Membrane and Water Treatment, *Vol. 15, No. 3 (2024) 139-152*
https://doi.org/10.12989/mwt.2024.15.3.139

Tuning the surface charge of mixed matrix membranes using novel chemistry

Priyanka Mistry[a] and C.N. Murthy*

Macromolecular Materials Laboratory, Applied Chemistry Department, Faculty of Technology and Engineering,
The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India, 390001

(Received May 27, 2024, Revised July 24, 2024, Accepted July 24, 2024)

Abstract. Mixed matrix membranes have gained significant recognition in the wastewater treatment industry for their effectiveness in removing dyes, proteins, and heavy metals from water sources. Researchers have developed an innovative technique to enhance properties of these membranes by incorporating amine-functionalized carbon nanotubes into the polymer matrix. This approach introduces amine functional groups onto the membrane surface, which are then modified with trimesoyl chloride and cyanuric chloride. The modified membranes are characterized by XPS to confirm successful bonding of amines with the trimesoyl chloride and cyanuric chloride. The surface charge of the modified membrane also plays a role in the modification process; the membrane modified with trimesoyl chloride has a negative surface charge, while the one modified with cyanuric chloride has a more positive charge. At the same acidic pH, the positive or negative charge of the mixed matrix membranes assists in enhancing the rejection of heavy metals. This results in improved antifouling properties for both modified membranes. The heavy metal rejection for all modified membranes is higher than for unmodified membranes, due to both adsorption and complexation abilities of the functional groups on the membrane surface with heavy metal ions. As the membrane surface functionalities increase through modification, the separation due to complexation also increases. The bulk morphology of the membrane remains unchanged, while roughness slightly increases due to the surface treatment.

Keywords: antifouling property; bulk morphology; heavy metal rejection; mixed matrix membrane; surface charge

1. Introduction

Heavy metals, such as mercury, cadmium, chromium, copper, lead, and arsenic, can be highly toxic even at low content, originating from industrial processes and natural sources. Effective regulation and remediation efforts are crucial to mitigate their impact on ecosystems and human health (Briffa *et al*. 2020, Jaishankar *et al*. 2014, Kumar *et al*. 2021, Qasem *et al*. 2021, Tchounwou *et al*. 2012). Membrane filtration, including nanofiltration and reverse osmosis, efficiently removes heavy metals like lead and copper from wastewater. Factors affecting efficacy include pH, ionic strength, and membrane type. Surface charge modification and temperature optimization enhance rejection efficiency. Recent research has highlighted the effectiveness of modified polysulfone nanofiltration membranes in the efficient seperation of heavy metals and salts from wastewater, particularly at elevated temperatures (Al-Rashdi *et al*. 2013, Gholami *et al*. 2022, Samavati *et al*. 2023).

Recent research focused on mixed matrix membranes, particularly those incorporating carbon nanotubes, as a promising solution for heavy metal removal. Comprehensive assessments also highlight advancements in nanofiltration and adsorptive nanocomposite membranes for effectively removing heavy metal-contaminated water sources (Alotaibi *et al*. 2021, Chandrashekhar Nayak *et al*. 2020, Damiri *et al*. 2022, Ibrahim *et al*. 2020, Mahmoud and Mostafa, 2023, Pandey *et al*. 2022, Wang *et al*. 2023). Functionalized carbon nanotubes are incorporated into the polysulfone matrix to introduce crucial functional groups facilitating heavy metal rejection through processes like adsorption or complexation. These functional groups enable additional modifications on the membrane surface, enhancing metal rejection by increasing the number of functionalities. Techniques such as click chemistry, combined with reversible addition-fragmentation chain transfer radical polymerization, offer novel approaches to graft functional groups onto membrane surfaces, improving separation characteristics and antifouling properties (Gupta *et al*. 2015, Nikita *et al*. 2019a, b, 2020, 2022, Shah and Murthy 2013, Upadhyaya *et al*. 2018, Wu *et al*. 2012).

The enhancement of the separation and antifouling properties of membranes involves the utilization of trimesoyl chloride (TMC) and cyanuric chloride for surface modification. TMC is commonly used as a monomer to create thin film composite (TFC) membranes (Farahbakhsh *et al*. 2021). On the other hand, cyanuric chloride enables the formation of a polymer that lacks hydrolysis-prone amide bonds, resulting in enhanced membrane stability (Elshof *et al*. 2021). Interfacial polymerization is a widely employed technique for membrane modification. For instance, TMC in combination with 1,3,5-(tris-piperazine)-triazine was used to fabricate poly(s-triazine-amine) NF membranes (Lee *et al*. 2017). Another method involved manipulation of the properties and performance of polyethyleneimine nanofiltration membranes through the

---

*Corresponding author, Ph.D., Professor
E-mail: chivukula_mn@yahoo.com
[a] Ph.D. Student, E-mail: pm35315@gmail.com

http://www.techno-press.org/?journal=mwt&subpage=7

ISSN: 2005-8624 (Print), 2092-7037 (Online)

use of polyethylenimine-dextran conjugate (Bera *et al*. 2016). Systematic characterization of the modified membranes was conducted to evaluate the changes in properties and separation performance, with experimental results indicating an overall improvement in membrane performance.

Both cyanuric chloride and trimesoyl chloride offer distinct advantages in the field of membrane modification. Cyanuric chloride is recognized for its stability and pH-resistance, making it a favourable option. On the other hand, trimesoyl chloride finds widespread use in the fabrication of thin film composite (TFC) membranes. Trimesoyl chloride offers several advantages in membrane modification, including its widespread application in the fabrication of thin film composite (TFC) membranes, utilization in interfacial polymerization techniques, and the ability to enhance membrane properties and performance. However, it is important to consider the limitations associated with trimesoyl chloride. These limitations include concerns regarding toxicity, high costs, and challenges related to handling and disposal. The selection of the appropriate monomer depends on the specific application requirements and the desired properties of the membrane. The utilization of cyanuric chloride for membrane modification presents certain drawbacks, such as its limited reactivity and the relatively limited amount of research conducted in comparison to other monomers. Nevertheless, limitations in reactivity can be overcome by combining cyanuric chloride with various amines. It is important to note that the application of cyanuric chloride in membrane modification is a relatively recent research area, and there is still much to explore its performance and properties in comparison with other monomers.

In this work a polyether sulphone and polysulphone/ amine-MWCNTs mixed matrix membrane having an amine functional group on the membrane surface was treated with trimesoyl chloride and cyanuric chloride for surface modification. The reaction mechanism between trimesoyl chloride and an amine involves nucleophilic addition-elimination. The amine functional groups on the membrane surface act as nucleophiles, attacking the electrophilic carbonyl carbon of trimesoyl chloride. This led to the formation of an amide linkage on the surface of the membrane. In contrast, the reaction between cyanuric chloride and amines follows a nucleophilic substitution mechanism. Nucleophiles, such as amine groups on the membrane surface, easily displace chloride ions in cyanuric chloride. However, under the extreme pH conditions encountered in industrial operations, the amide bonds (C=O or C-N) in the membranes are susceptible to attack and degradation by H^+ and OH^- ions. This hydrolysis process leads to the production of amidogen and carboxyl groups, resulting in a significant reduction in the membrane rejection performance (Dalwani *et al*. 2011a, 2011b). To address this issue, researchers have explored the use of cyanuric chloride (CC) as an alternative monomer to trimesoyl chloride (TMC) to develop pH-stable organic polymer nanofiltration (NF) membranes. In this approach, a compact polyamidoamine layer is created on the surface of the selective layer to protect it from H^+ and OH^- attack. The mechanism behind this protection involves electron-donating groups and electron-withdrawing groups, which can hinder the vulnerability of the amide bond to attack by H^+ or OH^- ions under acidic or alkaline conditions (Lee *et al*. 2015, Wang and Wang, 2016). We conducted a study where we tuned the surface charge of a mixed matrix membrane by using polyethylenimine (PEI), resulting in a positive charge on the membrane surface due to the presence of amine functional groups. Under acidic pH conditions, this positively charged mixed matrix membrane exhibited enhanced heavy-metal rejection and improved antifouling properties (Mistry and Murthy 2023).

The novel aspect of this research is the focus on improving the membrane functionality through straight-forward chemical reactions using trimesoyl chloride and cyanuric chloride to modify the membrane surface. The primary purpose of membrane surface modification is to increase the functionality of the membrane surface and tune the surface charge, which in turn enhances its ability to efficiently reject heavy metals and provides other desirable properties, such as antifouling. By modifying the surface of the membrane, 1,3,5-triazines and 1,3,5-benzenetricarbonyls functional groups with an affinity for heavy metals can be incorporated. These functional groups can selectively interact with heavy metal ions, facilitating their adsorption and retention on the membrane surface due to the surface charge. This allows for effective separation and removal of heavy metals from the feed solution passing through the membrane. The presence of these functionalities enhances the separation characteristics of the membrane, leading to improved heavy metal rejection efficiency. In addition to improving heavy metal rejection, surface modification can enhance the antifouling properties of the membrane.

2. Experimental section

2.1 Materials

Polyether sulphone (PES) (ULTRASON E6020 with M_w 72000 g mol^{-1}) and Polysulphone (PSU) (ULTRASON S6010 with M_w 62000 g mol^{-1}) purchased from Permionics Membranes Pvt. Ltd. Vadodara, India. Multiwalled Carbon nanotubes (MWCNT) (Purity: >99%, Average Diameter: 10-15 nm, Average length: 5 µm surface area: 400 m^2/g) purchased from Ad-nano technologies private limited, Shimoga, Karnataka, India, Trimesoyl Chloride (TMC, 98%) and Cyanuric chloride (CC, 99%) were purchased from Sigma-Aldrich, Thionyl chloride, Ethylenediamine, Sodium hydroxide (NaOH), Dimethyl Formamide (DMF), Hexane were purchased from Loba Chemie Pvt Ltd.

2.2 Membrane preparation

18% dope solutions of PES (polyether sulphone) and PSU (polysulfone) were prepared by dissolving in Dimethyl formamide, which served as the solvent. As fillers, 1% of amine-functionalized MWCNT (multi-walled carbon nanotubes), prepared based on a previous study, were added to the polymeric dope solution. To prepare the membranes, these dope solutions were cast onto a glass plate using an applicator and then submerged in a coagulation bath. Following the wet phase inversion technique, the membranes were formed. Subsequently, the prepared membranes were

Table 1 A comparative case study of membranes in relation to our previous research

Membrane Type	Heavy Metals Rejection Rate	Key Findings	Ref.
Pristine Membranes PES PSU PSU/f-MWCNT Mixed Matrix Membranes PES/f-MWCNT Mixed Matrix Membranes	~10-15 % ~20-25 % ~93-95 % ~90-94 %	The use of pristine membranes, which have larger pore size and lack functional groups, results in lower heavy metal rejection despite the high pure water flux. The incorporation of f-MWCNTs into the polymeric matrix improved the rejection of heavy metals, resulted in smaller pore size but higher porosity, which led to increased pure water flux, and functional groups were present on the membrane surface.	(Gupta *et al*. 2015, Nikita *et al*. 2019a, b, 2022, Shah and Murthy 2013)
Click modified PSU/Az-MWCNT Mixed Matrix Membrane Click modified PES/Az-MWCNT Mixed Matrix Membrane	~95-98 % ~92-96 %	The membranes that have azide groups attached to them undergo a click reaction to form a triazole ring, which improves their ability to reject heavy metals and prevents fouling compared to unmodified membranes	(Mistry *et al*. 2023, Nikita *et al*. 2020)
PES/Ox-CNT membrane modified with polyethylenimine (PEI) PSU/Ox-CNT membrane modified with polyethylenimine (PEI)	~92-98% ~93-98%	The membrane having a carboxylic functionality on the surface treated with polyethylenimine (PEI), and forms amide linkages. Amines groups introduced on the membrane surface which facilitates the positive charge on the membrane surface	(Mistry and Murthy 2023)
PES/Am-CNT membrane modified with trimesoyl chloride (TMC) PSU/Am-CNT membrane modified with trimesoyl chloride (TMC) PES/Am-CNT membrane modified with cyanuric chloride (CC) PSU/Am-CNT membrane modified with cyanuric chloride (CC)	~97-99 %	The membrane, which had amine functional groups on its surface, was chemically modified using TMC and CC. This modification introduced both 1,3,5-triazines and 1,3,5-benzenetricarbonyls functional groups to the membrane surface, resulting in enhanced heavy metal rejection as well as antifouling properties due to surface charge	This Article

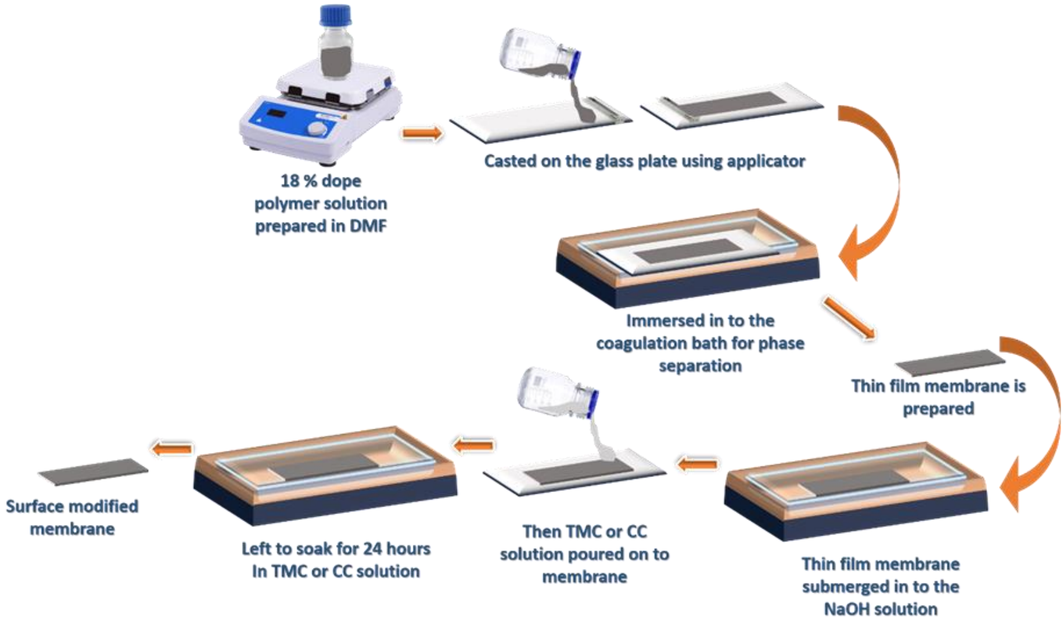

Fig. 1 Schematic diagram of membrane preparation and surface modification using TMC and CC

washed with deionized water to remove any residual solvent. Afterward, it was air dried for 24 hours and subjected to further surface modification.

2.3 Surface modification of membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

The surface modification process of polyether sulphone and polysulphone/amine-MWCNTs mixed matrix membranes involves the use of trimesoyl chloride (TMC) and cyanuric chloride (CC) as follows. As shown in Fig. 1, Initially, the prepared mixed matrix membranes were immersed in a 0.01 M NaOH solution, where NaOH acts as an acid receptor. This step helps deprotonate the amine groups on the membrane surface, rendering them more nucleophilic and facilitating their reaction with trimesoyl chloride and cyanuric chloride (Zhou *et al*. 2014). Subsequently, any excess NaOH solution was removed using a rubber roller. Subsequently, an organic solution containing 1% of trimesoyl chloride and cyanuric chloride was poured onto

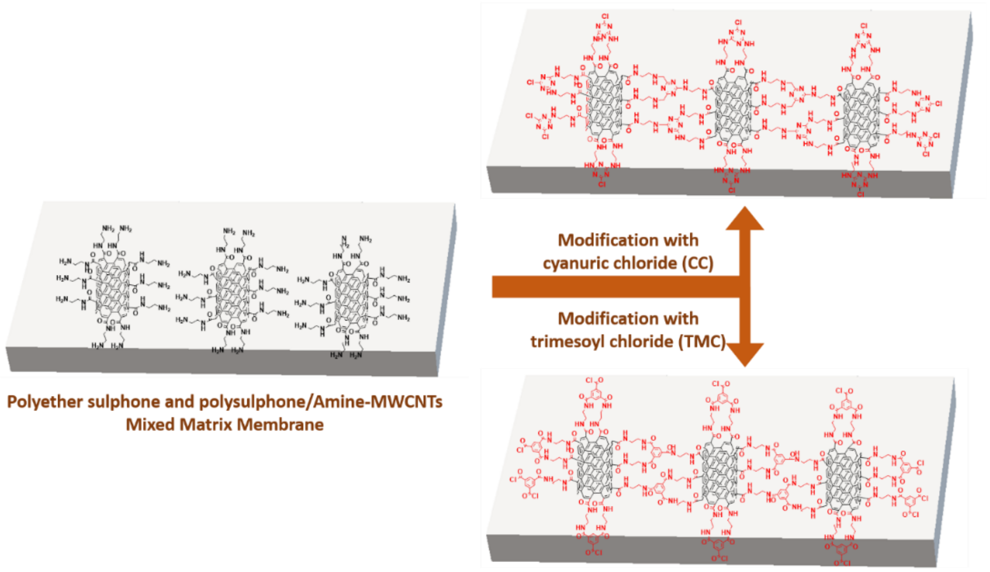

Fig. 2 Surface Modification of membranes with cyanuric chloride (CC) and trimesoyl chloride (TMC)

Table 2 Composition of prepared membranes

Membranes	Composition
Pristine PES	Pristine polyether sulphone
Pristine PSU	Pristine polysulphone
PES/Am-CNT	Polyether sulphone mixed matrix membrane incorporated with amine functionalised multiwalled carbon nanotubes
PSU/Am-CNT	Polysulphone mixed matrix membrane incorporated with amine functionalised multiwalled carbon nanotubes
PES/Am-CNT/TMC	PES/Am-CNT membrane modified with trimesoyl chloride (TMC)
PSU/Am-CNT/TMC	PSU/Am-CNT membrane modified with trimesoyl chloride (TMC)
PES/Am-CNT/CC	PES/Am-CNT membrane modified with cyanuric chloride (CC)
PSU/Am-CNT/CC	PSU/Am-CNT membrane modified with cyanuric chloride (CC)

the membrane surface and left to soak for approximately 24 hours. Once again, excess organic solution was eliminated from the membrane surface using a rubber roller. The membrane was then allowed to air dry at room temperature, to ensure the complete evaporation of the organic solvent. The resulting modified membrane was thoroughly washed with distilled water and stored in distilled water until use. The reaction takes place on the membrane surface after the surface modification shown in Fig. 2.

2.4 Characterisation

The modified and unmodified polyether sulphone and polysulphone/amine-MWCNT mixed matrix membranes surface functional groups of both modified and unmodified membranes with sample size 8 mm X 2 mm were analysed using Physical Electronics PHI 5000 VersaProbe III X-ray Photoelectron spectrophotometer. The zeta potential of the modified and unmodified membranes was measured using SurPass electrokinetic analyser (Anton Paar GmbH, Austria). Rejection of heavy metals and bovine serum albumin (BSA) protein was performed on stainless steel membrane test cell fabricated in house. A membrane with the surface area 0.00785 m^2 placed in to the membrane test cell, and the metal or protein solution was passed through the cell using a pump. Membrane cell usually stabilize for 1 hour at a transmembrane pressure of 50 psi for membrane compaction and a stable feed flow rate, which is 20 ml/min. The filtration experiments were carried out in cross-flow mode to minimize membrane stress and remove some trapped particles. For the separation experiments, solutions of metallic salts including potassium dichromate, copper sulphate, lead nitrate, calcium chloride, and mercuric chloride were prepared at a concentration of 1000 ppm.

The rejection of heavy metal and protein was calculated by following formula:

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

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®. Concentration of the bovine serum albumin (BSA) protein is determined using the UV spectrophotometer.

The fouling behaviour of the membrane was examined using a 1 ppm aqueous solution of bovine serum albumin

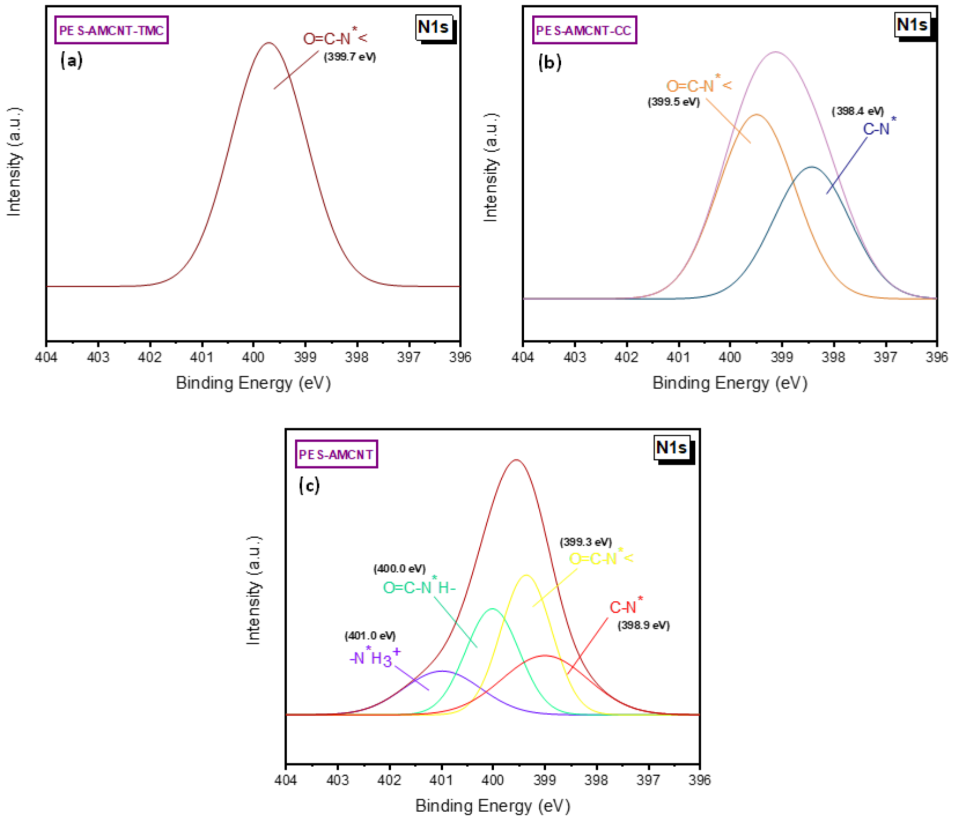

Fig. 3 N1s XPS spectra of (a) modified polyether sulphone/amine-MWCNT membrane using TMC (b) modified polyether sulphone/amine-MWCNT membrane using CC (c) unmodified polyether sulphone/amine-MWCNT membrane

(BSA). After rejection of BSA through the membrane, it was backwashed with distilled water for 30 minutes and the flux (J_2) was measured. The Flux Recovery Ratio (FRR) and Irreversible Fouling Ratio (Rir) were measured using the following formulas, and the antifouling performance of the membranes was investigated.

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

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

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.

4. Result and discussion

4.1 X-ray Photoelectron Spectroscopy (XPS)

The N1s XPS spectra for both the unmodified and modified polyether sulphone/amine-MWCNT mixed matrix membranes are presented in the Fig. 3. The unmodified polyether sulphone/amine-MWCNT mixed matrix membrane exhibits four distinct peaks in the X-ray photoelectron spectroscopy (XPS) analysis: 399.3 eV for O=C-N*, 398.9 eV for C-N*, 400.0 eV for O=C-N*H-, and 401.0 eV for protonated NH_2 ($-NH_3^+$) (Fig. 3(c)) (Deng *et al.* 2021, Dwight *et al.* 1981). After undergoing modification with trimesoyl chloride and cyanuric chloride, the peaks at 400.0 eV and 401.0 eV disappear. When examining the modified membranes, the trimesoyl chloride-treated membrane displays a single peak at 399.7 eV, attributed to O=C-N*, indicating the formation of an amide bond on the surface (Fig. 3 (a)). On the other hand, the membrane treated with cyanuric chloride shows two peaks at 399.5 eV and 398.4 eV, attributed to O=C-N* from the amide linkage and C-N* arising from the triazine ring of cyanuric chloride respectively (Fig. 3 (b)) (Chen *et al.* 2019). Similarly, the N1s XPS spectra for the modified and unmodified polysulphone/ amine-MWCNT mixed matrix membrane exhibit similar peaks (Fig. 4 (a,b,c)). This suggests that the membrane surface containing amine functional groups has been successfully modified using trimesoyl chloride and cyanuric chloride. The XPS spectra provide a clear understanding of the modifications that occur on the membrane surface (Ghosh *et al.* 2008, Jiang *et al.* 2019, Lee *et al.* 2015, Liu *et al.* 2012).

4.2 Zeta potential studies

Zeta potential studies of unmodified and modified membranes were conducted with an adjustable-gap cell. The membranes were soaked in 0.1 M KCl water for 1 h. The membranes were cut to 2x1 cm size and fixed on the

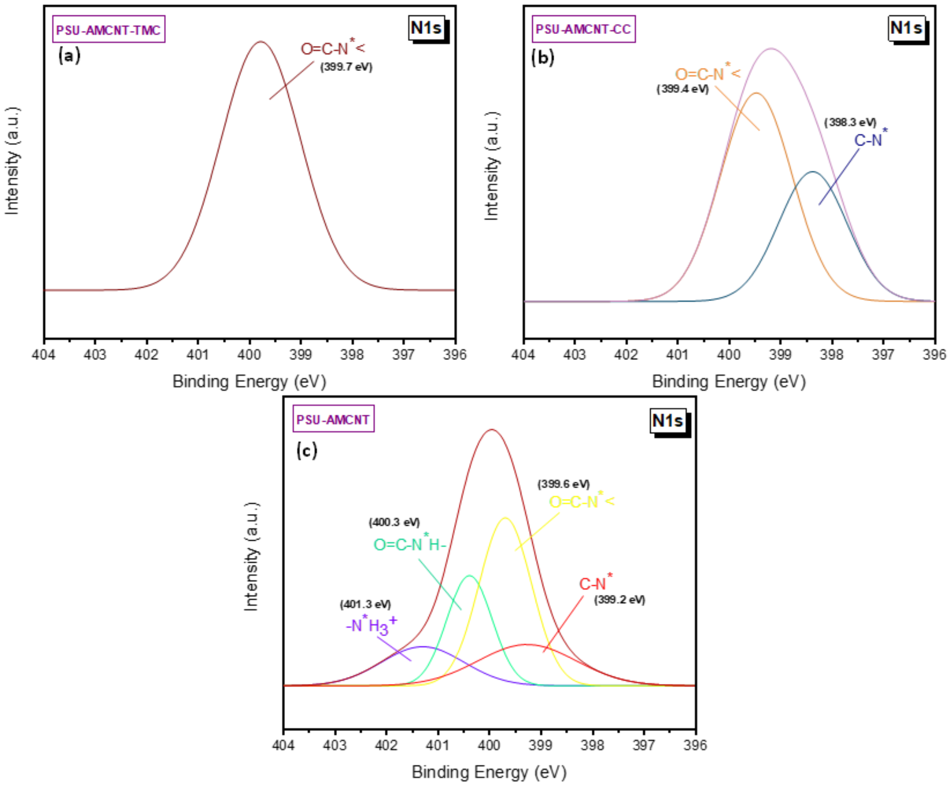

Fig. 4 N1s XPS spectra of (a) modified polysulphone/amine-MWCNT membrane using TMC (b) modified polysulphone/amine-MWCNT membrane using CC (c) unmodified polysulphone/amine-MWCNT membrane

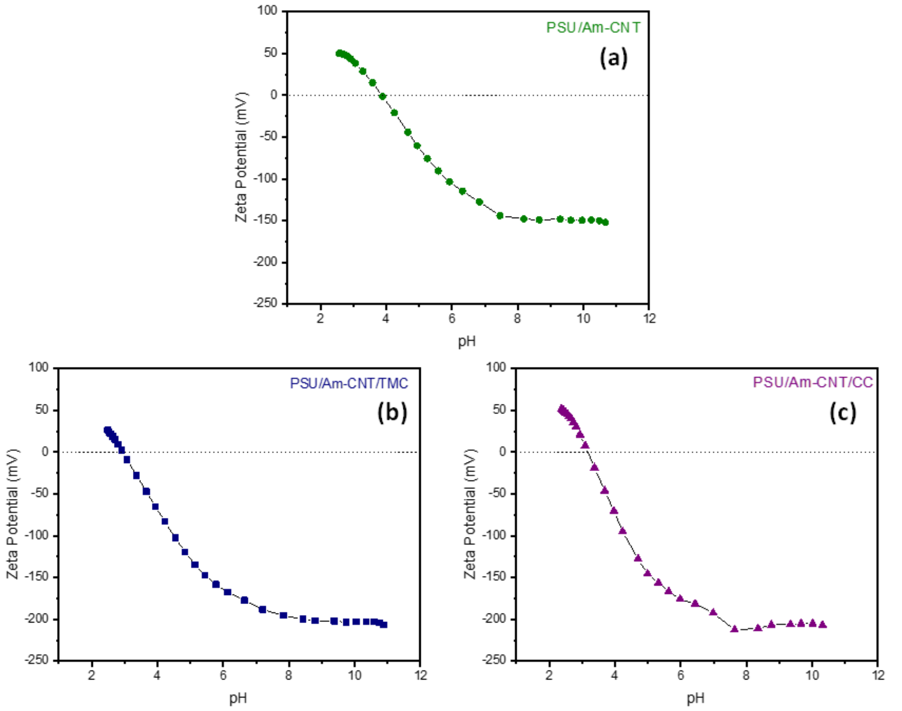

Fig. 5 Zeta potential of (a) unmodified polysulphone/Am-CNT membranes, (b) modified polysulphone/Am-CNT membranes with TMC, (c) modified polysulphone/Am-CNT membranes with CC

measurement holder using double-sided adhesive tape. 0.1 M KCl was used as the electrolyte. The pH of the electrolyte was increased to 11 by adding 1 M NaOH and was titrated against 0.05 M HCl for a sweep to pH 2-3. The streaming potential was measured by pumping the electrolyte by a pair of syringe pumps through the adjustable gap cell in both flow directions. The rinsing and flow check was performed at an increasing pressure of up to 300 mbar and the

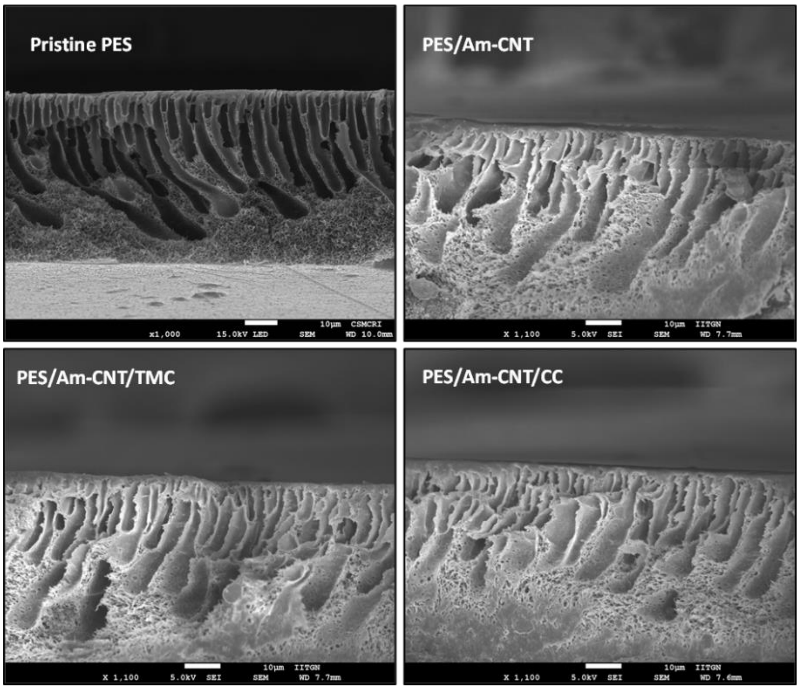

Fig. 6 (a) SEM images of unmodified and modified polyether sulphone/amine-MWCNT membrane

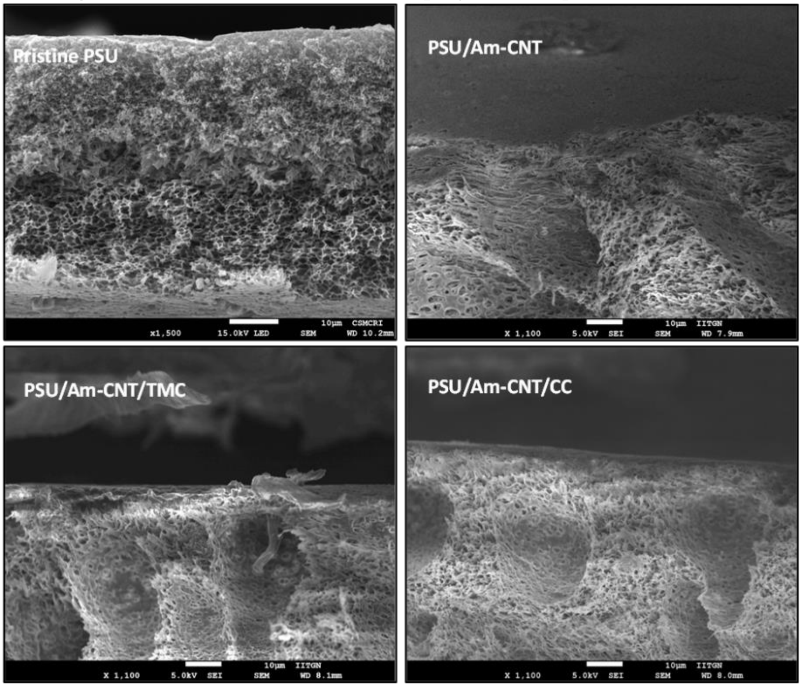

Fig. 6 (b) SEM images of unmodified and modified polysulphone/amine-MWCNT membrane

measurement was performed at 200 mbar. The pH and conductivity sensors were calibrated before the measurement. The zeta potential was obtained from the measured streaming potential in the SurPass software Attract (Anton Paar GmbH) based on Helmholtz–Smoluchowski equation. The zeta potential of unmodified and modified polysulfone mixed matrix membranes are presented in Fig. 5.

The isoelectric points of the membranes PSU/Am-CNT (3.86), PSU/Am-CNT/TMC (2.95), and PSU/Am-CNT/CC (3.17) indicate variations in their surface charge properties, which can affect their interactions with ions and particles in solution. For PSU/Am-CNT at low pH values, the zeta potential was observed to be positively charged. This observation can be attributed to the protonation of the amine groups on the membrane surface. As pH increased, the number of available protons decreased, leading to a gradual decrease in the positive zeta potential. This pH-dependent behaviour can be explained through the principles of acid-base equilibria, where amine groups are more likely to be protonated under acidic conditions (Gupta *et al.* 2015). When the PSU/Am-CNT membranes were treated with trimesoyl chloride, a significant change in the zeta potential behaviour was observed. Trimesoyl chloride

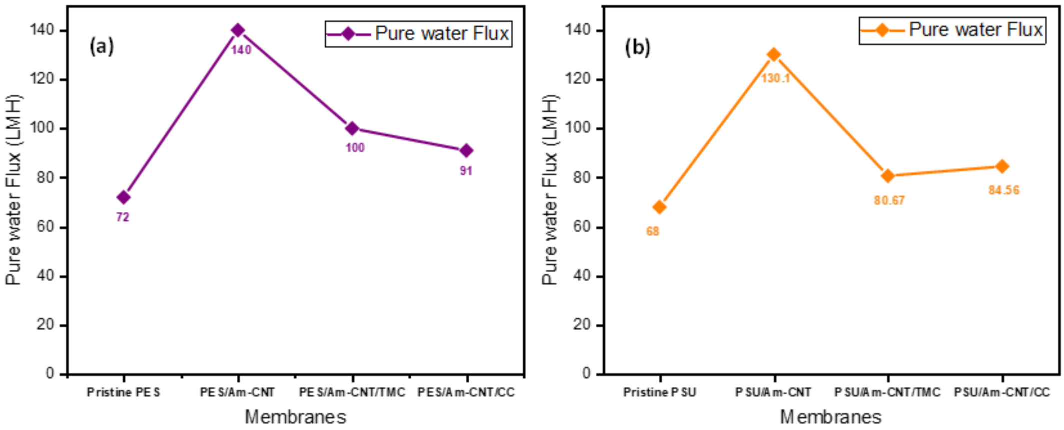

Fig. 7 Pure water flux of (a) Pristine, unmodified and modified polyether sulphone membranes (b) Pristine, unmodified and modified polysulphone membranes

introduces acyl functional groups to the membrane surface. These groups are susceptible to hydrolysis, which leads to the formation of carboxylic acid groups. Importantly, the carboxylic acid groups exhibited less positive zeta potentials, particularly at acidic pH values. This change in the zeta potential can be attributed to changes in the charge distribution caused by the conversion of the amine groups to carboxylic acid groups. Therefore, the membrane surface charge becomes less positive under acidic conditions. Conversely, when the PSU/Am-CNT membranes were modified with cyanuric chloride, a different zeta-potential change was observed. Cyanuric chloride introduces a nitrogen containing triazine ring structure on the membrane surface. This unique structure of triazine, possesses protonatable sites that can interact with protons, leading to an enhanced positive surface charge at low pH than acyl functional groups. This behaviour is consistent with the principles of pH-dependent protonation, in which triazine ring protonation enhances positive zeta potential. As a result, cyanuric chloride modification imparts a higher degree of positive charge to the membrane surface than those modified with trimesoyl chloride (Lee *et al*. 2015, Liu *et al*. 2012, Xie *et al*. 2011, Zhang *et al*. 2017, Zhou *et al*. 2014).

4.3 Permeation studies of modified and unmodified membranes

The pure water flux of the two types of membranes, Pristine PES with a finger-like structure (Fig. 6(a)) and PSU with a sponge-like structure (Fig. 6(b)), (Dong *et al*. 2021, Mistry *et al*. 2023, Nikita *et al*. 2020, Tan and Rodrigue, 2019) along with the incorporation of amine-functionalised CNTs (Am-CNT) and its surface modification with trimesoyl chloride, and cyanuric chloride are shown in Fig. 6. The pristine PES membrane possessed a finger-like structure, providing a relatively high initial water flux of 72 LMH (L/m²/h or LMH). This structure allows water molecules to pass through the membrane more easily, resulting in enhanced flux. On the other hand, the PSU membrane features a sponge-like structure, which exhibits a slightly lower pure water flux of 68 LMH. The differences in the flux of these two membranes can be attributed to their distinct morphological characteristics, with the finger-like structure of the PES allowing for greater water flow. For the PES mixed matrix membrane incorporated with Am-CNT (PES/Am-CNT), the water flux significantly increased to 140 LMH. The incorporation of Am-CNTs into the membrane matrix created nanochannels that facilitated water transport. This enhancement in water flux can be attributed to the increased surface area and altered pore size distribution, which reduced the flow resistance and improved permeability. Similarly, the PSU-Am-CNT membrane demonstrated enhanced water flux at 130.1 LMH compared to the pristine PSU membrane. This improvement was attributed to the creation of pores within the sponge-like structure, resulting in better water flow through the membrane.

Surface modification plays a crucial role in tailoring membrane properties. When the PES/Am-CNT membrane was modified with trimesoyl chloride, water flux decreased to 100 LMH. This reduction in flux can be attributed to the partial blockage of pores due to the surface reaction, which slightly reduced the effective pore size and increased resistance to water flow. Modification with trimesoyl chloride alters the surface chemistry and pore structure, impacting the overall water transport. While surface modification of the PES/Am-CNT with cyanuric chloride led to a flux of 91 LMH. The modification with trimesoyl chloride likely forms a less obstructive surface layer compared to cyanuric chloride, allowing for slightly improved water transport than pristine PES membrane, while still affecting the overall pore structure. For the PSU/Am-CNT membrane, surface modification with trimesoyl chloride resulted in a flux of 80.67 LMH. The impact of this modification on the water flux is more significant compared to PES, which are more affected by surface modifications. Cyanuric chloride modification of the PSU/Am-CNT membrane has a flux of 84.56 LMH. This modification likely interacts differently with the sponge-like structure compared to the finger-like structure of PES, leading to a moderate increase in the water flux. Although the pure water flux experiment lasted for 24 hours, there was minimal change observed in the pure water flux throughout.

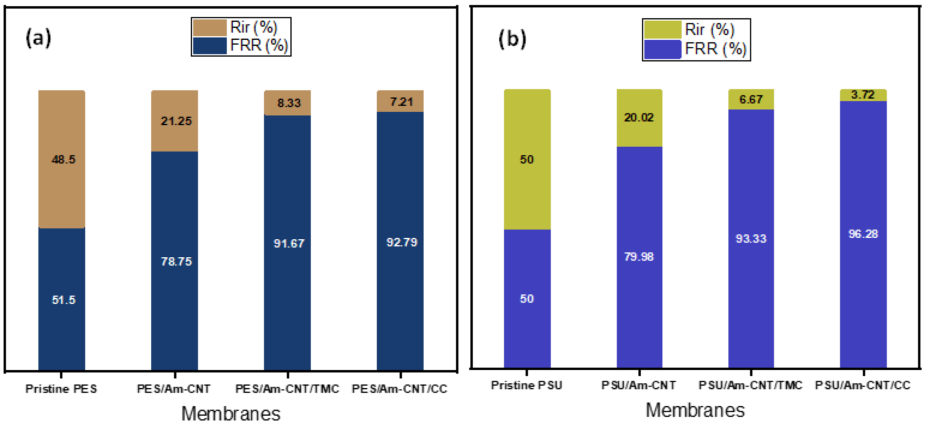

Fig. 8 Flux recovery ratio (FRR) and Irreversible Fouling ratio (Rir) (a) Pristine, unmodified and modified polyether sulphone membranes (b) Pristine, unmodified and modified polysulphone membranes

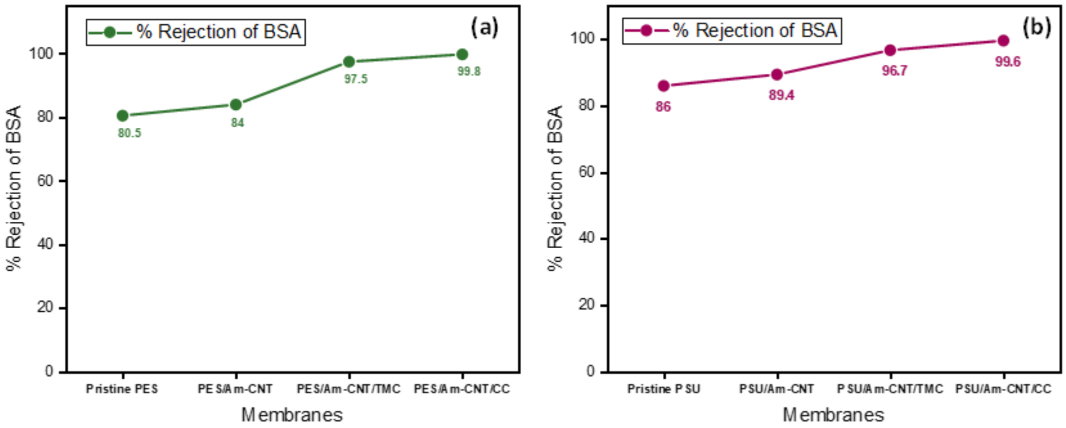

Fig. 9 BSA Rejection of (a) Pristine, unmodified and modified polyether sulphone membranes (b) Pristine, unmodified and modified polysulphone membranes

4.4 Antifouling studies

The Figs 8 and 9 show the flux recovery ratio (FRR) and irreversible ratio (Rir) and Bovine serum Albumin (BSA) rejection of the unmodified and modified membranes. These pristine membranes exhibited relatively low BSA rejection percentages (80.5% for pristine PES and 86.0% for pristine PSU) and reduced FRR (51.5% and 50%, respectively). Similar Rir values of 48.5% and 50% indicated comparable fouling over time. The introduction of amine-functionalised carbon nanotubes (Am-CNT) into PSU and PES membranes demonstrates a significant enhancement in performance of the membrane. PSU/Am-CNT exhibited a higher BSA rejection percentage (89.4%) and more substantial FRR (79.98%) and Rir (20.02%) compared to the pristine PSU membrane. The increased FRR suggests that the addition of amine-CNT is effective in inhibiting fouling, likely due to the ability of amine-CNT to alter surface characteristics and hinder foulant attachment. Similarly, PES/Am-CNT demonstrated improved BSA rejection (84.0%) and FRR (78.75%) and Rir (21.25%) compared to pristine PES. This result reaffirms that Am-CNT incorporation enhances membrane fouling resistance. It is important to note that the addition of Am-CNT significantly improved both BSA rejection and fouling resistance in these membranes. The surface modifications using trimesoyl chloride (TMC) and cyanuric chloride (CC) on the membrane surface with amine functional groups demonstrated more enhanced BSA rejection for PSU/Am-CNT/TMC is 96.7% and for PES/ Am-CNT/TMC is 97.5%, similarly for PSU/Am-CNT/CC and PES/Am-CNT/CC BSA rejection enhanced up to 99.6% and 99.8%, respectively. The FRR of 93.33% for PSU/Am-CNT/TMC and 91.67% for PES/Am-CNT/TMC underscores the success of the modification using TMC on the membrane surface. Same goes with the PSU/Am-CNT/ CC and PES/ Am-CNT/CC the FRR is 96.28% and 92.79%, respectively.

The antifouling characteristics of a membrane can be affected by its surface charge and surface roughness. In this context, the modified membranes exhibited a slightly increased surface roughness compared to the unmodified membranes (Gholami *et al.* 2022, Hebbar *et al.* 2018, Kang *et al.* 2007, Li *et al.* 2014, Mistry *et al.* 2023, Nikita *et al.* 2022, Sianipar *et al.* 2017, Wu *et al.* 2013). This change was attributed to the reaction between the amine functional groups on the membrane surface and trimesoyl chloride and cyanuric chloride. However, it is important to note that the surface charge also plays a significant role in determining

Table 3 Heavy metal rejection of unmodified PES/Am-CNT and modified with trimesoyl chloride (TMC) and cyanuric chloride (CC) mixed matrix membrane

Membranes	% Rejection of Metals				
	Cr(VI)	Cu(II)	Pb(II)	Cd(II)	Hg(II)
Pristine PES	35.67 ± 0.33	78.83 ± 0.71	44.83 ± 0.44	43.8 ± 0.58	34.3 ± 1.07
PES/Am-CNT	85.7 ± 0.86	95.6 ± 0.81	92.4 ± 0.61	83.5 ± 0.26	92.2 ± 0.61
PES/Am-CNT/TMC	96.0 ± 0.81	98.2 ± 0.42	96.9 ± 0.62	95.4 ± 0.83	96.9 ± 0.67
PES/Am-CNT/CC	96.3 ± 0.58	98.2 ± 0.85	97.6 ± 0.61	95.3 ± 0.29	97.6 ± 0.47

Table 4 Heavy metal rejection of unmodified PSU/Am-CNT and modified with trimesoyl chloride (TMC) and cyanuric chloride (CC) mixed matrix membraner

Membranes	% Rejection of Metals				
	Cr(VI)	Cu(II)	Pb(II)	Cd(II)	Hg(II)
Pristine PES	37.0±1.3	77.0±1.5	47.0±1.4	44.0 ± 2.08	36.0 ± 0.82
PES/Am-CNT	86.9 ± 3.2	96.6 ± 0.82	90.6 ± 0.62	84.5 ± 0.56	92.4 ± 0.51
PES/Am-CNT/TMC	94.6 ± 0.42	98.8 ± 0.41	95.3 ± 0.60	95.96 ± 0.56	97.2 ± 0.79
PES/Am-CNT/CC	95.2 ± 0.59	98.9 ± 0.52	96.7 ± 0.65	96.5 ± 0.63	97.8 ± 0.79

membrane antifouling behaviour. Bovine Serum Albumin (BSA) was used to investigate membrane fouling. BSA carries a negative charge, which leads to its interaction with the membrane surface being dependent on the surface charge. Specifically, in the case of membranes modified with trimesoyl chloride resulting in a negatively charged surface, BSA molecules—also negatively charged—experience a repulsive force, causing them to avoid deposition onto the membrane surface. Conversely, when the membranes are modified with cyanuric chloride, resulting in a positively charged surface, BSA may adhere to the membrane due to electrostatic attractions (Rana and Matsuura, 2010). Importantly, in both cases BSA was easily detached from the membrane surface after simple washing. This outcome highlights the antifouling nature of the membrane. Therefore, surface modification evidently enhances membrane performance in terms of BSA rejection and fouling resistance. Modified and unmodified polysulphone mixed matrix membranes exhibit better antifouling properties compared to modified and unmodified polyether sulphone mixed matrix membranes. The reason for this is that polysulphone membranes have a sponge-like structure while polyether sulphone membranes have a finger-like structure, as explained in a morphological study.

Sewage water contains proteins and other pathogens that can pose a risk of infection, including human pancreatic α-amylase, which was found to be the most abundant protein in the wastewater soluble fraction. Other proteins detected in sewage water include human keratins and pancreatic elastase. In seawater, pathogenic viruses such as enteroviruses, hepatitis A viruses, noroviruses, reoviruses, adenoviruses, and rotaviruses have been identified, which can cause a range of infections when people are exposed to them through recreational water use. Some of these viruses, such as enteroviruses and hepatitis A viruses, have negative charges, while others, such as noroviruses, have positive charges (Carrascal *et al*. 2023, Corpuz *et al*. 2020). To remove these proteins and viruses, membranes can be used based on their charges. By selecting membranes with positive or negative surface charges, specific types of proteins and viruses present in sewage or seawater can be effectively removed.

4.5 Heavy metal rejection study

This heavy metal rejection study carried out at 50 psi transmembrane pressure at acidic pH (2.6 pH) at 25°C, room temperature. This is the optimum condition for the rejection study as reported earlier by Prachi et al. (Shah and Murthy 2013). At acidic pH protons interact with heavy metal ions, resulting in high rejection. Because of the functional groups like amine, benzenecarbonyl and triazine present on the membrane surface, adsorption also occurs which helps to reject heavy metal ions. In addition, the complexation ability of these functional groups also contributes to higher rejection.

The rejection mechanism of heavy metal ions by modified membranes depends on a combination of two key processes: high charge density and size exclusion effect. These membranes possess surfaces that are either positively or negatively charged, creating an electrostatic environment that plays a crucial role in heavy metal ion removal. Firstly, heavy metal ions are typically charged species, either positively or negatively. The modified membranes, with their high charge density, establish strong electrostatic interactions with these ions. Positively charged metal ions are attracted to negatively charged membrane surfaces, and repelled by positively charged membrane surfaces. This attraction facilitates the adhesion of heavy metal ions to the membrane, effectively reducing their concentration in the feed solution. Secondly, the size exclusion effect comes into play. The porous structure of the modified membranes features specific pore sizes that allow smaller water

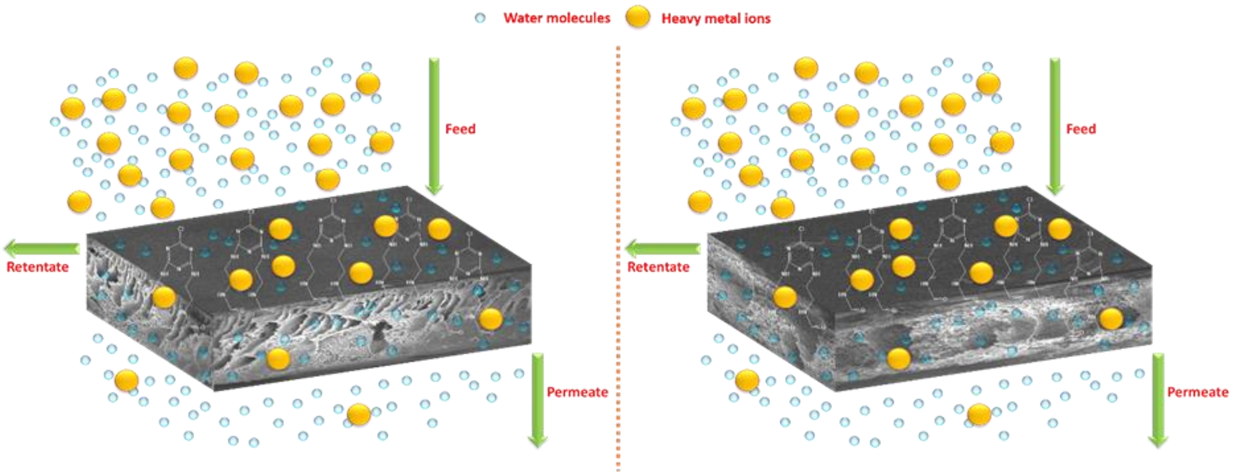

Fig. 10 Representation of heavy metal rejection thorough modified membrane due to adsorption as well as complexation

molecules to pass through while hindering the passage of larger heavy metal ions. Pore sizes of the porous membranes were measured using a novel SANS technique. (Agarwal *et al*. 2022, McCoy 1995, Mistry *et al*. 2023, Nikita *et al*. 2020, 2019a). This size-based selectivity further contributes to the efficient removal of heavy metal ions. The combination of electrostatic repulsion and size exclusion effect makes these positively charged modified membranes highly effective in removing heavy metal ions from contaminated solutions (Abedi *et al*. 2023, Li *et al*. 2023).

As shown in Table 3 and 4 modified mixed membrane has enhanced heavy metal rejection than the unmodified membrane. This was because of the introduction of surface functional groups on the membranes. As seen in the table modified membrane with cynuric chloride has better rejection than the modified with trimesoyl chloride. This can be explained by the structure difference between cynuric chloride and trimesoyl chloride, as with the cynuric chloride 1,3,5-triazine ring introduced on the membrane surface while with trimesoyl chloride 1,3,5-benzene-tricarbonyl ring was introduced on the membrane surface. This affected the rejection of the modified membranes than the unmodified membrane. Here. 1,3,5-triazine act as a ligand which is six membered heterocyclic compounds, the electronic structure of 1,3,5-triazine, including its pyridine-N donors, electron-deficient ring, and heterocyclic aromatic ring, contributes to its ability to act as a good ligand. Cynuric chloride reacts with the amine functional groups on the membrane surface, however, it cannot be predicting how many chlorines displaced from cynuric chloride to form an amide linkage. However, it is generally accepted that a triazine ring has been introduced on the membrane surface, which formed a complex with heavy metal ions. Therefore, before modification with cynuric chloride only one N-donor atom available to form a complex, but after the modification the number of N-donor atoms three times increases. Similarly, 1,3,5-benzenetricarbonyl also acts as a ligand to form a complex with heavy metals, through carboxylate groups which can serve as a donor atom, binding to the metal centre through the oxygen atom of the carbonyl group (C=O). After reacting the amine functional groups with trimesoyl chloride, these groups were introduced onto the membrane surface. Here, the modification allows the donor atoms to increase in number also, which facilitates the formation of a complex.

Polysulphone and polyether sulphone mixed matrix membrane with amine-MWCNTs modified with cynuric chloride gives ~95.2% and ~96.3% rejection for Cr(VI), which improved from unmodified membrane having amine functional groups. This explains by the complex formation with triazine ring, however, Cr(VI) doesn't form a complex, but in acidic pH it reduces to Cr(III) which forms a complex with triazine ring present on the membrane surface (Maxim *et al*. 2010, Wietzke *et al*. 1999). Similarly, modified with trimesoyl chloride gives ~94.6% and ~96.0% rejection for Cr(VI), due to the formation of Cr(III) complex with 1,3,5-benzenetricarbonyl (Klangwart *et al*. 2022). Chromium contamination is an important environmental problem that has a detrimental effect on the environment and natural resources, specifically water and soil. Industrial effluents/ wastewater are the main source of Cr(VI) pollutants in the environment. Cr(VI) is the most hazardous form of chromium. Membrane-based processes are effective for removing chromium from water, and the specific method used depends on the type of chromium contamination and the desired level of removal.

Copper contamination can have significant repercussions on the ecosystem, especially for aquatic life and plant variety. It may interact with the environment through human as well as natural processes such as copper mine, agriculture, and industry. Various membrane filtration techniques, such as ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), are suitable to remove copper from water. And these modified membrane gives improved rejection for Cu(II) upto ~99% with 1,3,5-triazine ring on the membrane surface while ~98% with 1,3,5-benzenetricarbonyl functional groups, due to the adsorption as well as complex formation of Cu(II) with available functional groups on the membrane surface. Copper has a high complexation ability and can form complexes with a variety of ligands, including amines. However, Copper ions have a greater affinity for nitrogen atoms than for oxygen atoms, hence copper rejection observed less for the polysulphonesamine-MWCNT mixed matrix membranes modified with trimesoyl chloride than the modified with cynuric chloride (Demeshko *et al*. 2004).

These modified membranes also give higher rejection rates for lead (Pb(II)) than the unmodified membranes. At very high levels, lead poisoning can be fatal, as it affects the children mental and physical development. The membranes, such as nanofiltration and thin film composite reverse osmosis membranes, can effectively reject lead ions from water. These membranes play a crucial role in the water treatment processes, ensuring the production of lead-free water. Polysulphone/Am-CNT and polyether sulphone/Am-CNT mixed matrix membrane modified with cyanuric chloride gives ~96.7% and ~97.6% rejection, respectively, which is higher than the unmodified membranes and pristine membranes. The reason for this higher rejection is support the absorption and complex formation of lead with surface functional groups on the membrane surface (Banerjee *et al*. 2013).

Other heavy metal rejection also enhanced after the surface modification with trimesoyl chloride and cyanuric chloride. The polysulfone membrane, when modified with cyanuric chloride, demonstrated approximately ~96.5% and ~97.8% rejection rates for cadmium (Cd(II)) and mercury (Hg(II)), respectively. On the other hand, the polysulfone membrane modified with trimesoyl chloride exhibited approximately ~95.96% and ~97.2% rejection for the same heavy metals. Similarly, the polyether sulfone mixed matrix membrane, after being modified with cyanuric chloride, achieves rejection rates of about ~95.3% and ~97.6% for Cd(II) and Hg(II), while modification with trimesoyl chloride resulted in rejection rates of roughly ~95.4% and ~96.9%. It is evident that the heavy metal rejection rates for all modified membranes improved than those of their respective unmodified membranes. This enhancement in rejection performance is attributed to the introduction of functional groups onto the membrane surface through modifications. These functional groups possess adsorption and complexation capabilities, allowing them to interact with heavy metal ions effectively. As the surface functionalities of the membranes increase due to modification, complexation-based separation also improves, leading to higher heavy metal rejection rates. Overall, the modified membranes demonstrated exceptional potential for efficient heavy metal ion separation and purification applications, promising advancements in environmental and industrial processes. However, these membranes show the ability to reject heavy metal ions at acidic pH levels. Consequently, by maintaining an acidic pH in the feed solution, these membranes can be utilized for separation processes.

4. Conclusions

Polyether sulphone and polysulphone/Am-CNT mixed matrix membranes were modified with trimesoyl chloride and cyanuric chloride to increase the functionalities on the membrane surface. This was confirmed through XPS, and zeta potential measurements.

- The surface charge of the membrane changed to negative after treatment with trimesoyl chloride due to the presence of acyl groups on the membrane surface. The membranes modified with cyanuric chloride, became more positively charged due to the protonation of amine functional groups under acidic conditions.
- The modified membrane with trimesoyl chloride and cyanuric chloride showed improved antifouling properties and higher heavy metal rejection compared to the unmodified membrane. The antifouling property improved due to the surface charge and structure of the membrane.
- The heavy metal rejection for all modified membranes was higher than that of the unmodified membranes due to the adsorption and complexation ability of the functional groups on the membrane surface with heavy metal ions. As the membrane surface functionalities increased through modification, separation due to complexation also increased.

Acknowledgments

The authors acknowledge to SHODH-ScHeme Of Developing High quality research, Education Department, Gujarat State, for their valuable support throughout the course of this study.

References

Abedi, F., Dubé, M.A., Kruczek, B. (2023), “Adsorption of heavy metals on the surface of nanofiltration membranes: “A curse or blessing”?”, *J. Membr. Sci*., **685**, 121988. https://doi.org/10.1016/j.memsci.2023.121988.

Agarwal, C., Das, S., Pandey, A.K. (2022), “Study on pore size distributions of microporous polymer membranes having different physical architecture using capillary flow porometry”, *Mater. Today Chem*., **23**, 100652. https://doi.org/10.1016/j.mtchem.2021.100652.

Alotaibi, A.A., Shukla, A.K., Mrad, M.H., Alswieleh, A.M., Alotaibi, K.M., (2021), “Fabrication of polysulfone-surface functionalized mesoporous silica nanocomposite membranes for removal of heavy metal ions from wastewater”, *Membranes*, **11**, 935. https://doi.org/10.3390/membranes11120935.

Al-Rashdi, B.A.M., Johnson, D.J., Hilal, N. (2013), “Removal of heavy metal ions by nanofiltration”, *Desalination*, **315**, 2-17. https://doi.org/10.1016/j.desal.2012.05.022.

Banerjee, R., Pace, N.J., Brown, D.R., Weerapana, E. (2013), “1,3,5-Triazine as a Modular Scaffold for Covalent Inhibitors with Streamlined Target Identification”, *J. Am. Chem. Soc*., **135**, 2497-2500. https://doi.org/10.1021/ja400427e.

Bera, A., Trivedi, J.S., Jewrajka, S.K., Ghosh, P.K. (2016), “In situ manipulation of properties and performance of polyethyleneimine nanofiltration membranes by polyethylenimine-dextran conjugate”, *J. Membr. Sci*., **519**, 64-76. https://doi.org/10.1016/j.memsci.2016.07.038.

Briffa, J., Sinagra, E., Blundell, R. (2020), “Heavy metal pollution in the environment and their toxicological effects on humans”, *Heliyon*, **6**, e04691. https://doi.org/10.1016/j.heliyon.2020.e04691.

Carrascal, M., Sánchez-Jiménez, E., Fang, J., Pérez-López, C., Ginebreda, A., Barceló, D., Abian, J. (2023), “Sewage protein information mining: Discovery of large biomolecules as biomarkers of population and industrial activities”, *Environ. Sci. Technol*., **57**, 10929-10939. https://doi.org/10.1021/acs.est.3c00535.

Chandrashekhar Nayak, M., Isloor, A.M., Inamuddin, Lakshmi, B., Marwani, H.M., Khan, I. (2020), "Polyphenylsulfone/ multiwalled carbon nanotubes mixed ultrafiltration membranes: Fabrication, characterization and removal of heavy metals Pb^{2+}, Hg^{2+}, and Cd^{2+} from aqueous solutions", *Arab. J. Chem.*, **13**, 4661-4672. https://doi.org/10.1016/j.arabjc.2019.10.007.

Chen, T., Li, W.Q., Hu, W.B., Hu, W.J., Liu, Y.A., Yang, H., Wen, K. (2019), "Direct synthesis of covalent triazine-based frameworks (CTFs) through aromatic nucleophilic substitution reactions", *RSC Adv.*, **9**, 18008-18012. https://doi.org/10.1039/C9RA02934F.

Corpuz, M.V.A., Buonerba, A., Vigliotta, G., Zarra, T., Ballesteros, F., Campiglia, P., Belgiorno, V., Korshin, G., Naddeo, V. (2020), "Viruses in wastewater: occurrence, abundance and detection methods", *Sci. Total Environ.*, **745**, 140910. https://doi.org/10.1016/j.scitotenv.2020.140910.

Dalwani, M., Bargeman, G., Hosseiny, S.S., Boerrigter, M., Wessling, M., Benes, N.E. (2011), "Sulfonated poly(ether ether ketone) based composite membranes for nanofiltration of acidic and alkaline media", *J. Membr. Sci.*, **381**, 81-89. https://doi.org/10.1016/j.memsci.2011.07.018.

Dalwani, M., Benes, N.E., Bargeman, G., Stamatialis, D., Wessling, M. (2011), "Effect of pH on the performance of polyamide/polyacrylonitrile based thin film composite membranes", *J. Membr. Sci.*, **372**, 228-238. https://doi.org/10.1016/j.memsci.2011.02.012.

Damiri, F., Andra, S., Kommineni, N., Balu, S.K., Bulusu, R., Boseila, A.A., Akamo, D.O., Ahmad, Z., Khan, F.S., Rahman, Md.H., Berrada, M., Cavalu, S. (2022) "Recent advances in adsorptive nanocomposite membranes for heavy metals ion removal from contaminated water: A comprehensive review", *Materials*, **15**, 5392. https://doi.org/10.3390/ma15155392.

Demeshko, S., Leibeling, G., Dechert, S., Meyer, F. (2004), "1,3,5-Triazine-based tricopper(ii) complexes: structure and magnetic properties of threefold-symmetric building blocks", *Dalton Trans.*, **21**, 3782. https://doi.org/10.1039/b407598f.

Deng, L., Li, S., Qin, Y., Zhang, L., Chen, H., Chang, Z., Hu, Y. (2021), "Fabrication of antifouling thin-film composite nanofiltration membrane via surface grafting of polyethyleneeimine followed by zwitterionic modification", *J. Membr. Sci.*, **619**, 118564. https://doi.org/10.1016/j.memsci.2020.118564.

Dong, X., Lu, D., Harris, T.A.L., Escobar, I.C. (2021), "Polymers and solvents used in membrane fabrication: A review focusing on sustainable membrane development", *Membranes*, **11**, 309. https://doi.org/10.3390/membranes11050309.

Dwight, D.W., Fabish, T.J., Thomas, H.R. (1981), *Photon, Electron, and Ion Probes of Polymer Structure and Properties*, ACS Symposium Series, American Chemical Society, Washington, D.C., U.S.A. https://doi.org/10.1021/bk-1981-0162.

Elshof, M.G., Maaskant, E., Hempenius, M.A., Benes, N.E. (2021), "Poly(aryl cyanurate)-based thin-film composite nanofiltration membranes", *ACS Appl. Polym. Mater.*, **3**, 2385-2392. https://doi.org/10.1021/acsapm.0c01366.

Farahbakhsh, J., Vatanpour, V., Khoshnam, M., Zargar, M. (2021), "Recent advancements in the application of new monomers and membrane modification techniques for the fabrication of thin film composite membranes: A review", *React. Funct. Polym.*, **166**, 105015. https://doi.org/10.1016/j.reactfunctpolym.2021.105015.

Gholami, F., Asadi, A., Zinatizadeh, A.A. (2022), "Efficient heavy metals and salts rejection using a novel modified polysulfone nanofiltration membrane", *Appl. Water Sci.*, **12**, 146. https://doi.org/10.1007/s13201-022-01671-x.

Gholami, S., Llacuna, J.L., Vatanpour, V., Dehqan, A., Paziresh, S., Cortina, J.L. (2022), "Impact of a new functionalization of multiwalled carbon nanotubes on antifouling and permeability of PVDF nanocomposite membranes for dye wastewater treatment", *Chemosphere*, **294**, 133699. https://doi.org/10.1016/j.chemosphere.2022.133699.

Ghosh, A.K., Jeong, B.H., Huang, X., Hoek, E.M.V. (2008) "Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties", *J. Membr. Sci.*, **311**, 34-45. https://doi.org/10.1016/j.memsci.2007.11.038.

Gupta, S., Bhatiya, D., Murthy, C.N. (2015), "Metal removal studies by composite membrane of polysulfone and functionalized single-walled carbon nanotubes", *Sep. Sci. Technol.*, **50**, 421-429. https://doi.org/10.1080/01496395.2014.973516.

Hebbar, R.S., Isloor, A.M., Prabhu, B., Inamuddin, Asiri, A.M., Ismail, A.F. (2018), "Removal of metal ions and humic acids through polyetherimide membrane with grafted bentonite clay", *Sci Rep.*, **8**, 4665. https://doi.org/10.1038/s41598-018-22837-1.

Ibrahim, S., Mohammadi Ghaleni, M., Isloor, A.M., Bavarian, M., Nejati, S. (2020), "Poly(homopiperazine-amide) thin-film composite membrane for nanofiltration of heavy metal ions", *ACS Omega*, **5**, 28749-28759. https://doi.org/10.1021/acsomega.0c04064.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N. (2014), "Toxicity, mechanism and health effects of some heavy metals", *Interdiscipl. Toxicol.*, **7**, 60-72. https://doi.org/10.2478/intox-2014-0009.

Jiang, Z., Miao, J., He, Y., Hong, X., Tu, K., Wang, X., Chen, S., Yang, H., Zhang, L., Zhang, R. (2019), "A pH-stable positively charged composite nanofiltration membrane with excellent rejection performance", R*SC Adv.*, **9**, 37546-37555. https://doi.org/10.1039/C9RA06528H.

Kang, G., Liu, M., Lin, B., Cao, Y., Yuan, Q. (2007), "A novel method of surface modification on thin-film composite reverse osmosis membrane by grafting poly(ethylene glycol)", *Polymer*, **48**, 1165-1170. https://doi.org/10.1016/j.polymer.2006.12.046.

Klangwart, N., Ruijs, C., Hawes, C.S., Gunnlaugsson, T., Kotova, O. (2022), "Tripodal 1,3,5-benzenetricarboxamide ligand with dipicolinic acid units and its binding with Eu(III) ions", *Supramol. Chem.*, **34**, 10-19. https://doi.org/10.1080/10610278.2023.2177162.

Kumar, M., Seth, A., Singh, A.K., Rajput, M.S., Sikandar, M. (2021), "Remediation strategies for heavy metals contaminated ecosystem: A review", *Environ. Sust. Indicat.*, **12**, 100155. https://doi.org/10.1016/j.indic.2021.100155.

Lee, K.P., Bargeman, G., De Rooij, R., Kemperman, A.J.B., Benes, N.E. (2017), "Interfacial polymerization of cyanuric chloride and monomeric amines: pH resistant thin film composite polyamine nanofiltration membranes", *J. Membr. Sci.*, **523**, 487-496. https://doi.org/10.1016/j.memsci.2016.10.012.

Lee, K.P., Zheng, J., Bargeman, G., Kemperman, A.J.B., Benes, N.E. (2015), "pH stable thin film composite polyamine nanofiltration membranes by interfacial polymerisation", *J. Membr. Sci.*, **478**, 75-84. https://doi.org/10.1016/j.memsci.2014.12.045.

Li, F., Meng, J., Ye, J., Yang, B., Tian, Q., Deng, C. (2014), "Surface modification of PES ultrafiltration membrane by polydopamine coating and poly(ethylene glycol) grafting: Morphology, stability, and anti-fouling", *Desalination*, **344**, 422-430. https://doi.org/10.1016/j.desal.2014.04.011.

Li, M., Zhang, W., Zhang, X., Guo, H., Liang, Y. (2023), "Recent advanced development of acid-resistant thin-film composite nanofiltration membrane preparation and separation performance in acidic environments", *Separations*, **10**, 20. https://doi.org/10.3390/separations10010020.

Liu, M., Zheng, Y., Shuai, S., Zhou, Q., Yu, S., Gao, C. (2012), "Thin-film composite membrane formed by interfacial polymerization of polyvinylamine (PVAm) and trimesoyl chloride (TMC) for nanofiltration", *Desalination*, **288**, 98-107. https://doi.org/10.1016/j.desal.2011.12.018.

Mahmoud, A.E.D., Mostafa, E. (2023), “Nanofiltration membranes for the removal of heavy metals from aqueous solutions: preparations and applications”, *Membranes*, **13**, 789. https://doi.org/10.3390/membranes13090789.

Maxim, C., Matni, A., Geoffroy, M., Andruh, M., Hearns, N.G.R., Clérac, R., Avarvari, N. (2010), “C3 symmetric tris (phosphonate)-1,3,5-triazine ligand: homopolymetallic complexes and its radical anion”, *New J. Chem*., **34**, 2319. https://doi.org/10.1039/c0nj00204f.

McCoy, B.J. (1995), “Membrane sieving of a continuous polydisperse mixture through distributed pores”, *Sep. Sci. Technol*., **30**, 487-507. https://doi.org/10.1080/01496399508225606.

Mistry, P., Murthy, C.N. (2023), “Positively charged polysulfone and polyether sulfone mixed matrix membranes modified with polyethylenimine: Enhancing heavy metal rejection and antifouling properties”, *ACS EST Water*, **3**, 4168-4182. https://doi.org/10.1021/acsestwater.3c00585.

Mistry, P., Nikita, K., Aswal, V.K., Kumar, S., Murthy, C.N. (2023), “Modification of surface characteristics of functionalized multi-walled carbon nanotubes containing mixed matrix membrane using click chemistry”, *Desal. Water Treat*., **295**, 42-51. https://doi.org/10.5004/dwt.2023.29589.

Nikita, K., Karkare, P., Ray, D., Aswal, V.K., Singh, P.S., Murthy, C.N. (2019), “Understanding the morphology of MWCNT/PES mixed-matrix membranes using SANS: interpretation and rejection performance”, *Appl Water Sci*., **9**, 154. https://doi.org/10.1007/s13201-019-1035-4.

Nikita, K., Kumar, S., Aswal, V.K., Kanchan, D.K., Murthy, C.N. (2019), “Porous structure studies of the mixed-matrix polymeric membranes of polyether sulfone incorporated with functionalized multiwalled carbon nanotubes”, *Desal. Water Treat*., **146**, 29-38. https://doi.org/10.5004/dwt.2019.23624.

Nikita, K., Ray, D., Aswal, V.K., Murthy, C.N. (2020), “Surface modification of functionalized multiwalled carbon nanotubes containing mixed matrix membrane using click chemistry”, *J. Membr. Sci*., **596**, 117710. https://doi.org/10.1016/j.memsci.2019.117710.

Nikita, K., Swetha, D.C., Murthy, C.N. (2022), “Uniquely modified polyethersulphone and f-CNTs mixed matrix membranes for enhanced water transport and reduced biofouling”, *Desal. Water Treat*., **245**, 16-34. https://doi.org/10.5004/dwt.2022.27980.

Pandey, R.P., Ouda, M., Abdul Rasheed, P., Banat, F., Hasan, S.W. (2022), “Surface decoration of bis-aminosilane cross-linked multiwall carbon nanotube ultrafiltration membrane for fast and efficient heavy metal removal”, *NPJ Clean Water*, **5**, 44. https://doi.org/10.1038/s41545-022-00189-8.

Qasem, N.A.A., Mohammed, R.H., Lawal, D.U. (2021), “Removal of heavy metal ions from wastewater: a comprehensive and critical review”, *NPJ Clean Water*, **4**, 1-15. https://doi.org/10.1038/s41545-021-00127-0.

Rana, D., Matsuura, T. (2010), “Surface modifications for antifouling membranes”, *Chem. Rev*., **110**, 2448-2471. https://doi.org/10.1021/cr800208y.

Samavati, Z., Samavati, A., Goh, P.S., Fauzi Ismail, A., Sohaimi Abdullah, M. (2023), “A comprehensive review of recent advances in nanofiltration membranes for heavy metal removal from wastewater”, *Chem. Eng. Res. Des*., **189**, 530-571. https://doi.org/10.1016/j.cherd.2022.11.042.

Shah, P., Murthy, C.N. (2013), “Studies on the porosity control of MWCNT/polysulfone composite membrane and its effect on metal removal”, *J. Membr. Sci*., **437**, 90-98. https://doi.org/10.1016/j.memsci.2013.02.042.

Sianipar, M., Hyun Kim, S., Khoiruddin, Iskandar, F., Gede Wenten, I. (2017), “Functionalized carbon nanotube (CNT) membrane: Progress and challenges”, *RSC Adv*., **7**, 51175-51198. https://doi.org/10.1039/C7RA08570B.

Tan, X., Rodrigue, D. (2019), “A review on porous polymeric membrane preparation. Part I: Production techniques with polysulfone and poly (vinylidene fluoride)”, *Polymers*, **11**, 1160. https://doi.org/10.3390/polym11071160.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J. (2012), “Heavy metals toxicity and the environment”, *EXS*, **101**, 133-164. https://doi.org/10.1007/978-3-7643-8340-4_6.

Upadhyaya, L., Qian, X., Ranil Wickramasinghe, S. (2018), “Chemical modification of membrane surface — overview”, *Curr. Opin. Chem. Eng*., **20**, 13-18. https://doi.org/10.1016/j.coche.2018.01.002.

Wang, H., Zheng, L., Yuan, B., Guo, S., Yuan, C. (2023), “How polyvinyl alcohol-based interlayers affect the performance of polyamide nanofiltration membranes prepared by polyethylene-imine”, *Sep. Sci. Technol*., **58**, 2369-2382. https://doi.org/10.1080/01496395.2023.2255737.

Wang, L.Y., Wang, M.J. (2016), “Removal of heavy metal ions by poly(vinyl alcohol) and carboxymethyl cellulose composite hydrogels prepared by a freeze-thaw method”, *ACS Sust. Chem. Eng*., **4**, 2830-2837. https://doi.org/10.1021/acssuschemeng.6b00336.

Wietzke, R., Mazzanti, M., Latour, J.M., Pécaut, J. (1999), “Crystal structure and solution fluxionality of lanthanide complexes of 2,4,6,-Tris-2-pyridyl-1,3,5-triazine”, *Inorg. Chem*., **38**, 3581-3585. https://doi.org/10.1021/ic990122w.

Wu, H., Li, X., Zhao, C., Shen, X., Jiang, Z., Wang, X. (2013), “Chitosan/sulfonated polyethersulfone-polyethersulfone (CS/SPES-PES) composite membranes for pervaporative dehydration of ethanol”, *Ind. Eng. Chem. Res*., **52**, 5772-5780. https://doi.org/10.1021/ie303437r.

Wu, X.M., Wang, L.L., Wang, Y., Gu, J.S., Yu, H.Y. (2012), “Surface modification of polypropylene macroporous membrane by marrying RAFT polymerization with click chemistry”, *J. Membr. Sci*., **421-422**, 60-68. https://doi.org/10.1016/j.memsci.2012.06.033.

Xie, H., Saito, T., Hickner, M.A. (2011), “Zeta potential of ion-conductive membranes by streaming current measurements”, *Langmuir*, **27**, 4721-4727. https://doi.org/10.1021/la105120f.

Zhang, R., Yu, S., Shi, W., Wang, W., Wang, X., Zhang, Z., Li, L., Zhang, B., Bao, X. (2017), “A novel polyesteramide thin film composite nanofiltration membrane prepared by interfacial polymerization of serinol and trimesoyl chloride (TMC) catalyzed by 4-dimethylaminopyridine (DMAP)”, *J. Membr. Sci*., **542**, 68-80. https://doi.org/10.1016/j.memsci.2017.07.054.

Zhou, C., Shi, Y., Sun, C., Yu, S., Liu, M., Gao, C. (2014), “Thin-film composite membranes formed by interfacial polymerization with natural material sericin and trimesoyl chloride for nanofiltration”, *J. Membr. Sci*., **471**, 381-391. https://doi.org/10.1016/j.memsci.2014.08.033.

JL