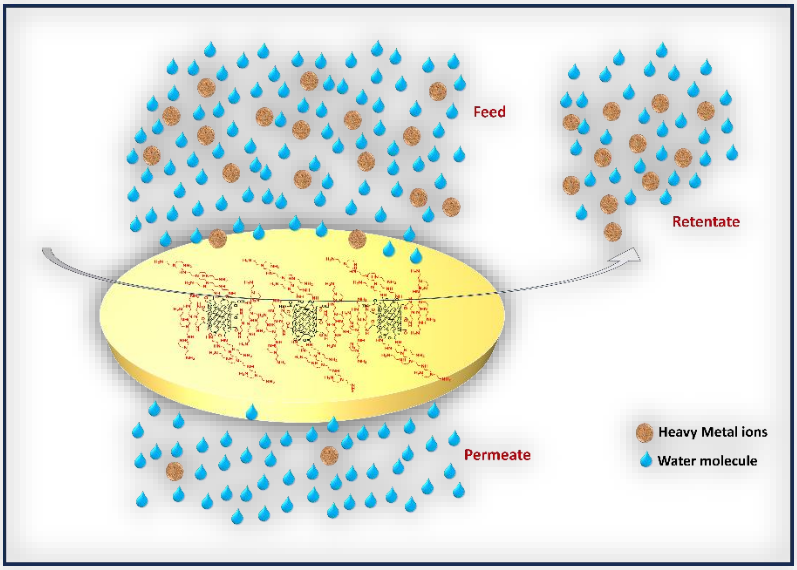
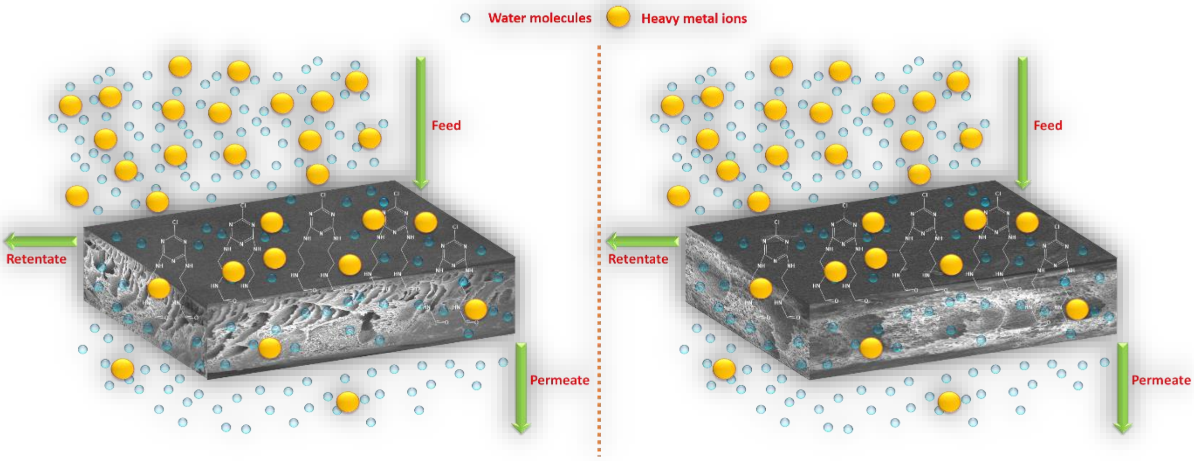


Chapter 4
Membrane Performance



4.1 Permeation Studies of Modified and Unmodified Membranes

4.1.1 Pure water flux of unmodified and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

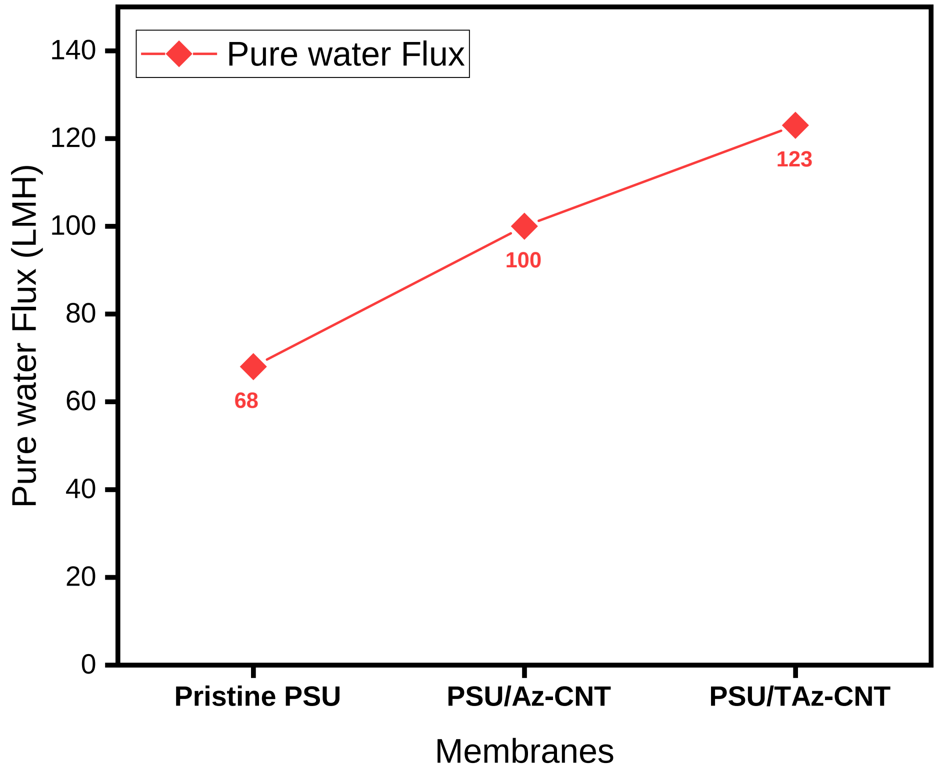


Figure 4.1. Pure water flux of pristine polysulphone, unmodified and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

The pure water flux of the pristine polysulfone membrane was initially measured at 68 LMH (L/m²/h or LMH). Polysulphones are known for their inherent properties; however, their pure water flux can be improved through modifications. When azide-functionalized multi-walled carbon nanotubes (MWCNTs) are introduced into the polysulfide matrix, we observed a notable increase in the pure water flux, which reached 100 LMH. This enhancement can be attributed to the higher porosity of the mixed-matrix membranes. The incorporation of azide functionalized MWCNTs in to the polysulphone matrix also contributed to this improvement, as these groups interacted with water molecules on the membrane surface, facilitating more efficient water flow[82,84,86]. Furthermore, after the modification via a click reaction, the pure water flux experienced a further enhancement, reaching 123 LMH. This notable increase was attributed to the formation of triazole rings on the membrane surface during the click reaction. These triazole rings provide additional sites for water interactions, leading to an even higher pure water flux. In summary, the introduction of azide-functionalized MWCNTs into the polysulphone matrix enhances the pure water flux owing to increased porosity and the interaction of azide functional groups with water molecules. Subsequent modification through a click reaction resulted in the formation of triazole rings on the membrane surface, further improving the pure water flux and making it a promising approach to optimize membrane performance for water filtration applications[146,147].

4.1.2 Pure water flux of unmodified and modified polyether sulphone and polysulphones/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

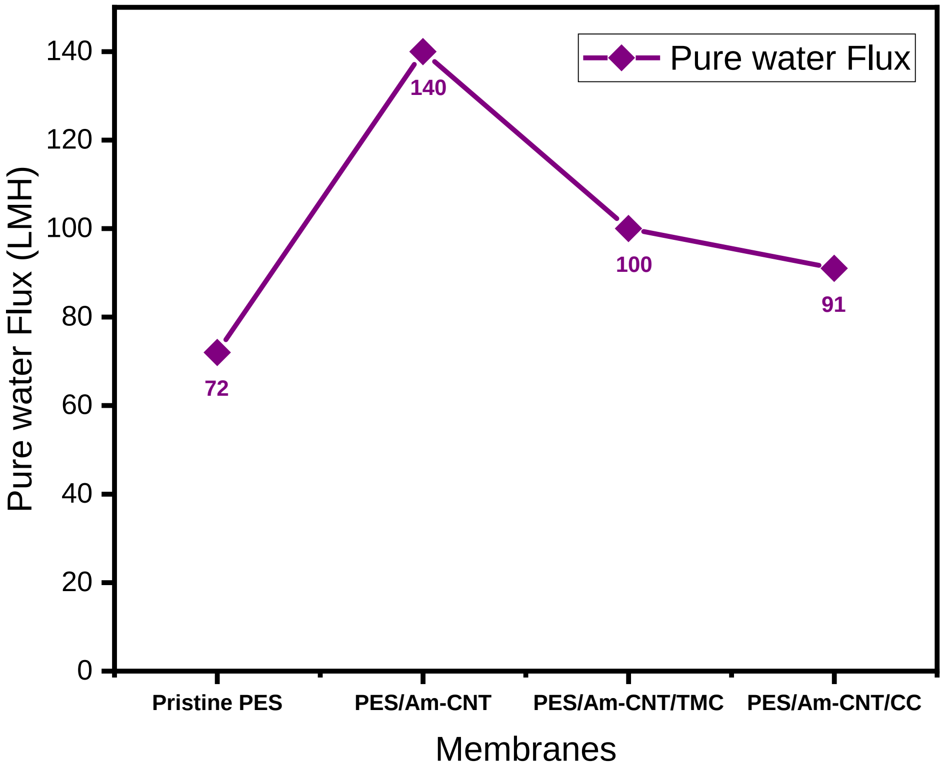


Figure 4.2. Pure water flux of pristine polyether sulphone, unmodified and modified polyether sulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

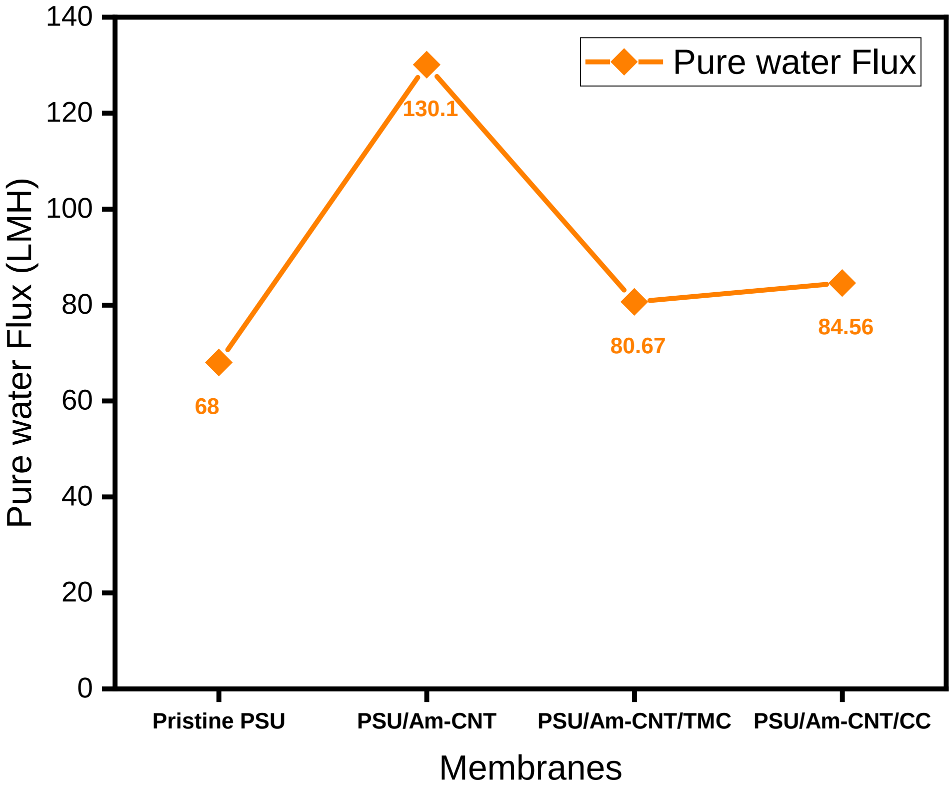


Figure 4.3. Pure water flux of pristine polysulphone, unmodified and modified polysulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

The two types of membranes, Pristine PES with a finger-like structure and PSU with a sponge-like structure, as well as the incorporation of amine-functionalized CNTs (Am-CNT) along with their surface modification with trimesoyl chloride and cyanuric chloride, are depicted in Figures 4.2 and 4.3. The pristine PES membrane, with its finger-like structure, possess a high initial water flux of 72 LMH than pristine PSU membrane. because finger like structure of PES enables water molecules to pass through the membrane more easily, resulting in an enhanced flux. Conversely, the PSU membrane, with its sponge-like structure, exhibits a considerably lower pure water flux of 68 LMH. The difference in the flux of these two membranes can be attributed to their different morphological characteristics, with the finger-like structure of PES facilitating greater water flow. The incorporation of amine MWCNTs into the PES membrane increases pure water flux to 140 LMH. This increase is because of the formation of nanochannels, which enhance water transport, resulting from the increased surface area and altered pore size distribution, reducing flow resistance and improving permeability.

Similarly, the PSU/Am-CNT membrane outperforms the pristine PSU membrane with a water flux of 130.1 LMH. This improvement is attributed to the formation of pores within the sponge-like structure, leading to better water flow through the membrane.

Surface modification plays a critical role in altering the characteristics of the membrane. Modifying the PES/Am-CNT membrane with trimesoyl chloride reduces the pure water flux to 100 LMH. This reduction in flux is attributed to the partial blockage of pores caused by the surface reaction, which slightly reduces the effective pore size and increases resistance to water flow. Similarly, modifying the membrane surface with cyanuric chloride leads to a flux of 91 LMH. This modification likely forms a less obstructive surface layer compared to trimesoyl chloride, allowing for slightly improved water transport while still affecting the overall pore structure. Modifying the PSU/Am-CNT membrane with trimesoyl chloride results in a flux of 80.67 LMH. However, the impact of this modification on water flux is less severe compared to PES because of the inherently larger pores in the sponge-like structure of PSU, which are less affected by surface modifications. In contrast, modifying the PSU/Am-CNT membrane with cyanuric chloride 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, results a moderate increase in water flux.

4.1.3 Pure water flux of unmodified and modified polyether sulphone and polysulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

The pure water flux of membranes is influenced by their distinct structures and various modifications. Enhancement of pure water flux can be achieved by incorporating oxidized-MWCNTs (Ox-CNT) into the polymer matrix. However, surface modifications, such as with PEI, can either positively or negatively impact the water flux. The pristine PES membrane, with its finger-like structure, has a pure water flux of 72 LMH. This structure enhances water flow by forming preferential pathways for water molecules. In contrary, the pristine PSU membrane, with a sponge-like structure, has a relatively lower pure water flux of 68 LMH. The difference in distribution of the pore size and overall porosity between these two membrane types is responsible for this variance in flux.

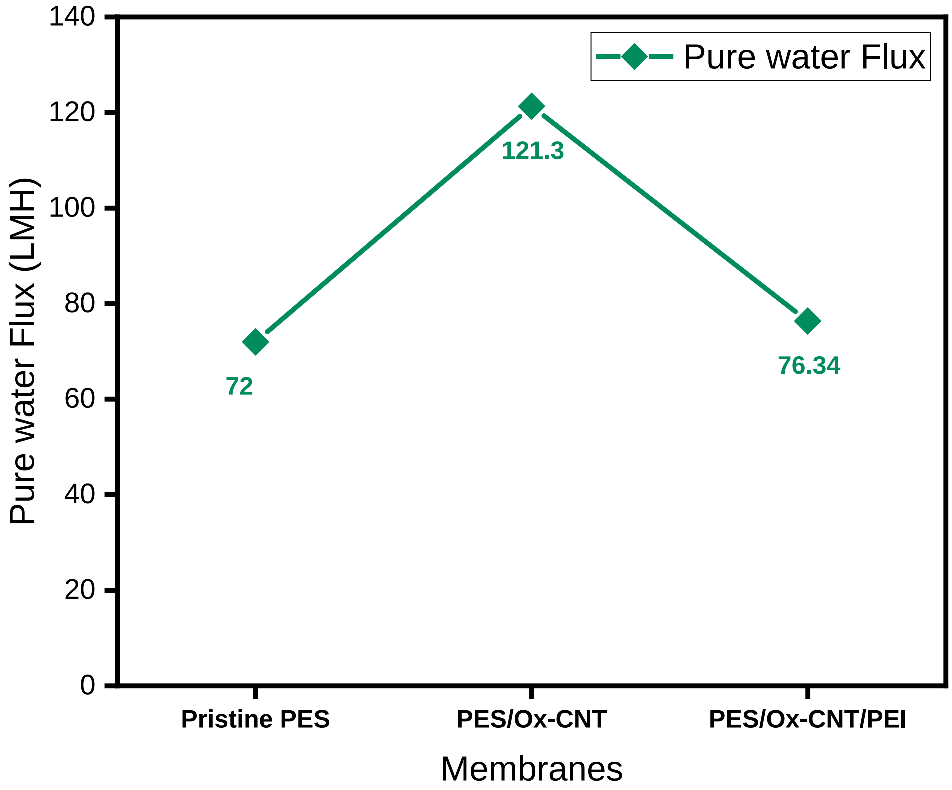


Figure 4.4. Pure water flux of pristine polyether sulphone, unmodified and modified polyether sulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

Incorporating oxidized MWCNTs into the PES membrane leads to a significant increase in water flux. The PES/Ox-CNT membrane has a flux of 121.3 LMH. This enhancement can be attributed to the unique properties of oxidized MWCNTs, such as their high surface area and hydrophilicity. The oxidized MWCNTs create nanochannels within the membrane matrix, reducing flow resistance and facilitating faster water transport. The PSU/Ox-CNT membrane displays a pure water flux of 106.19 LMH compared to the pristine PSU membrane. The presence of oxidized MWCNTs within the sponge-like structure enables the formation of pathways for water molecules, resulting in an improved water flux.

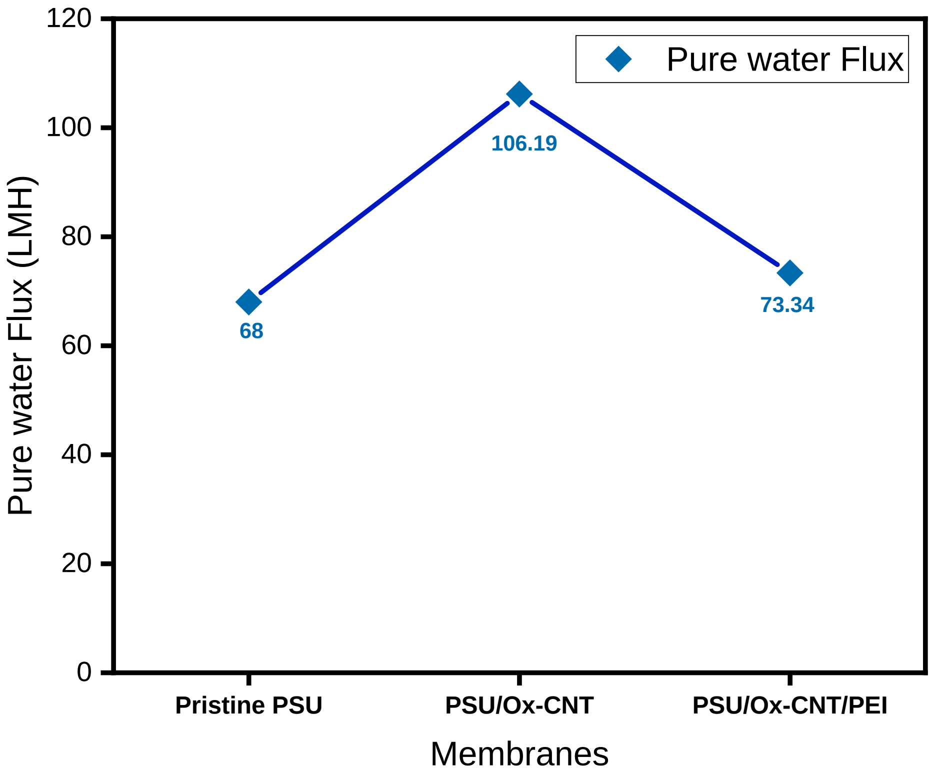


Figure 4.5. Pure water flux of pristine polysulphone, unmodified and modified polysulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

The surface modifications of the PES/Ox-CNT and PSU/Ox-CNT membranes play a crucial role in tailoring their membrane properties to specific applications. For instance, the surface modification of the PES/Ox-CNT membrane with PEI results in a significant reduction of water flux to 76.3 LMH. The interaction between PEI and the carboxylic group on the membrane surface is responsible for the observed decrease. Similarly, the surface modification of the PSU/Ox-CNT membrane with PEI results in a flux of 73.34 LMH. This reduction in water flux demonstrates that surface modifications can have varying effects on different membrane structures, and in the case of the sponge-like PSU membrane, the modification with PEI likely leads to changes in the pore structure, resulting in a decrease in water transport. The possible reason for the significant decline in pure water flux following treatment with PEI could be due to the surface reaction that caused partial blockage of pores, which in turn led to a slight reduction of the effective pore size.

4.2 Antifouling Studies of Modified and Unmodified Membranes

4.2.1 Fouling Studies of unmodified and modified polysulphone/azide- MWCNTs mixed matrix membrane via click reaction

The antifouling properties of the membranes were studied using bovine serum albumin (BSA), as shown in Figure 4.6 and 4.7. Following surface modification, membrane fouling decreases significantly. The pristine polysulphone membrane demonstrated 86% rejection of BSA with a flux recovery ratio of 50%, and also showed an irreversible fouling ratio. However, the addition of azide functionalized CNT improved the performance, resulting in 88% rejection of BSA with a higher flux recovery ratio of 70% and a reduced irreversible fouling ratio of 30%. The click reaction modification of the polysulphone/azide-CNT membrane resulted in an increase in BSA rejection up to 92%, as well as an increase in flux recovery ratio and a significant decrease in irreversible fouling to 9%. This means that the azide MWCNTs antifouling properties are enhanced by the introduction of triazole moiety on the surface of the modified membrane, resulting in improved performance after the click reaction[146,147].

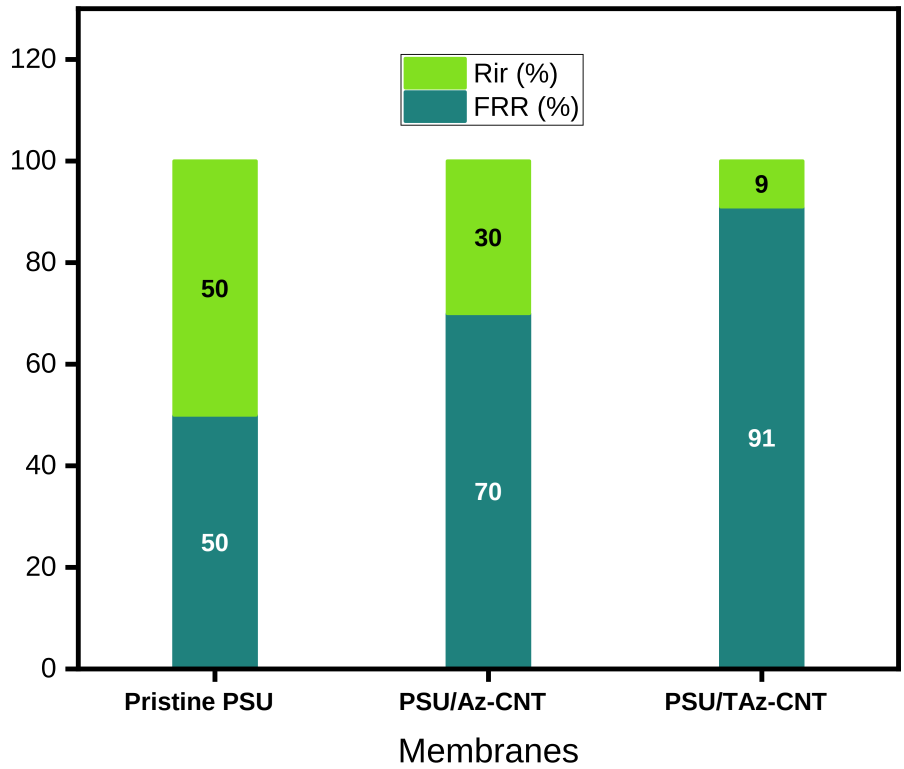


Figure 4.6. Flux recovery ratio (FRR) and Irreversible Fouling ratio (Rir) of pristine polysulphone, unmodified polysulphone/azide-MWCNTs mixed matrix membrane and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

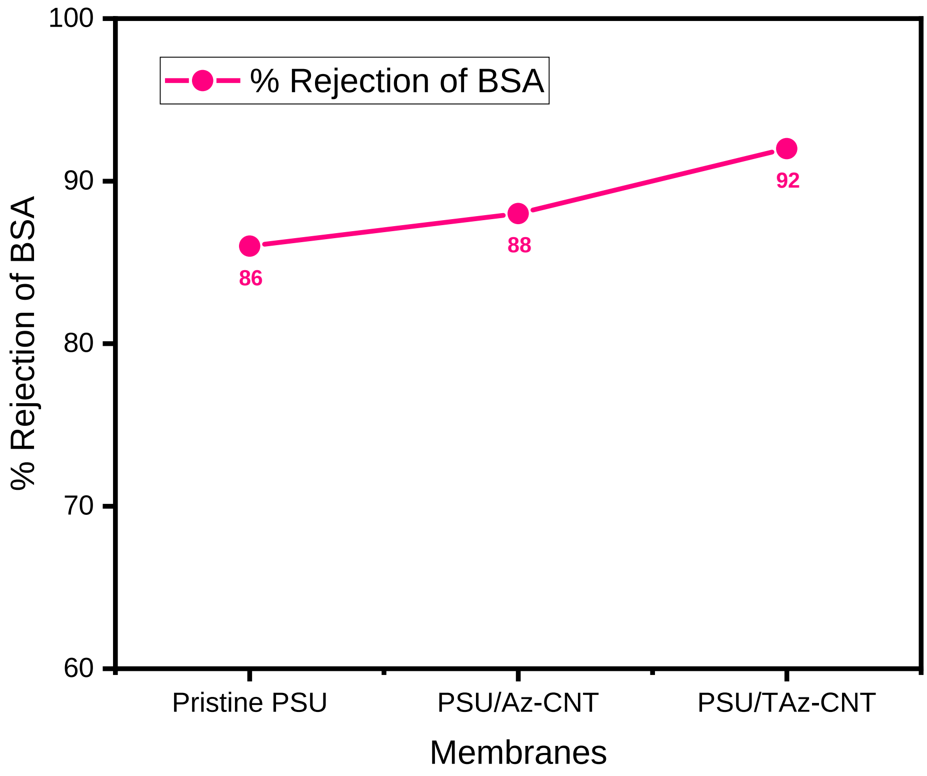


Figure 4.7. Bovine serum albumin rejection of pristine polysulphone, unmodified polysulphone/azide-MWCNTs mixed matrix membrane and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

Although the surface roughness increased, fouling decreased, which is a critical phenomenon that requires explanation. However, as seen in the surface parameters, after modification, there were lesser peaks than valleys on the modified membrane, which indicates that there was no specific site available for protein deposition on the surface. As a result, the modified membrane was easily cleaned by washing. In summary, surface roughness affects the fouling property of the membrane, but because of the surface modification, fouling decreases even though the surface roughness increases.

4.2.2 Fouling Studies of unmodified and modified polyether sulphone and polysulphones/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

The Figure 4.8 and Figure 4.9 illustrate the flux recovery ratio (FRR) and irreversible ratio (Rir) along with the rejection of Bovine serum Albumin (BSA) by unmodified and modified membranes. These pristine membranes exhibit relatively lower BSA rejection percentages, with 80.5% for pristine PES and 86.0% for pristine PSU. Additionally, they show reduced FRR, with 51.5% and 50%, respectively. The similar Rir values of 48.5% and 50% suggest comparable fouling over time. The incorporation of amine-functionalized carbon nanotubes (Am-CNT) into polysulphone (PSU) and polyether sulphone (PES) membranes has shown a notable improvement in their performance. Specifically, PSU/Am-CNT membranes exhibit a higher rejection percentage of bovine serum albumin (BSA) (84.4%) and a more significant flux recovery ratio (FRR) (79.98%) and rejection ratio (Rir) (20.02%) compared to the pristine PSU membrane. These results implies that the addition of amine-MWCNTs is effective in inhibiting fouling, likely because the ability of amine-MWCNTs to alter surface characteristics and prevent foulant attachment. Similarly, PES/Am-CNT membranes demonstrate improved BSA rejection (84.0%) and FRR (78.75%) and Rir (21.25%) compared to pristine PES. This confirms that amine-MWCNTs incorporation enhances the membranes fouling resistance. It is important to mention that the addition of amine-MWCNTs significantly improves both BSA rejection and fouling resistance in these membranes. The surface modifications using trimesoyl chloride (TMC) and cyanuric chloride (CC) on the membrane having amine functional groups show improved rejection of BSA for both PSU/Am-CNT/TMC (96.7%) and PES/Am-CNT/TMC (97.5%). Similarly, for PSU/Am-CNT/CC and PES/Am-CNT/CC, the rejection of BSA is enhanced up to 99.6% and 99.8%, respectively. The low FRR of 93.33% for PSU/Am-CNT/TMC and 91.67% for PES/Am-CNT/TMC indicates the success of modification using TMC on the membrane surface. The same is true for PSU/Am-CNT/CC and PES/Am-CNT/CC, with FRR values of 96.28% and 92.79%, respectively.

The surface charge and surface roughness of a membrane can impact its antifouling characteristics. Modified membranes exhibit a slightly increased surface roughness compared to unmodified membranes, which is because of the reaction between amine functional groups and trimesoyl chloride and cyanuric chloride. Nonetheless, the surface charge also significantly affects the membrane's antifouling behaviour. Since BSA carries a negative charge, its interaction with the membrane surface is influenced by the surface charge. When the membrane is modified with trimesoyl chloride, resulting in a negatively charged surface, BSA molecules experience a repulsive force and avoid deposition onto the membrane surface. Conversely, when the membrane is modified with cyanuric chloride, resulting in a positively charged surface, BSA may adhere to the membrane due to electrostatic attractions[202]. Notably, in both situations, BSA can be easily removed from the surface of the membrane with simple washing, demonstrating the antifouling properties of the membrane. This conclusion indicates that surface modification has a positive impact on the membrane's performance, improving BSA rejection and fouling resistance. The modified and unmodified polysulphone mixed matrix membranes display better antifouling properties compared to their counterparts with polyether sulphone. This is because polysulphone membranes possess a sponge-like structure, while polyether sulphone membranes have a finger-like structure, as revealed by a morphological analysis.

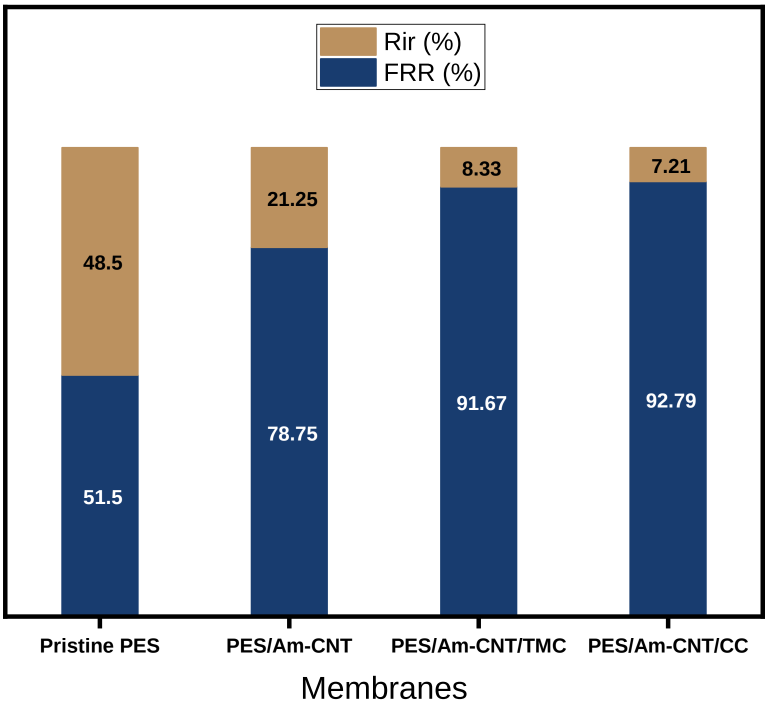


Figure 4.8. Flux recovery ratio (FRR) and Irreversible Fouling ratio (Rir) of pristine polyether sulphone, unmodified polyether sulphone/amine-MWCNTs mixed matrix membrane and modified polyether sulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

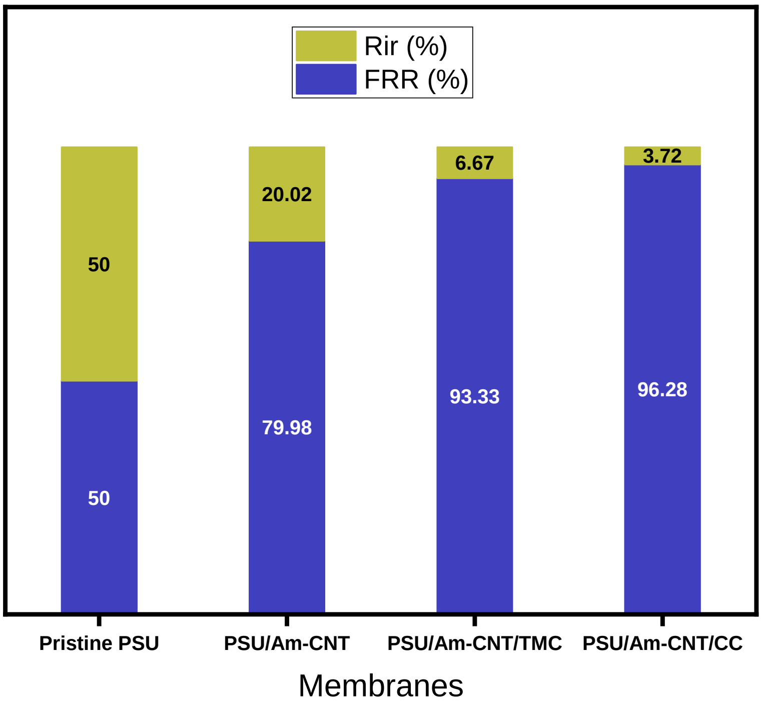


Figure 4.9. Flux recovery ratio (FRR) and Irreversible Fouling ratio (Rir) of pristine polysulphone, unmodified polysulphone/amine-MWCNTs mixed matrix membrane and modified polysulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

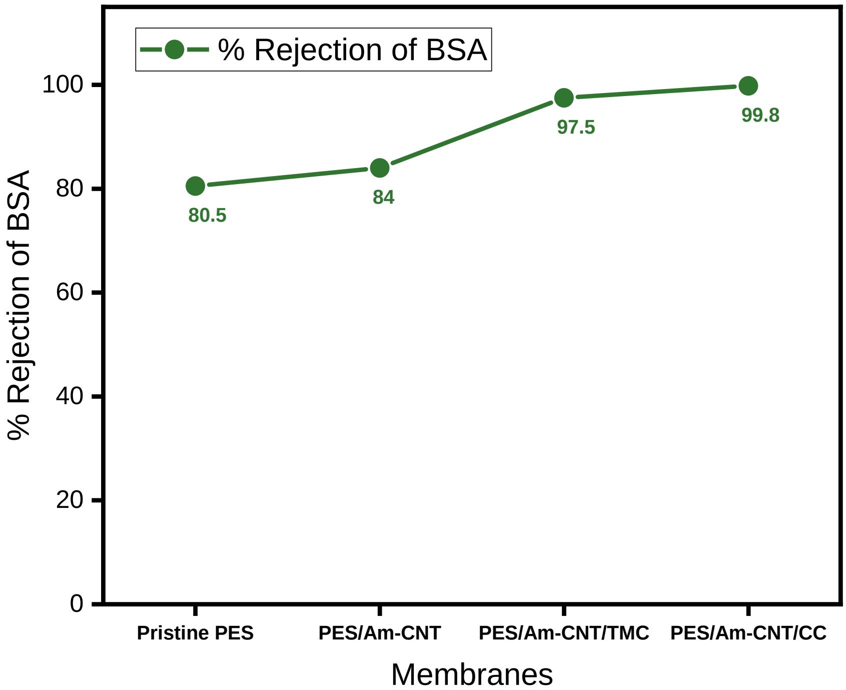


Figure 4.10. Bovine serum albumin rejection of pristine polyether sulphone, unmodified polyether sulphone/amine-MWCNTs mixed matrix membrane and modified polyether sulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

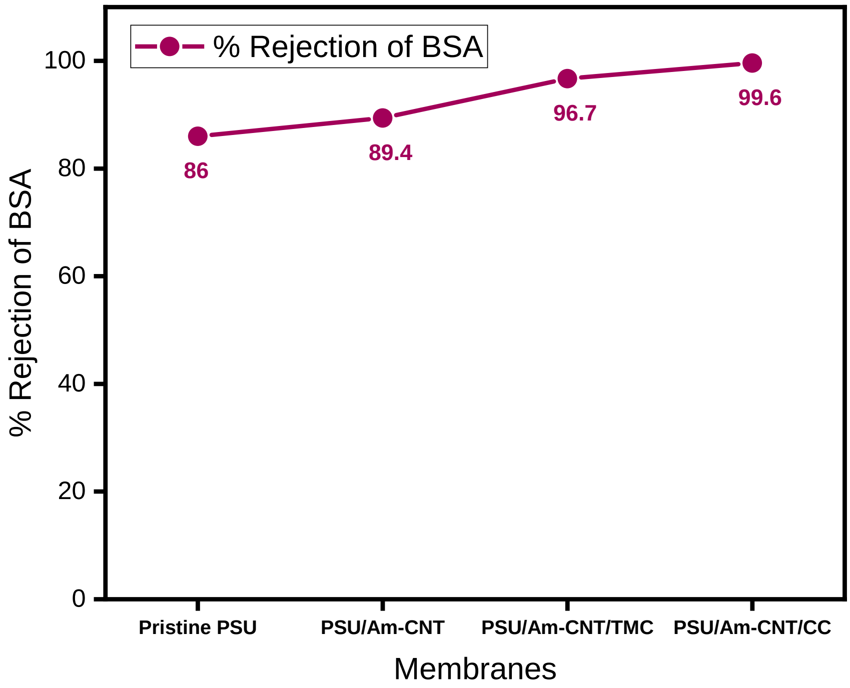


Figure 4.11. Bovine serum albumin rejection of Pristine polysulphone, unmodified polysulphone/amine-MWCNTs mixed matrix membrane and modified polysulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

4.2.3 Fouling Studies of unmodified and modified polyether sulphone and polysulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

The two figures, 4.11 and 4.12, examine the improvement in the performance of polysulphone (PSU) and polyether sulphone (PES) membranes resulting from the incorporation of oxidized-MWCNTs and the surface modification with polyethylenimine (PEI). Initially, the pristine PSU and PES membranes showed Bovine Serum Albumin (BSA) rejection rates of 86% and 80.5%, respectively, with flux recovery ratios (FRR) of 50% and 51.5%, and irreversible fouling ratios (Rir) of 50% and 48.5%. However, after adding Oxidized-MWCNTs to the polymer matrix, the BSA rejection rates increased to 89.9% for PSU/Ox-CNT and 85.5% for PES/Ox-CNT, with FRR values of 67.97% and 66.58%, and Rir values of 32.03% and 33.42%, respectively. After treatment with PEI, both types of membranes showed significant improvements. The PSU/Ox-CNT/PEI membranes had a remarkable BSA rejection of 95.2%, an FRR of 86.39%, and an Rir of 13.61%, while the PES/Ox-CNT/PEI membranes achieved a BSA rejection of 94.52%, an FRR of 85.98%, and an Rir of 14.02%. The improvements in performance for the modified membranes were attributed to the structural differences between the polymers, which affected pore size and solute transport, as well as the surface modifications introduced by PEI, which increased rejection, hydrophilicity, and anti-fouling properties through the introduction of amine groups. When compared to the pristine membranes, the modified membranes consistently outperformed in terms of BSA rejection, FRR, and Rir, demonstrating the synergistic benefits of nanotube incorporation and surface modification in enhancing membrane performance for various separation processes.

The antifouling properties of membranes are influenced by their surface charge and surface roughness. Modification with polyethyleneimine (PEI) caused a slight increase in surface roughness because of the formation of amide linkages. This change resulted from the introduction of more amine functional groups. However, the surface charge remains the primary factor affecting the antifouling behaviour. The PEI treatment resulted in a high positive surface charge, which had a significant impact on the interaction between the membrane and Bovine Serum Albumin (BSA), a negatively charged protein used to study membrane fouling. The electrostatic attractions between the positively charged membrane and negatively charged BSA caused the protein to attach to the membrane surface[202,203]. To address the fouling issue, a straightforward cleaning method involving backwashing with distilled water was employed, which effectively removed the adsorbed BSA from the membrane surface. In comparison to the unmodified PES/Ox-CNT and modified with PEI mixed matrix membrane, the mixed matrix membrane composed of unmodified PSU/Ox-CNT, as well as the membrane modified with PEI, demonstrated superior antifouling properties. This improvement can be assigned to the structural differences elucidated by Scanning Electron Microscopy (SEM) analysis, and the effect of surface charge, surface roughness, and composition on the membranes antifouling efficacy. In conclusion, the interplay between these factors plays a crucial role in determining the antifouling performance of the membranes.

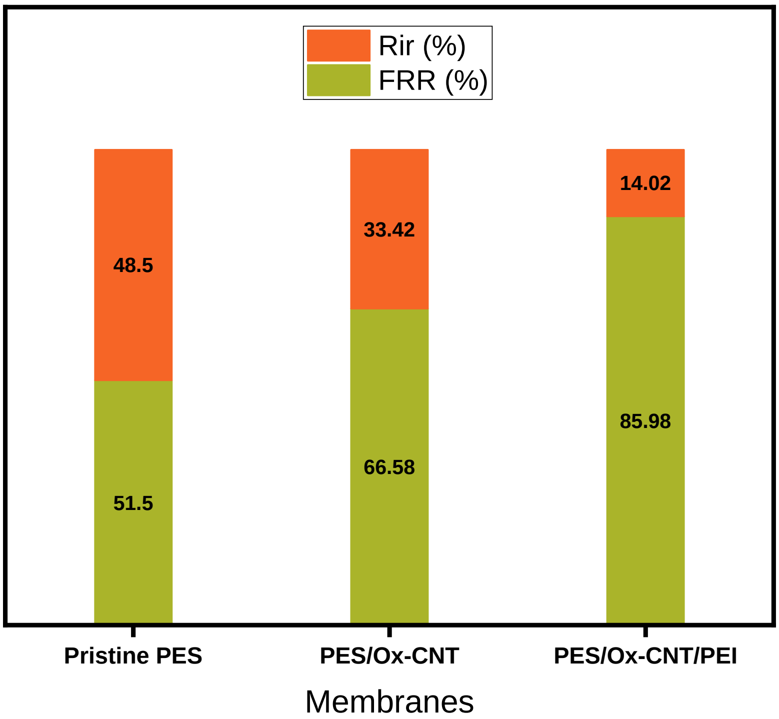


Figure 4.12. Flux recovery ratio (FRR) and Irreversible Fouling ratio (Rir) of pristine polyether sulphone, unmodified polyether sulphone/oxidized-MWCNTs mixed matrix membrane and modified polyether sulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

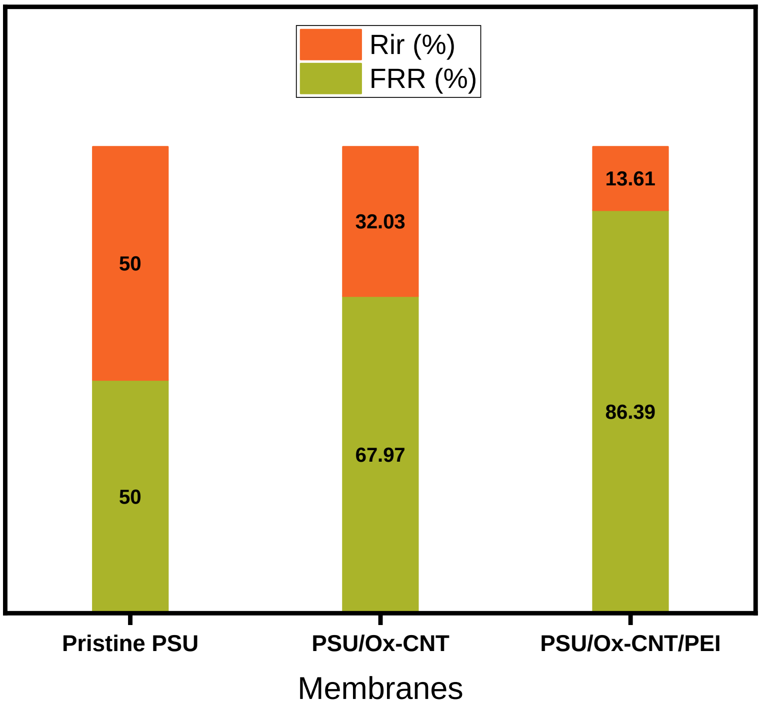


Figure 4.13. Flux recovery ratio (FRR) and Irreversible Fouling ratio (Rir) of pristine polysulphone, unmodified polysulphone/oxidized-MWCNTs mixed matrix membrane and modified polysulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

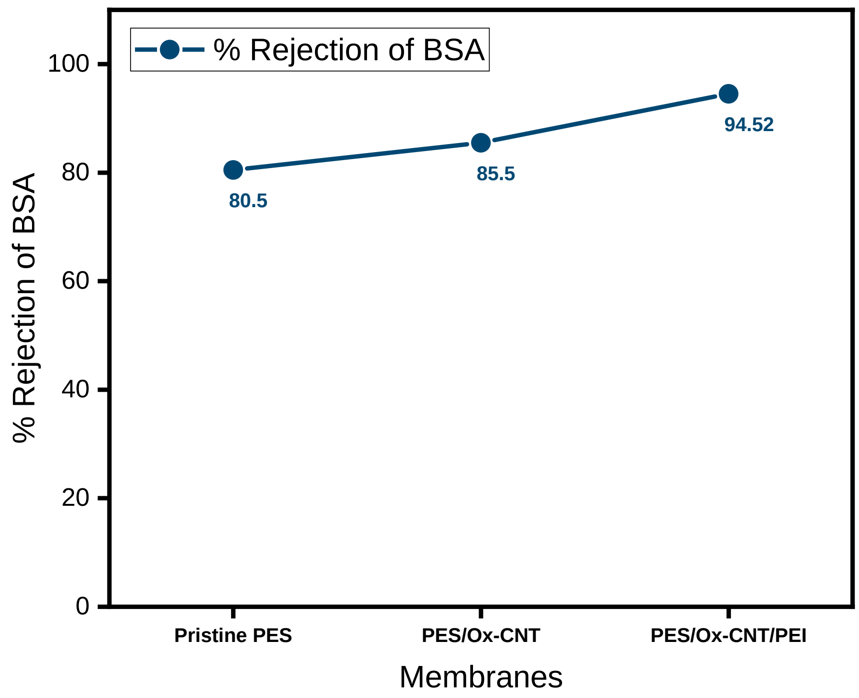


Figure 4.14. Bovine serum albumin rejection of Pristine polyether sulphone, unmodified polyether sulphone/oxidized-MWCNTs mixed matrix membrane and modified polyether sulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

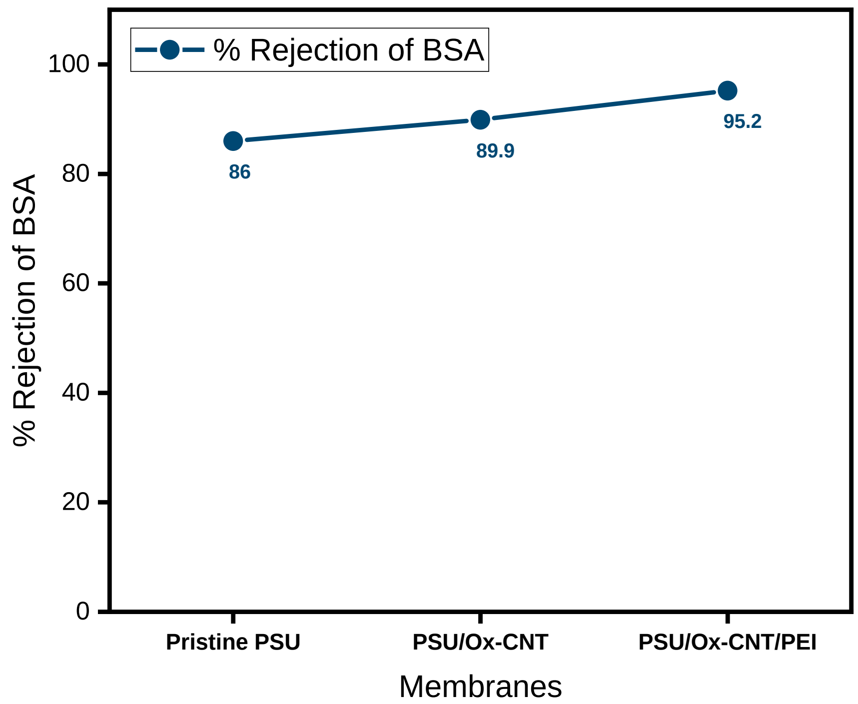


Figure 4.15. Bovine serum albumin rejection of pristine polysulphone, unmodified polysulphone/oxidized-MWCNTs mixed matrix membrane and modified polysulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

4.3 Heavy Metal Rejection studies of Modified and Unmodified Membranes

The heavy metal rejection study was conducted at a transmembrane pressure of 50 psi and an acidic pH of 2.6 at 25℃, which are the optimal conditions reported earlier by Prachi et al[82]. At acidic pH, protons interact with heavy metal ions, leading to high rejection. The presence of functional groups such as azide, triazole, amine, carboxylic, benzenecarbonyl, and triazine on the membrane surface enables adsorption, which helps to reject heavy metal ions. Additionally, the complexation ability of these functional groups also contributes to the higher rejection.

The rejection of heavy metal ions by modified membranes relies on two crucial processes: high charge density and the size exclusion effect. These membranes have surfaces that are either positively or negatively charged, which creates an electrostatic environment that is vital for 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, 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 molecules to pass through while hindering the passage of larger heavy metal ions. This size-based selectivity further contributes to the effectual removal of heavy metal ions. The combination of electrostatic attraction and size exclusion effect makes these modified membranes highly effective in rejecting heavy metal ions from contaminated solutions[204,205].

4.3.1 Heavy Metal Rejection of unmodified and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

Based on Table 4.1, it can be observed that the modification resulted in an increase in the rejection percentage of heavy metals. Specifically, for the pristine polysulphone membrane, the rejection of heavy metals is lower compared to the polysulphone/azide-MWCNT membrane. The modified polysulphone/azide-MWCNT membrane via click reaction exhibited 99% rejection of Cu(II), surpassing the unmodified membrane, because of the presence of triazole rings on its surface, which enhanced the separation or rejection of heavy metal ions through adsorption and complexation with azide and triazole functional groups on the membrane surface. The report stated that the incorporation of azide CNTs and the presence of azide and triazole groups in the membrane enhanced its adsorptive properties[82]. The triazole ring serves as a soft ligand that has a strong π acceptor interaction and a weaker σ donor interaction. This property results in its higher complexation ability for Cu(II). Other metals like Pb(II) and Cr(VI) also show higher rejection after surface modification of the membrane via the click reaction. Copper is selectively rejected at a higher percentage. It is worth noting that copper pollution is a significant concern due to its toxicity to the environment. In addition, copper contamination in drinking water is also a problem, which can occur due to corrosion in water pipes. Modified membranes may provide an effective solution for wastewater treatment.

Table 4.1. Heavy metal rejection study of pristine polysulphone, unmodified polysulphone/azide-CNT mixed matrix membrane and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

Membranes	**% REJECTION OF METALS**				
	Cr(VI)	Cu(II)	Pb(II)	Cd(II)	Hg(II)
Pristine PSU	37.0±1.3	77.0±1.5	47.0±1.4	44.0 ± 2.08	36.0 ± 0.82
PSU/Az-CNT	89.0±1.7	96.0±1.8	81.0±1.2	75.3 ± 1.00	78.33 ± 1.15
PSU/TAz-CNT	95.0±1.6	98.0±1.0	90.0±1.5	89.0 ± 0.82	94.7 ± 0.33

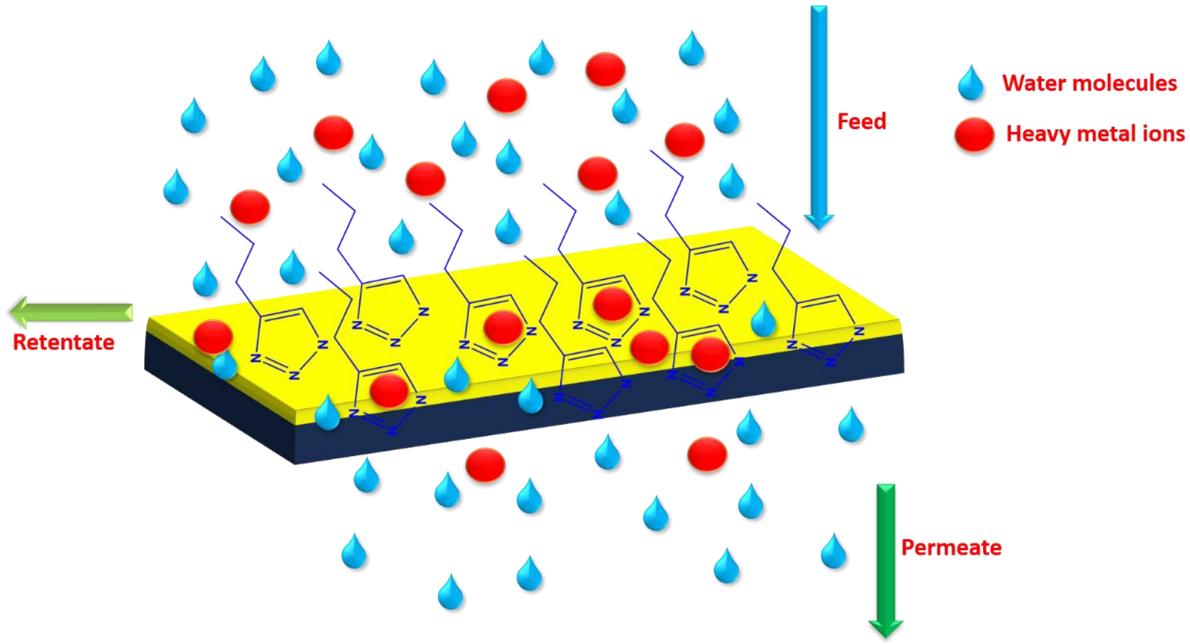


Figure 4.16. Representation of heavy metal rejection thorough modified polysulphone/azide-MWCNTs membrane via click reaction due to adsorption as well as complexation

4.3.2 Heavy Metal Rejection of unmodified and modified polyether sulphone and polysulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

Table 4.2 and Table 4.3 demonstrate that the modified mixed membrane exhibits improved heavy metal rejection compared to the unmodified membrane. This is due to the introduction of surface functional groups on the membranes. The table shows that the modified membrane with cynuric chloride has better rejection compared to the modified membrane with trimesoyl chloride. This can be attributed to the different structures of these two modifiers, as cynuric chloride introduces a 1,3,5-triazine ring on the membrane surface, while trimesoyl chloride introduces a 1,3,5-benzenetricarbonyl ring. This results in a higher rejection rate for the modified membranes compared to the unmodified membrane. 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 serve as a good ligand. Cynuric chloride reacts with the amine functional groups on the membrane surface, but it is difficult to predict how many chlorines are displaced to form an amide linkage. However, it is commonly accepted that a triazine ring is introduced on the membrane surface, which forms a complex with heavy metal ions. Before modification with cynuric chloride, only one N-donor atom was available to form a complex, but after modification, the number of N-donor atoms increases threefold. Benzene tricarbonyl, with the molecular formula 1,3,5-benzenetricarbonyl, can act as a ligand by forming a complex with heavy metals through its carboxylate groups. These groups can function as a donor atom and bind to the metal center via the oxygen atom of the carbonyl group (C=O). After reacting the amine functional groups with trimesoyl chloride, these groups are introduced onto the membrane surface. This modification increases the number of donor atoms, which in turn facilitates the formation of a complex.

The PES and PSU/amine-MWCNTs modified membrane with cynuric chloride showed improved rejection levels of ~95.2% and ~96.3% for Cr(VI), compared to the unmodified membrane with amine functional groups. This is due to the complex formation between the triazine ring and Cr(VI), although Cr(VI) itself does not form a complex. However, in acidic pH, Cr(VI) reduces to Cr(III), which then forms a complex with the triazine ring present on the membrane surface[206,207]. Modified with trimesoyl chloride, ~94.6% and ~96.0% rejection for Cr(VI) was observed because of the formation of Cr(III) complex with 1,3,5-benzenetricarbonyl[208]. Chromium contamination is a significant environmental issue that negatively impacts water and soil resources through its harmful effects. Industrial effluents/wastewater are primarily responsible for the chromium pollutants present in the environment, with hexavalent chromium being the most hazardous form. Membrane-based processes are highly effective in removing chromium from water, and the specific method utilized depends on the type and level of contamination. It is certainly feasible to use modified membranes for chromium removal from contaminated industrial wastewater.

Copper contamination can have significant consequences for the ecosystem, particularly for aquatic life and plant diversity. This may occur through both human activities, like copper mining and industrial processes, as well as natural processes. To mitigate the impacts of copper contamination, various membrane filtration techniques can be employed, including ultrafiltration, nanofiltration, and reverse osmosis, which are effective at removing copper from water. The modified membranes showed improved rejection of Cu(II) up to 99% with 1,3,5-triazine ring on the membrane surface, compared to 98% with 1,3,5-benzenetricarbonyl functional groups, due to both adsorption and complex formation of Cu(II) with available functional groups on the surface. While copper has a high affinity for forming complexes with different ligands, including amines, its ions exhibit a higher affinity for nitrogen atoms than oxygen atoms. This is why the observed copper rejection is less for the PES and PSU/amine-

MWCNT mixed matrix membranes which have been modified with trimesoyl chloride compared to those modified with cynuric chloride[209].

The modified membranes demonstrate a higher rejection rate for lead (Pb(II)) compared to unmodified membranes. At elevated levels, lead toxicity can prove fatal, as it impairs the mental and physical development of children. Nanofiltration and thin film composite reverse osmosis (RO) membranes are particularly effective in rejecting lead ions from water, thereby playing a substantial role in the production of lead-free water and ensuring its safety for consumption. The modified polysulphone/amine-CNT and polyether sulphone/amine-CNT membranes showed a higher rejection rate of approximately 96.7% and 97.6%, respectively, compared to both unmodified and pristine membranes. The improved rejection rate is attributed to the support provided by the surface functional groups for the absorption and complex formation of lead[210].

The rejection of other heavy metals increased after surface modification with trimesoyl chloride and cyanuric chloride. The polysulphone membrane, when modified with cyanuric chloride, shows approximately 96.5% and 97.8% rejection rates for cadmium (Cd(II)) and mercury (Hg(II)), respectively. The polysulphone membrane modified with trimesoyl chloride, on the other hand, displays around 95.96% and 97.2% rejection rates for the same heavy metals. The polyether sulphone mixed matrix membrane, after being modified with either cyanuric chloride or trimesoyl chloride, exhibits rejection rates of approximately 95.3% and 97.6% for Cd(II) and Hg(II), respectively. It is clear that the rejection rates of heavy metals improved for all modified membranes compared to their unmodified membranes. This improvement in rejection performance can be attributed to the introduction of functional groups on the membrane surface through modification. These functional groups have the ability to adsorb and complex with heavy metal ions, resulting in more effective interaction. The modified membranes showed an increase in surface functionalities, which led to better complexation-based separation and higher rejection rates for heavy metals. These membranes have exceptional potential for efficient heavy metal ion separation and purification applications, and they could bring advancements in environmental and industrial processes.

Table 4.2. Heavy metal rejection study of pristine polyether sulphone, unmodified polyether sulphone/amine-MWCNTs mixed matrix membrane and modified polyether sulphone/amine-CNT mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

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

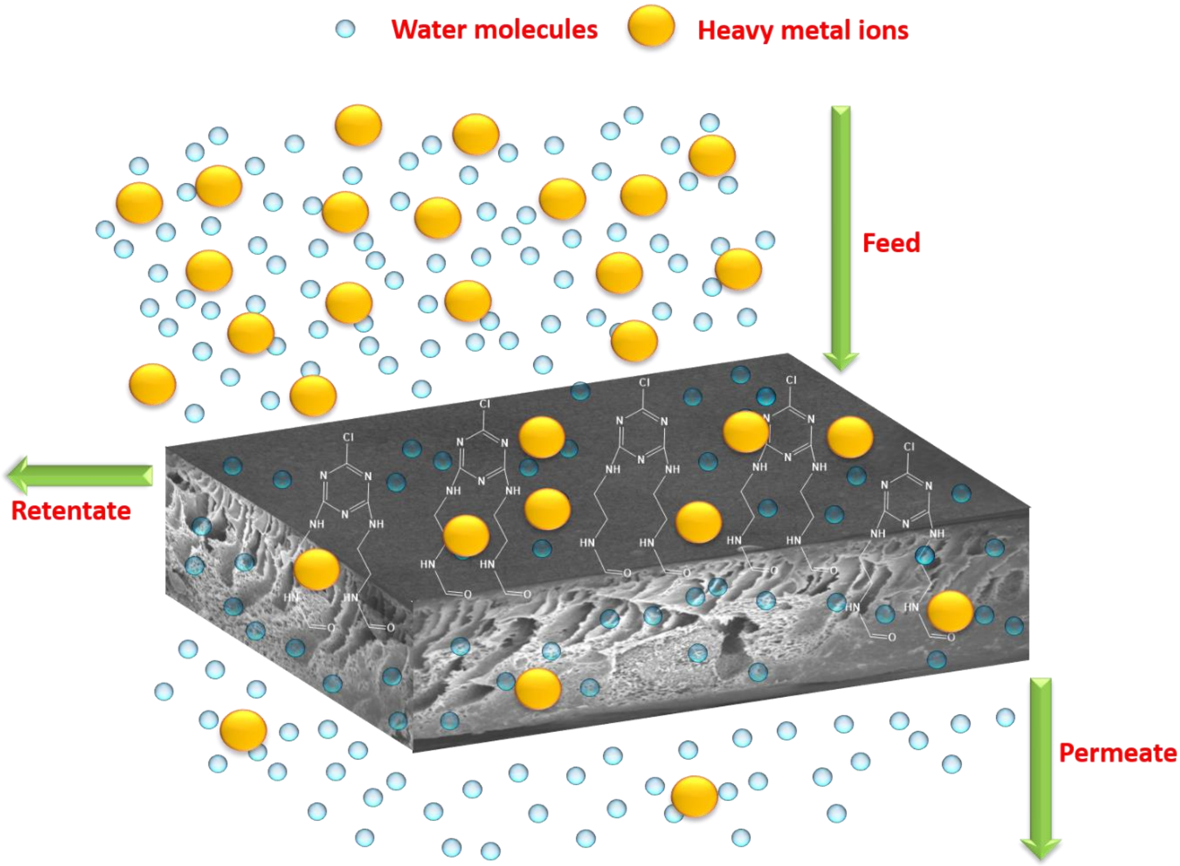


Figure 4.17. Representation of heavy metal rejection thorough modified polyether sulphone/amine-MWCNTs membrane using TMC and CC due to adsorption as well as complexation

Table 4.3. Heavy metal rejection study of pristine polysulphone, unmodified polysulphone/amine-MWCNTs mixed matrix membrane and modified polysulphone/amine-CNT mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

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

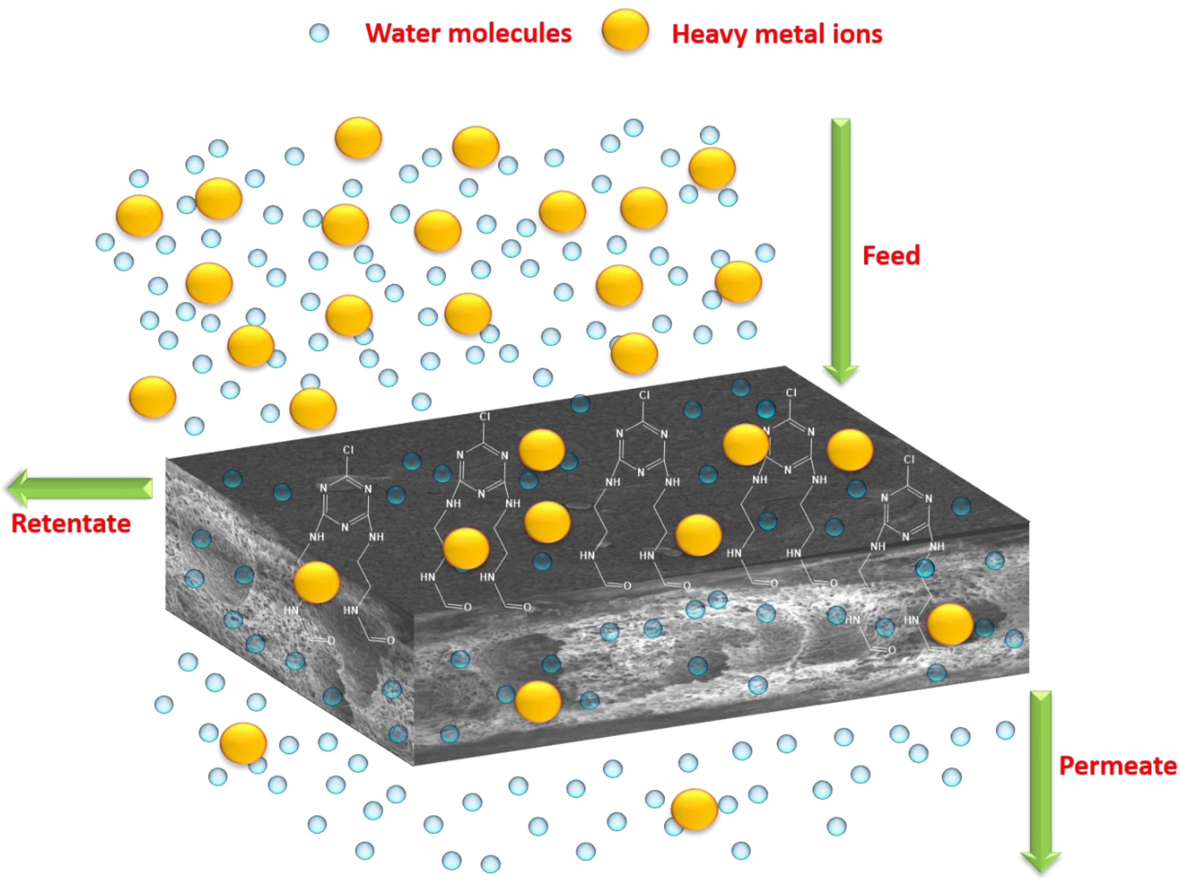


Figure 4.18. Representation of heavy metal rejection thorough modified polysulphone/amine-MWCNTs membrane using TMC and CC due to adsorption as well as complexation

4.3.3 Heavy Metal Rejection of unmodified and modified polysulphones/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

Table 4.4 and Table 4.5 illustrate the percentage of heavy metal rejection for membranes. The rejection percentages for heavy metals were found to be 35.67% ± 0.33 for Cr(VI), 78.83% ± 0.71 for Cu(II), 44.83% ± 0.44 for Pb(II), 43.8% ± 0.58 for Cd(II), and 34.3% ± 1.07 for Hg(II) for Pristine PES membranes. Similarly, for Pristine PSU membranes, the rejection percentages were 37.0% ± 1.3 for Cr(VI), 77.0% ± 1.5 for Cu(II), 47.0% ± 1.4 for Pb(II), 44.0% ± 2.08 for Cd(II), and 36.0% ± 0.82 for Hg(II). However, upon the addition of oxidized-MWCNTs to the polymeric matrix, substantial enhancements were observed in the rejection percentages. For PES membranes, the rejection percentages changed to 70.43% ± 0.47 for Cr(VI), 78.63% ± 0.32 for Cu(II), 35.93% ± 0.27 for Pb(II), 50.0% ± 0.08 for Cd(II), and 45.67% ± 0.27 for Hg(II). Similarly, upon incorporating oxidized-MWCNTs into PSU membranes, substantial enhancements were observed in rejection percentages: 85.43% ± 0.14 for Cr(VI), 71.93% ± 0.28 for Cu(II), 50.23% ± 0.16 for Pb(II), 71.83% ± 0.41 for Cd(II), and 68.43% ± 0.29 for Hg(II). However, a significant improvement in rejection percentages was achieved after the treatment with PEI on membrane surface creating amide linkage and more functionalities, resulting in 95.93% ± 0.19 rejection of Cr(VI), 98.1% ± 0.08 rejection of Cu(II), 97.1% ± 0.09 rejection of Pb(II), 92.1% ± 0.12 rejection of Cd(II), and 97.27% ± 0.27 rejection of Hg(II). The highest rejection percentages were achieved with PSU/oxidized-MWCNTs membranes modified with PEI, showing values of 94.83% ± 0.1 for Cr(VI), 98.27% ± 0.16 for Cu(II), 96.2% ± 0.29 for Pb(II), 93.87% ± 0.12 for Cd(II), and 98.23% ± 0.16 for Hg(II).

The research found that incorporating oxidized-MWCNTs into PES and PSU membranes led to a substantial increase in the rejection of heavy metal ions. This effect was further improved by treating the membrane surface with polyethyleneimine (PEI), which can be attributed to the functional groups on the surface that can adsorb and form a complex with heavy metal ions[82,85,104]. The membrane modifications that were made resulted in an increased number of surface functionalities, which led to better separation through complexation. This research highlights the importance of these modifications for efficient heavy metal ion separation and purification, with potential applications in environmental and industrial processes.

The surface modification with PEI on the PES and PSU/Ox-CNT mixed matrix membrane created amine functional groups, which resulted in the formation of amide linkages.

However, the presence of amine groups on the surface could result in the formation of complexes with heavy metal ions which are ultimately rejected by the membranes. XPS data and zeta potential studies indicate that some protonated amines are present on the surface, creating a positive charge. Positively charged membranes have been found to be highly effective in removing heavy metals from wastewater because of the electrostatic repulsion between the positively charged surface and the positively charged heavy metal ions[211,212].

Table 4.4. Heavy metal rejection study of pristine polyether sulphone, unmodified polyether sulphone/oxidized-MWCNT mixed matrix membrane and modified polyether sulphone/oxidized-MWCNT mixed matrix membrane using polyethylenimine (PEI)

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/Ox-CNT	70.43 ± 0.47	78.63 ± 0.32	35.93 ± 0.27	50.0 ± 0.08	45.67 ± 0.27
PES/Ox-CNT/PEI	95.93 ± 0.19	98.1 ± 0.08	97.1 ± 0.09	92.1 ± 0.12	97.27 ± 0.27

Table 4.5. Heavy metal rejection study of pristine polysulphone, unmodified polysulphone/oxidized-MWCNT mixed matrix membrane and modified polysulphone/oxidized-CNT mixed matrix membrane using polyethylenimine (PEI)

Membranes	**% Rejection Of Metals**				
	Cr(VI)	Cu(II)	Pb(II)	Cd(II)	Hg(II)
Pristine PSU	37.0±1.3	77.0±1.5	47.0±1.4	44.0 ± 2.08	36.0 ± 0.82
PSU/Ox-CNT	85.43 ± 0.14	71.93 ± 0.28	50.23 ± 0.16	71.83 ± 0.41	68.43 ± 0.29
PSU/Ox-CNT/PEI	94.83 ± 0.1	98.27 ± 0.16	96.2 ± 0.29	93.87 ± 0.12	98.23 ± 0.16

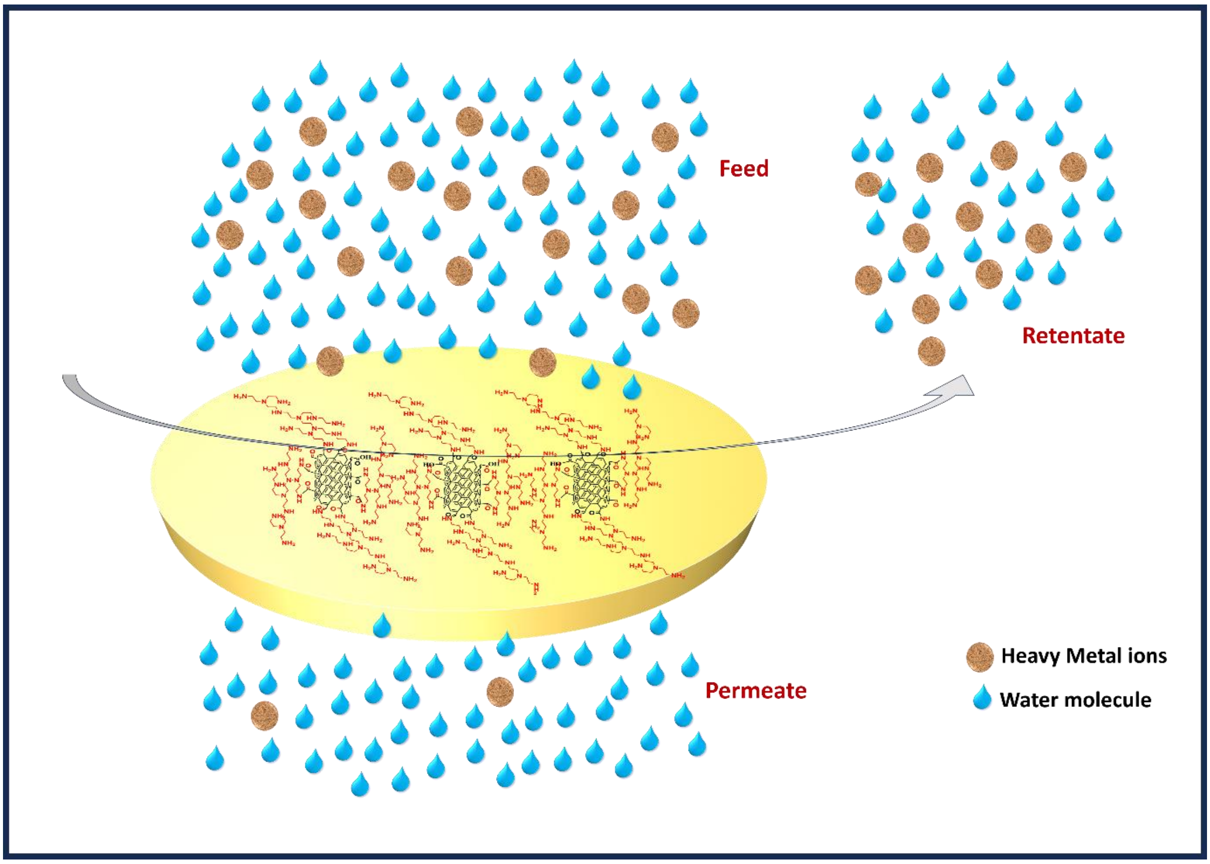


Figure 4.19. Representation of heavy metal rejection thorough modified PES or PSU/amine-MWCNTs membrane using PEI due to adsorption as well as complexation