different polymer, that is, polysulfone. These two pristine polymers, when cast from the solution by the phase inversion process, show distinct bulk morphologies. Polyethersulfone shows a fingerlike structure, whereas polysulfone has a sponge-like structure resulting from its chemical backbone, which is quite different. This work attempts to show the effect of f-CNTs and their further modification on the bulk morphologies of these two.

2. Experimental set-up

2.1. Materials

PSU was procured from M/s Permionics Membranes Pvt., Ltd., Vadodara, India. Multi-walled carbon nanotubes (MWCNT) (purity: >99%, average diameter: 10–15 nm, average length: 5 μm surface area: 400 m^2/g, supplied by Adnano Technologies, Simonga, Karnataka, India), thionyl chloride (>99%, Sigma-Aldrich, Bommasandra Jigani Link Road,

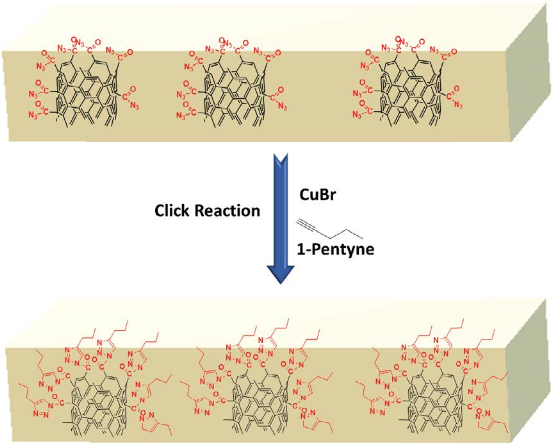

Fig. 1. Surface modification of membrane via click reaction.

Industrial Area, Anekal Taluk, Bangalore, Karnataka 560010 IN), sodium azide (>99%, Sigma-Aldrich), 1-pentyne ((>99%, Sigma-Aldrich) copper bromide (>99%, Sigma-Aldrich), dimethylformamide (>99%, Sigma-Aldrich) were used as received.

2.2. Functionalization of MWCNT

The functionalisation of MWCNT was carried out according to our procedure developed in our laboratory. In brief, purification of MWCNT was done using 50% HCl, followed by oxidation using concentrated H_2SO_4 and concentrated HNO_3. These oxidised MWCNTs were treated with thionyl chloride and subsequently treated with sodium azide (NaN_3) for azide functionalisation of MWCNT [40].

2.3. Preparation of PSU/azide-functionalized mixed matrix membrane

18% dope solution of PSU was prepared using dimethyl formamide as a solvent and 1% azide-functionalized MWCNT were added as fillers. This dope solution was casted on the glass plate using an applicator with gap size 200 μm and submerged into the coagulation bath. The prepared membrane was washed with deionized water for the removal of residual solvent, followed by air drying for 24 h and used for further surface modification.

2.4. Surface modification of membrane via click chemistry

PSU/azide-functionalized MWCNT mixed matrix membrane having azide functional groups on the surface of membrane was reacted with 1-pentyne in the presence of copper bromide (CuBr), where the azide functional group converted in to the triazole ring. Initially the membrane was submerged in water in a round bottom flask and inert atmosphere was maintained. After that CuBr added followed by the addition of 1-pentyne dropwise with the help of additional funnel at low temperature. After the addition the reaction was kept for about 3 h for complete conversion of the azide to triazole. During the reaction the colour of the solution changes from the light yellow to green which indicates the change in the oxidation state of the Cu(I) to Cu(II). The membrane was then washed with distilled water several times for removal of excess of unreacted CuBr and 1-pentyne, and air dried for 24 h to use for further characterisation [39]. The click reaction is essentially the cycloaddition reaction of azide and terminal alkyl, which is an exothermic reaction that then works well in water and is unlikely to be affected by other attached groups [41].

2.5. Characterization

The modified and unmodified polysulfone/azide-CNT mixed matrix membrane was characterized by X-ray photoelectron spectroscopy (XPS), to identify the surface functional groups and confirmation of the formation of triazole moiety from azide group. XPS is a quantitative method to evaluate the elemental composition on the surface of the material and it characterizes the modified molecular structure and determines its binding energy. Modified and unmodified membranes with sample size 8 mm × 2 mm were analyzed using Physical Electronics PHI 5000 VersaProbe III X-ray Photoelectron Spectrophotometer from ULVAC-PHI, Inc. TOP, 2500 Hagisono, Chigasaki, Kanagawa, 253-8522, Japan; Installed at IIT Roorkee, Uttarakhand, India in 2017. Field-emission gun-scanning electron microscopes (FEG-SEM) (JEOL JSM-7600F FEG-SEM) (IIT Bombay, Maharashtra, India) was used to study the surface and cross-section structure of the membranes, with 1,000–10,000 high resolution secondary images at the 10 kV accelerating voltage. Surface roughness and other surface parameters analyzed by atomic force microscopy using INTEGRA scanning probe microscope with modules including atomic force microscopy (AFM) (IIT Roorkee, Uttarakhand India). Small-angle neutron scattering experiments were carried out at the small-angle neutron scattering (SANS) diffractometer at Guide Tube Laboratory, Dhruva Reactor, Bhabha Atomic Research Centre, Mumbai, India. The intensity of scattered neutrons is measured as a function of magnitude of wave vector transfer Q (= $4\pi\sin\theta/\lambda$), where λ is the wavelength of the incident neutrons and 2θ is the scattering angle). The mean wavelength of the monochromatized beam from neutron velocity selector is 5.2 Å with a spread of $\Delta\lambda/\lambda$ ~ 15%. The angular distribution of neutrons scattered by the sample is recorded using a number of 1 m long one-dimensional He^3 position-sensitive detectors (PSDs) in crossed-geometry. The instrument covers a Q-range of 0.01–0.3 Å^{-1}. The data have been corrected for the contributions from background. Rejection of heavy metals and bovine serum albumin (BSA) protein performed on stainless steel membrane test cell fabricated in house. Membrane having the surface area 0.00785 m^2 placed into the membrane test cell, The metal or protein solution passed through the cell by using the pump. Membrane cell usually stabilized for 1 h at 50 psi transmembrane pressure for compaction of the membrane and stable flow rate. The rejection of heavy metal and protein calculated by following formula:

$$\text{Rejection}\left(\%\right) = \frac{C_f - C_p}{C_f} \times 100 \qquad (1)$$

where C_f is the concentration of the feed solution and C_p is the concentration of permeate solution, which determines using PerkinElmer Atomic Absorption Spectrometer PinAAcle™ 500. "PerkinElmer" from PerkinElmer, Inc., 940 Winter Street Waltham, MA 02451 USA. 298809 (012087B_01) PKI installed at Department of Environmental Studies, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India. Concentration of the BSA protein is determines using the UV spectrophotometer.

The fouling behaviour of the membrane was then examined using a 1 ppm aqueous solution of BSA. After rejection of the BSA through membrane, it was backwashed with distilled water for 30 min and the flux (J_2) was measured. The flux recovery ratio (FRR) and irreversible fouling ratio (R_{ir}) were measured using the following formulas below, and the antifouling performances of the membranes were investigated.

$$\text{Flux recovery ration}\left(\text{FRR}\right)\left(\%\right) = \frac{J_2}{J_1} \times 100 \qquad (2)$$

$$\text{Irreversible fouling ratio}\left(R_{\text{ir}}\right)(\%) = \frac{J_1 - J_2}{J_1} \times 100 \quad (3)$$

where J_1 is the pure water flux of membrane and J_2 is the pure water flux of cleaned membrane after the BSA rejection.

Hydrophilicity of the membranes was determined by measuring the contact angle using the contact angle meter ACAMNSC 03, Apex Instruments Co. Pvt. Ltd., using a sessile water drop method. "Apex Instruments Co., Pvt., Ltd.", from Ibrahimpur Road, Jadavpur Kolkata – 700032, West Bengal, India. An ISO 9001:2015 Company Installed at Raychem RPG Private Limited, Halol, Gujarat 389350.

3. Results and discussion

3.1. X-ray photoelectron spectroscopy

Both the unmodified and click reaction modified mixed matrix membrane was characterized by XPS to identify the surface group and to confirm the effective click coupling on the membrane surface.

Fig. 2 above shows the N1s XPS spectra of (a) the click reaction modified and (b) unmodified membrane. In the spectra of the unmodified membrane, Fig. 2b, having the azide functional group on the surface showed two peaks in XPS spectra. One at 399 and 403 eV, where two terminal nitrogen gives one single peak and center nitrogen gives one peak with 2:1 ratio because nitrogen consists of two different oxidation state in the azide functional group. The central electron deficient nitrogen atom gives less intense and higher energy peak at 403 eV, which is quite abnormal for the organic nitrogen atom therefore that peak consider for the central nitrogen in azide [42]. Modified membrane shows single peak at 399 eV, and disappearance of the peak at 403 eV, confirms the formation of triazole ring. The peak at 399 eV broadens which suggests that the different nitrogen atom present which is chemically different. Also, the area under the peaks of 399 and 403 eV (Fig. 2b) is similar to the area under the 399 eV (Fig. 2a) in the spectra. Therefore, the appearance and broadening of the peak at 399 eV and disappearance of the peak at 403 eV indicates the successful conversion of triazole ring from the azide functional group on the surface of the membrane [43–45].

XPS is a quantitative spectroscopic technique in which X-rays irradiated on the surface and Spectrum is obtained via measuring the intensity of the escaped electrons from the surface and binding energy. In this case, azide functional group gives two different peaks, one at 399 eV for two electron rich nitrogen atoms and one at 403 eV for electron deficient nitrogen atom. This also attributes the resonance structure of the azide groups. After it converted into the aromatic triazole ring which is the stable having 6π electrons delocalized around the ring gives a single peak at 399 eV.

In this study only nitrogen atoms environment is changing due to the ring formation. But if we talked about carbon and oxygen, their oxidation state and binding energy remains unaffected because click reaction is a simple cycloaddition reaction that occurs between the azide group and 1-pentyne.

3.2. Field-emission gun-scanning electron microscopes

The cross-section field-emission-scanning electron (FE-SEM) micrograph of mixed-matrix membranes were taken immediately after their cold fracture in liquid N_2. Fig. 3 shows the FE-SEM images of surface as well as cross section of the membrane of pristine polysulfone, polysulfone/azide-CNT membrane along with click reaction modified polysulfone/azide-CNT membrane. Polysulfone/azide-CNT membrane shows smaller pores than the pristine polysulfone membrane on the surface of the membrane as shown in Fig. 3. From the surface images of pristine polysulfone membrane it can be seen that it has comparatively larger pores, while polysulfone/azide-CNT membrane has smaller pores with greater number of pores. The reduction in size of the pores is depended on the rate of the solvent/non-solvent exchange during the phase inversion process, which become slower after the addition of the azide-functionalized CNTs. Cross-section of the both membrane shows sponge like structure, which indicated a homogenous distribution of azide-CNT in the membrane [40].

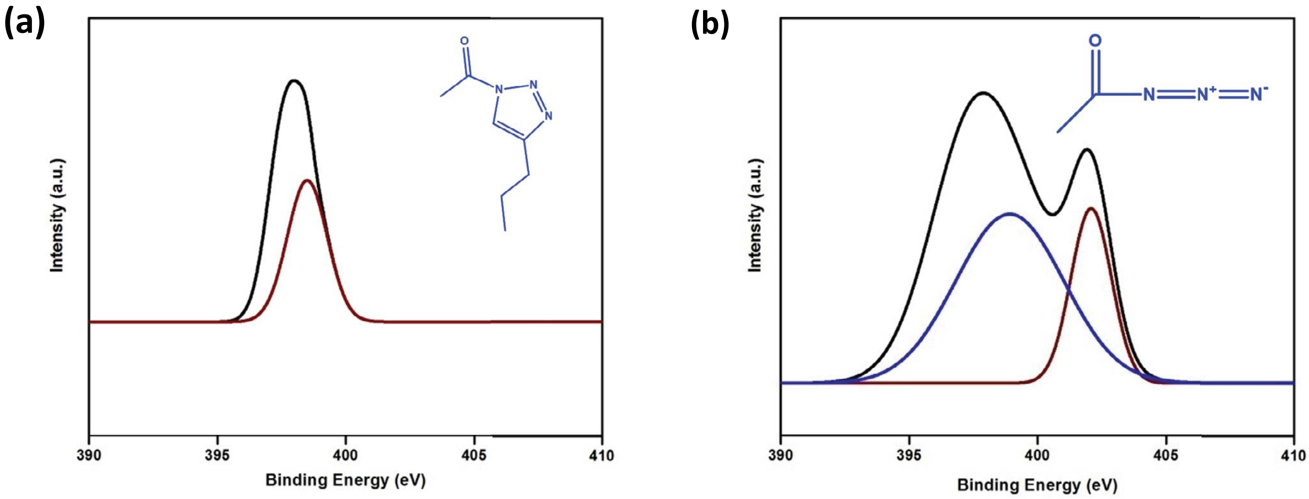

Fig. 2. N1s X-ray photoelectron spectroscopy of (a) modified membrane via click reaction and (b) unmodified membrane.

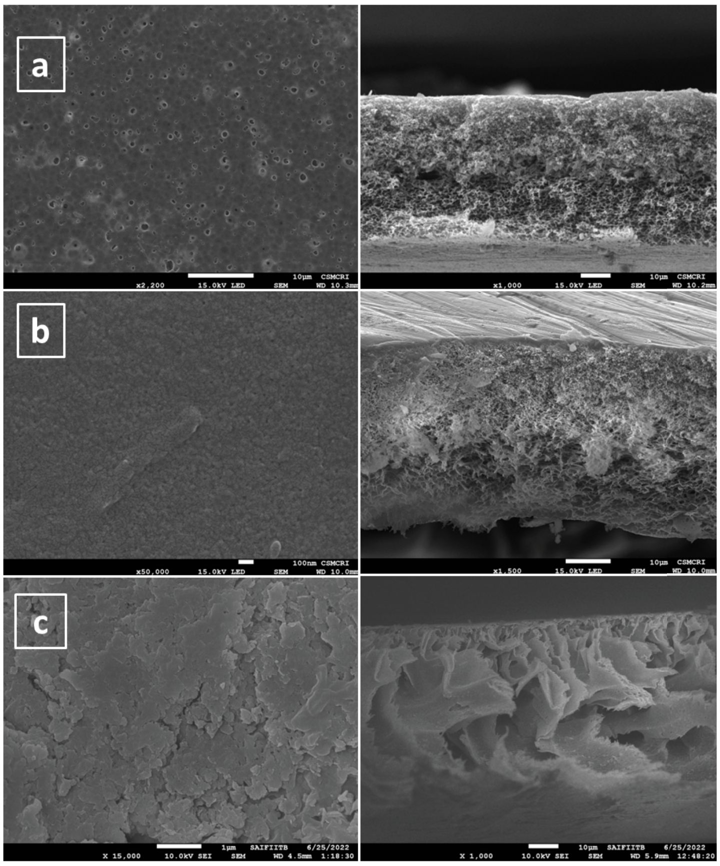

Fig. 3. Scanning electron microscopy images of (a) pristine PSU membrane, (b) PSU membrane with azide-functionalized CNT and (c) modified PSU membrane with azide-functionalized CNT via click reaction.

Surface of the click reaction modified membrane appears to be rougher than the unmodified membrane from the FE-SEM images. Surface of click reaction modified membrane has less porous structure as compared to unmodified membrane, which can be attributed to the formation of the triazole. Cross-section of the click reaction modified membrane shows more voids like asymmetric structure. The surface shows less porous structure, however the cross section of the membrane shows sponge like as well as macro voids with irregularities which facilitates porosity to the membrane. Therefore, it can be concluded that after the modification surface morphology alters however no significant change observed in bulk morphology of the modified membrane. As the roughness of the membrane increases following the click reaction that took place on the membrane surface, which generates more functional groups, the surface of the membrane shows significantly changed morphology. Bulk morphology is defined here as the cross section of the membrane that remains unchanged after the click reaction.

3.3. Atomic force microscopy

The morphology of the membrane illustrated from the AFM images (Fig. 4), gives the information about the surface roughness (S_a) of the membranes along with other parameters like root mean square (S_q), peak-to-peak (S_y), ten-point height (S_z), surface skewness (S_{sk}) and coefficient of kurtosis (S_{ka}), which is shown in Table 1.

Surface roughness is important parameter for the membrane surface studies, which describe the interaction of membrane surface with other components. The click reaction modified membrane showed higher average surface roughness than the unmodified membrane, which can be seen in Fig. 4. The other parameters like root mean square (S_q), which is standard deviation of height of the peak and peak-to-peak height (S_y), ten-point height (S_z) which gives the difference between the highest and lowest peak also increases after the modification. This indicates that there are many valleys and peaks available on the membrane surface. However, surface skewness (S_{sk}) and coefficient of kurtosis (S_{ka}) decreases. Surface skewness indicates the asymmetry in the height distribution, here in this membrane surface skewness is less than zero means that the membrane has porous surface and also the more valleys available than the peaks. Modified membrane surface skewness further decreases than the unmodified membrane, which also illustrates that the larger number of valleys available. Coefficient of kurtosis describes the sharpness of the highest peak, which is less than 3 in these membranes, indicates that there is a broad and heterogenous height distribution of the peaks on the membrane surface. After the modification

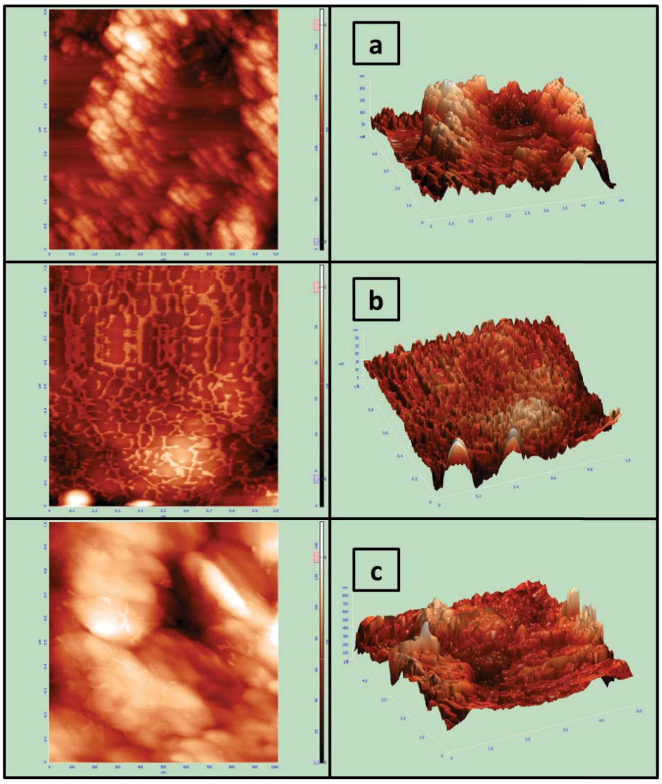

Fig. 4. Atomic force microscopy images of (a) pristine PSU membrane, (b) PSU membrane with azide-functionalized CNT and (c) modified PSU membrane with azide-functionalized CNT via click reaction.

Table 1
Roughness parameters of the membranes

Membranes	Average roughness, S_a (nm)	Root mean square, S_q (nm)	Peak-to-peak, S_y (nm)	Ten-point height, S_z (nm)	Surface skewness, S_{sk}	Coefficient of kurtosis, S_{ka}
PSU/M1	18.56	23.10	135.53	68.39	–0.05	–0.32
PSU/Az-M10	6.43	8.18	33.51	16.82	0.99	2.69
PSU/Caz-M10	17.15	21.76	155.16	77.59	–0.42	0.47

the coefficient of kurtosis decreases, which shows the more heterogenous height distribution than the unmodified membrane. These parameters explains that the membrane topography shows significant changes after the modification as the surface roughness increases but the peak height distribution becomes heterogenous, which means the surface have more blunt peaks. However, the unmodified membrane has more sharp peaks as well as less valley, whereas a modified membrane has more valleys and less peaks [46–49], which can also be shown in scanning electron microscopy (SEM) images (Fig. 3). A polysulfone membrane with azide-CNT shows less surface roughness than the pristine polysulfone membrane as expected, which indicates that the membrane becomes smoother after the addition of azide-functionalized CNT. However, after the modification of the polysulfone incorporated with azide-CNT membrane via click reaction, surface roughness increases due to formation of triazole moiety on the membrane surface. These results support that surface modification of the membrane has occurred.

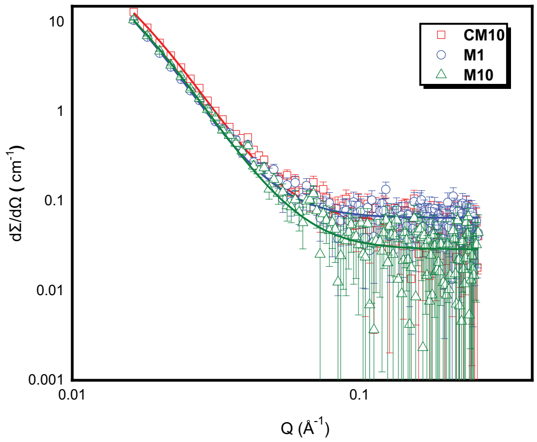

Fig. 5. SANS profile of pristine PSU (M1), 1 wt.% Az/PSU (M10) and click reaction modified 1 wt.% Az/PSU (CM10) membrane soaked in D_2O.

3.4. Small-angle neutron scattering

The SANS profiles of pristine and modified membranes are shown in Fig. 5. As shown in Table 2, pristine polysulfone membrane has 9.2 nm pore radius whereas the polysulfone incorporated with azide-functionalized MWCNT has 8.5 nm pore radius, which slightly decreases after the addition of the functionalized MWCNT and further reduced (8.1 nm) after click reaction on the membranes containing azide functional group on the surface. This may be attributed to the parallel alignment and uniform distribution of the nanotubes among the polysulfone matrix, which is in agreement with the previous studies. SANS is novel technique for the membrane characterization, where pore size, polydispersity of pores among the membrane surface as well as correlation length, which is the distance between the two pores are obtained. Here, in SANS data the scattering intensities for the different membrane samples are presented in the arbitrary unit and shifted vertically for the clarity of the presentation. Two models are considered, first, where the pores were considered to be spherical and surrounded by a matrix material, which is called the polydisperse sphere model and second, where the first phase is the pores and the second phase the surrounding matrix material, called the random two-phase model. This membrane SANS data follows the second model, which data are presented in Fig. 5 [50–52]. Consequently, there is possibility of further surface modification due to the availability of azide functional group on the membrane surface. The click reaction modified membrane shows higher metal rejection which may be due to the presence of triazole group. This subtle decrease in pore size after the modification supports the higher metal rejection for modified membrane than the unmodified membrane. Polydispersity is a dimensionless parameter, which is related to the size and distribution of the pores on the membrane surface. Here, polydispersity is found same for pristine, unmodified and modified membranes, which implies that non-uniform or polydisperse distribution of the pores with same pore size within the membrane. SEM images of the membrane surface support this explanation, that the pores appear to be in spherical shapes with inconsistent pore size distribution (Fig. 4).

Table 2
SANS data of the membranes soaked D_2O

Membrane	Pore radius (nm)	Polydispersity (σ)
PSU/M1	9.2	0.45
PSU/Az-M10	8.5	0.45
PSU/Caz-M10	8.1	0.45

3.5. Hydrophilicity of the membranes

Hydrophilicity of the membrane also enhances for the click reaction modified membrane, which supports the antifouling characteristics. The contact angle value was found to be 54.30° for PSU/azide-CNT which decreases to 34.48° for the click reaction modified membranes. Membrane becomes more hydrophilic after the modification as can be observed by the contact angles as shown in Fig. 6 [53,54].

3.6. Surface free energy of membranes using contact angle

Surface free energy is an important parameter of the solid surface which describes the membrane surface wettability and adhesion properties. Surface energy of the membrane was calculated by measuring the contact angle of the membrane via sessile drop method and using the Young–Dupres equation:

$$\left(1+\cos\theta\right)\gamma_L = W_A = \text{work of Adhesion or Surface energy} \quad (4)$$

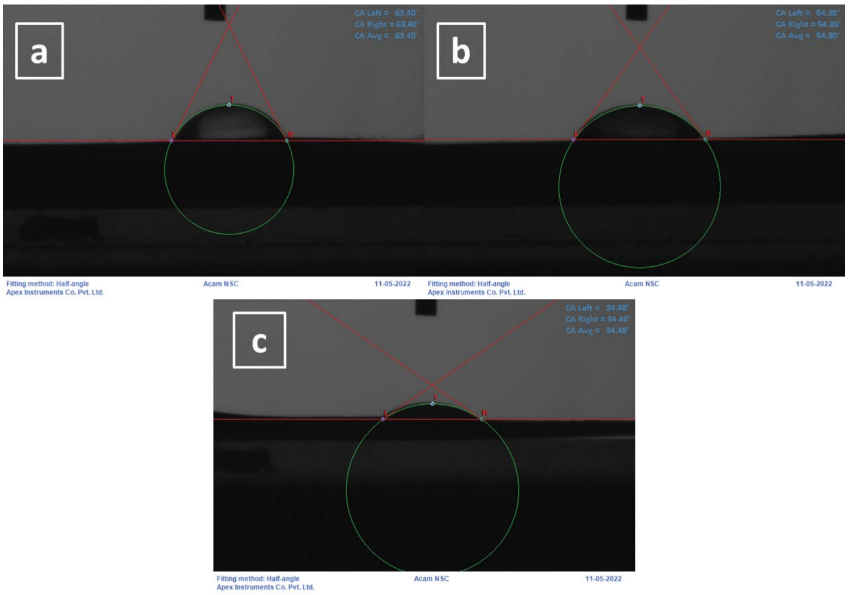

Fig. 6. Contact angles of the membrane.

Table 3
Contact angle of membrane and surface energy

Membrane	Contact angle	Surface energy (mJ/m^2)
PSU/M1	63.40	105.39
PSU/Az-M10	54.30	115.28
PSU/Caz-M10	34.48	132.81

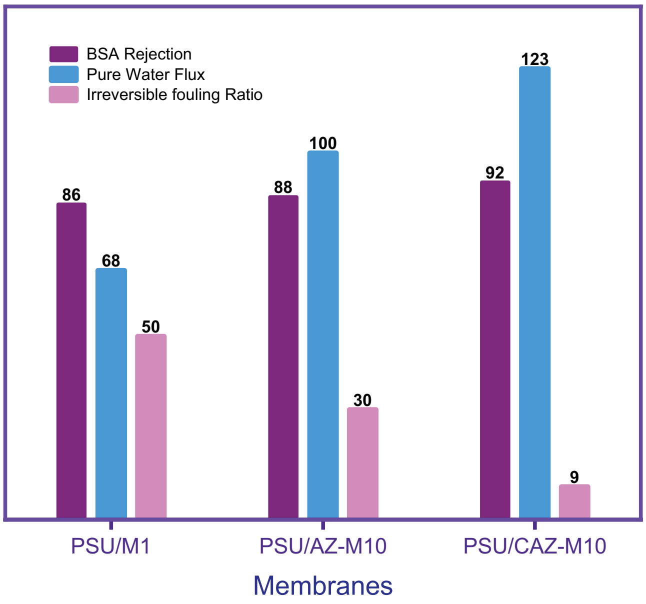

Fig. 7. Representation of fouling properties of the membranes.

Here, work of adhesion or surface energy is defined in this context as the work required to pull a water droplet from a square metre area of membrane surface, and γ_L is the surface tension of water which is 72.8 mJ/m^2. For the calculation of the surface energy of the membrane, the water contact angle (θ) must be measured at least three times using the sessile drop method [55,56]. Using the above equation surface energy was calculated and is reported in Table 3 below. From the table it seen that surface energy increase after the modification due to the decrease of contact angle. This explains that wetting property as well as adhesion of membrane is enhanced after the modification. Modification facilitates the polar functionalities on membrane surface. The contact angle decreases because the polar triazole group is introduced on the surface of membrane and hence surface energy increases. The rise in surface energy of membrane suggests that the surface become more active to pull water droplet towards the membrane surface.

3.7. Antifouling study of the membranes

BSA protein has been used to study antifouling properties of the membranes. As shown in Fig. 7, the fouling of the membrane drastically decreases after the surface modification. Pristine polysulfone membrane shows 86% rejection of BSA with 50% flux recovery ratio and irreversible fouling ratio as well, which further improves after the addition of azide-functionalized CNT, gives 88% of BSA rejection with enhanced flux recovery ratio 70% and 30% irreversible fouling. After the click reaction modification of polysulfone/azide-CNT membrane rejection of BSA increases up to 92%, flux recovery ratio also increases as well as irreversible fouling considerably decreases to 9%. Therefore, it explains as the addition of azide-CNT antifouling properties are enhanced, which is much improved after the surface modification, due to the triazole moiety on the surface of the click reaction modified membrane. Although the surface roughness increases fouling decreases, which is quite critical to explain. But as illustrated in the surface parameters that after modification there are less peaks compared to valleys on the modified membrane so there is no specific site available for the deposition of the protein on the surface. Therefore, modified membrane can easily be cleaned by simple washing. In simple words surface roughness affects the fouling property of the membrane, but because of the surface modification fouling decreases even though the surface roughness increases [25,39].

Table 4
% Rejection of metals of pristine polysulfone membrane along with unmodified and modified polysulfone/azide-CNT membrane

Membranes	% Rejection of heavy metals		
	Cu(II)	Pb(II)	Cr(VI)
PSU/M1	77.0 ± 1.5	47.0 ± 1.4	37.0 ± 1.3
PSU/Az-M10	96.0 ± 1.8	81.0 ± 1.2	89.0 ± 1.7
PSU/Caz-M10	98.0 ± 1.0	90.0 ± 1.5	95.0 ± 1.6

3.8. Heavy metal rejection

Heavy metal rejection study carried out on both click reaction modified and unmodified membranes at 50 psi transmembrane pressure in the membrane filtration cell. The percentage rejection studies of membrane with selected heavy metals are shown in Table 4.

From Table 4, rejection of heavy metals showed that the modification increases the rejection percentage. For the pristine polysulfone membrane heavy metal rejection is lower than the polysulfone/azide-CNT membrane. Modified membrane shows 99% rejection of the Cu(II), which is higher than the unmodified membrane, because of the presence of triazole ring on the surface of the membrane The separation or rejection of the heavy metal ions due to the adsorption as well as complexation ability of heavy metal with azide and triazole functional groups on membrane surface. It also reported that the because of the addition of azide-CNTs and presence of azide and triazole function groups the adsorptive nature of the membrane enhanced [40]. Triazole ring acts as a soft ligand with strong π acceptor interaction and weaker σ donor interaction, it is found to have higher complexation ability for Cu(II). Due to the same reasons other metals like Pb(II) and Cr(VI) also give higher rejection after the surface modification of the membrane via click reaction. As can be seen copper is selectively rejected at higher percentage. It is essential to note that copper pollution is a major concern due to its toxicity in the environment. Apart from this copper also contaminates drinking water due to corrosion in water pipes and modified membranes could be an effective solution in wastewater treatment.

4. Conclusions

Polysulfone/azide-CNT mixed matrix membrane was successfully modified via the click reaction using copper as catalyst and 1-pentyne. This cycloaddition reaction formed a 1,2,3-triazole ring on the surface of the membrane which has a good complexation ability with metals. After this modification hydrophilicity and antifouling property of the membrane has improved. Also due to the triazole moiety on the surface heavy metal rejection is enhanced. The modified membrane can be used for the selective removal of copper from contaminated water because the rejection of copper was found to be higher in this membrane, which can be used in places such as industries where copper pollution is a major concern. The bulk morphology of the modified membrane remains unchanged after the modification. Wetting and adhesion of the membrane also increases after the modification.

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