



Development and characterization of p-phenylenediamine/g-C₃N₄-based composite polysulfone (PSF) membranes for enhanced chromium (Cr(VI)) removal from wastewater

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Abstract

In this study, polysulfone (PSF)-based composite membranes were synthesised through phase inversion. These membranes were then dip-coated with non-functionalized and functionalized Graphitic Carbon Nitride (g-C₃N₄) to enhance Chromium (Cr(VI)) removal from a Cr(VI)-containing aqueous industrial water matrix. The effect of nanofiller loading and functionalization concentration on membrane morphology, thermal stability, hydrophilicity, porosity, pure water flux, and Cr(VI) rejection was systematically investigated. Thermogravimetric Analysis (TGA) depicted improved thermal stability upon incorporation of non-functionalized and functionalized g-C₃N₄, while Scanning Electron Microscopy (SEM) revealed structural modifications. Water Contact Angle (WCA) measurements demonstrated significant enhancement in surface hydrophilicity after g-C₃N₄ incorporation and further improvement upon its functionalization with Para-Phenylenediamine (PPD). Among the non-functionalized membranes, the membrane containing 0.2 g g-C₃N₄ exhibited optimal performance in terms of permeability and rejection. Functionalization of 0.2 g g-C₃N₄ with 0.054 mg PPD resulted in the highest porosity, maximum pure water flux of 56.12 L m⁻² h⁻¹ and superior Cr(VI) rejection of 95.69%. The results demonstrate that moderate non-functionalized and functionalized g-C₃N₄ loading significantly enhanced the membrane permeability–selectivity balance, making the optimized membrane highly suitable for Cr(VI) removal from aqueous industrial water matrices.

Keywords

Composite membrane, graphitic Carbon Nitride (g-C₃N₄), para-Phenylenediamine (PPD), Chromium (Cr(VI)) removal

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Introduction

Freshwater has been recognized as a valuable asset that sustains life on Earth and acts as a core input in various industrial processes.¹ Although approximately seven-tenths of the world's surface is covered by water, however only approximately 3% is categorized as fresh water and unfortunately the majority two-thirds of this amount is not fit for direct usage.² The United Nations projections indicate that two to seven billion people are projected to experience acute water shortages in the mid-twenty first century.³ Thus, the wastewater purification processes are a promising solution. Industrial wastewater involves a range of processes and mechanisms established by engineers to remediate effluents contaminated by industry.⁴ In recent times, membrane-based filtration technologies have emerged as a preferred method of water treatment due to their simplicity of operation and lower energy requirements compared with traditional methods.⁵ Conventional polymeric membrane substrates include polysulfone (PSF), polycarbonate (PC), polyacrylonitrile (PAN), etc. PSF is particularly preferred for membrane fabrication because it is accessible, easily modified, chemically stable, offers high mechanical strength, has an inherent

surface charge and a wide operational temperature and pH range.⁶ The presence of alkyl or aryl sulfone derivatives in PSF are responsible for its low cytotoxicity.⁷ The high

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amount of aromatic content in PSF is the reason of its high biocompatibility.⁸ Modifying PSF membranes by the introduction of hydrophilic functional groups represents an effective strategy to improve membrane performance.⁹

Nanoparticles are often used in membrane matrices to improve their hydrophilicity and performance.¹⁰ Nanoparticle-incorporated membranes benefit simultaneously from the inherent characteristics of the polymeric substrate but also from the nanoscale features brought by the filler. Membrane performance can be further improved by surface functionalization techniques where the main objective is the increase of hydrophilicity through surface coating.¹¹ Numerous nanoparticles have been investigated and functionalized for membrane surface modification. g-C₃N₄ has become a promising candidate owing to its impressive durability, charge density, hydrophilicity and chemical robustness. In the research scope of practical application, both surface-centred and bulk incorporation strategies are relevant (for example, blending) which are critical to the tailoring of high-performance membranes. g-C₃N₄ seems to be an ideal candidate for modifying both the skeleton structure and surface chemistry of polymeric membranes. Its abundant free amine groups (–NH₂) give it tunability and the triangular gaps made by sp²-hybridized C and N atoms act as inherent water-transport passages within the matrix.¹² Despite g-C₃N₄ enhances the hydrophilicity and separation efficacy of PSF membranes, the tendency of g-C₃N₄ to form agglomerates and poor interfacial compatibility with a polymer matrix can limit further improvement. In order to mitigate these challenges and to compact the chemical properties of the surface, g-C₃N₄ has been functionalized with amine groups (–NH₂), which improves the dispersion, interfacial interaction and improves the overall membrane performance.¹³

Functionalization of g-C₃N₄ with PPD allows the introduction of a high density of amine (–NH₂) surface-based functional groups on the layered carbon-nitride nanomaterial, significantly improving its physicochemical properties for Cr(VI)-containing aqueous matrix application. The use of PPD for the functionalization of g-C₃N₄ could lead to the introduction of extra amine-containing functional groups on the surface of g-C₃N₄, which may alter the surface polarity, hydrophilicity, and interaction sites. In the literature, amine-functionalized materials have been reported to interact with Cr(VI) species, especially under acidic conditions, when the amine groups can be protonated. In the present study, however, this interaction is not directly verified, but rather is considered as a possible/proposed contribution, as zeta potential analysis, adsorption kinetic/isotherm studies and post-filtration X-ray Photoelectron Spectroscopy (XPS) analysis were not conducted.¹⁴ Surface amination of carbon-based nanomaterials has been widely documented as an effective technique to facilitate heavy metal removal through promoting more active adsorption sites and improving dispersion stability.¹⁵ When dip-coating on PSF membranes, the amine-functionalized g-C₃N₄ demonstrates excellent interfacial compatibility with the polymer matrix by means of hydrogen bonding and π - π interactions, which leads to a lower agglomeration and a more homogeneous spatial distribution. This better dispersion reduces structural flaws and maintains membrane integrity, which is particularly important in maintaining structural, stable, long-term filtration performance.

In addition to facilitating the adsorption capacity, the amine functionalization plays an important role in improving the membrane's hydrophilicity along with its transport characteristics. The introduction of amine groups on the membrane surface form a more polar interface and thus substantially decreases the contact angle between water and membrane as well as strengthen the interaction between water and membrane and the development of the hydration layer. Increased hydrophilicity has been found to result in reduced mass transfer resistance and enhanced pure water flux without loss of rejection performance.¹⁶ A common challenge in membrane technology dilemma is the permeability/ selectivity trade-off in which typically an increase in flux can be at the cost of a reduced rejection efficiency.¹⁷ Nevertheless, careful surface functionalization in combination with optimized nanofiller dispersion can improve both permeability and selectivity at the same time. The addition of functionalized g-C₃N₄ onto PSF surfaces can be used to customize pore architecture and surface charge distribution, and can therefore increase Cr(VI) rejection, whilst keeping high water permeability.¹⁸ Outstanding interfacial bonding of the filler and polymer matrix lowers the formation of non-selective voids that usually leads to a selectivity loss in nanocomposite membranes. Consequently, amine-modified g-C₃N₄ coatings exhibit a synergistic enhancement of the membrane transport properties.

Furthermore, the surface hydrophilicity has been reported to be an important parameter affecting the fouling characteristics of the membrane, as hydrophilic surfaces might decrease hydrophobic interaction between the membrane surface and foulants. In the current research, surface hydrophilicity has been evaluated based on WCA measurement after introduction of g-C₃N₄ and PPD. Consequently, any enhancement in fouling resistance can be referred to as an assumption made because of improved hydrophilicity and increased uniformity in surface morphology. Hydrophilic membrane surfaces are more resistant to the adhesion of the foulants as a result of reduced hydrophobic interactions and the development of a persistent hydration layer that offers a physical barrier against contaminant deposition.¹⁹ Amine-functionalized surfaces also have better electrostatic repulsion to the negatively charged foulants, which further minimize the irreversible fouling and increase the flux recovery.²⁰ Enhanced thermal stability and structural robustness of nanocomposite systems, as seen in functionalized nanocomposite systems, aids in the improved lifespan and resistance of membrane structure under harsh operating conditions. Consequently, it is expected that dip-coating of PSF membranes with amine-functionalized g-C₃N₄ will enhance Cr(VI) adsorption capacity, increase the pure and wastewater flux, improve rejection efficiency and significantly reduce the fouling tendency. This high-permeability, selectivity, stability, and antifouling performance enhancement of amine-modified g-C₃N₄ -coated PSF membranes makes them a promising candidate as an advanced and sustainable solution for the treatment of heavy metals from complex wastewater systems.

In this study, g-C₃N₄ was functionalized with PPD to allow amine (–NHx) functional groups to be introduced to increase the adsorption capacity and surface reactivity. The functionalized g-C₃N₄ was then dip-coated onto a PSF

membrane to increase its hydrophilicity, permeability and selectivity for Cr(VI)-containing aqueous matrix applications. The performance of the modified membrane was assessed by determining the pure water flux to determine its permeability and then with Cr(VI) containing wastewater for determining the flux behaviour under actual conditions. Furthermore, the removal efficiency of Cr(VI) was studied to investigate the membrane's ability to reject heavy metals. For the amine-functionalized membrane, the enhanced Cr(VI) removal is expected to result from a combined effect of improved hydrophilicity, modified surface morphology, increased porosity, and possible interaction of Cr(VI) species with amine-containing groups, however, the electrostatic interaction contribution is not directly confirmed in this study. Therefore, it is discussed as a proposed mechanism.

Materials and methods

Materials

All chemicals used were of analytical grade and were used as received without further purification. PSF ($MW = 36000$ g mol⁻¹, 96% purity) was purchased from BASF, Germany. Melamine ($\geq 99\%$) was supplied by the company Sigma - Aldrich and it was used as a precursor for the preparation of g-C₃N₄. PPD $\geq 99\%$ and succinic acid ($\geq 99\%$) and ethanol ($\geq 99.8\%$, absolute) were also purchased from Sigma-Aldrich. N-methyl-2-pyrrolidone (NMP, 99%) was Chemical, Korea. Tetrahydrofuran (THF, $<99.0\%$) was provided by Merck KGaA, Germany. Deionized water was used for membrane preparation, washing, synthesis and filtration experiments during the whole study process. The in-house synthesis of g-C₃N₄ was done by thermal polymerization of melamine. A Cr(VI)-containing aqueous industrial water matrix was provided by Briter Engineering Company (Pvt) Ltd Pakistan for membrane filtration experiments, and the wastewater was fed to membranes for Cr(VI) removal performance. All quantitative measurements were performed in repeated trials, and the results are reported as mean $\pm$ standard deviation. Error bars in the figures represent the standard deviation of the repeated measurements.

Synthesis of g-C₃N₄

g-C₃N₄ was synthesized via a pyrolysis process using melamine as the precursor. First, 10 g of melamine (C₃H₆N₆) was introduced in a crucible of alumina and heated in air. The sample was heated at 10 °C per minute until it reached the desired temperature in the range of 400-600 °C and desired temperature was maintained for 2 h. During thermal treatment of melamine, stepwise condensation reactions occurred and intermediate species such as melem and melon were formed at intermediate temperatures, and then the condensation reaction was continued to form polymerization products as layered g-C₃N₄ structure at high temperatures. The crystallization of g-C₃N₄ was achieved during calcination at temperatures between 550 and 600 °C, but temperatures above 600 °C caused partial thermal decomposition of the material. The obtained product was collected as a yellow powder and used for further functionalization and membrane modification studies.²¹

Functionalization of g-C₃N₄ with PPD

Functionalization of g-C₃N₄ was done by using PPD through the polycondensation method. In a representative experiment, 0.2 g of pre-synthesized g-C₃N₄ was dispersed with a calculated amount of PPD in 5 ml of ethanol. The suspended solute was stirred until a homogeneous dispersion was obtained and then the ethanol was completely evaporated. The resulting dry powder was placed in a covered alumina crucible and heated to 400 °C at a ramp rate of 5 °C min⁻¹ for 2 h in a muffle furnace. After cooling, the finished product was isolated and ground into a fine powder so that it could be used later. Samples functionalized with different amounts of PPD were presented as CN-0.0108, CN-0.054, CN-0.27 and CN-0.54 corresponding to 0.0108, 0.054, 0.27 and 0.54 mg of PPD, respectively.²²

The functionalization was achieved through a polycondensation reaction between the amino groups (-NHx) on the g-C₃N₄ structure and the amine groups of PPD, leading to the incorporation of PPD units within the g-C₃N₄ framework.

Synthesis of composite nanofiltration membranes

PSF membranes were developed via the phase inversion method. A solution of 20 wt% PSF was synthesized by dissolving it in a blend of NMP and THF with a relative concentration of (wt:wt) 3:1. This solution was stirred at a thermal condition of 60 °C for 4 h to ensure complete dissolution, which was followed by an overnight stir at ambient temperature to make the solution homogenous and remove entrapped air. The casting dope was then uniformly distributed on a pristine and planar glass panel with the help of the casting knife, with a gap size of about 0.2 mm. The panel was then immersed and placed in a water bath at ambient temperature, which induced solvent/non-solvent exchange to give the PSF membrane. After being immersed, the membrane was detached washed thoroughly with distilled water and dehydrated at ambient temperature. The resulting membrane was then evaluated regarding to its physical/chemical properties.²³ The selection of a 3:1 NMP: THF solvent mixture ratio was chosen here to optimize the PSF solubility particularly and the membrane performance is based on the outcomes acquired from earlier phase inversion membrane research.

Dip-Coating of g-C₃N₄ and functionalized g-C₃N₄ on PSF membranes

The dip-coating method was applied for the purpose of refine the PSF membranes with g-C₃N₄ and functionalized g-C₃N₄. First, 5 g polyvinyl alcohol (PVA) was dissolved in 120 g water and stirred at 90 °C for 3 h to gain a homogeneous PVA solution. To prepare the g-C₃N₄ and functionalized g-C₃N₄ suspension, an appropriate quantity of g-C₃N₄ and functionalized g-C₃N₄ was suspended in 10 g of water and sonicated for 30 min to acquire a uniform dispersion. Subsequently, 1 g of succinic acid was introduced to the PVA solution, and the mixture was stirred for another 6 h at 90 °C to achieve full homogenization and formation of a stable PVA-g-C₃N₄ and PVA-functionalized-g-C₃N₄ suspension. Pre-prepared PSF membranes were soaked in PVA-g-C₃N₄ and PVA-functionalized-g-C₃N₄ suspension

Table 1. Composition of casting solutions and dip-coated membrane types.

Membrane type	PSF (wt %)	g-C ₃ N ₄ (g)	PPD (mg)	NMP + THF 3:1 (wt %)
M-0	20	0	0	80
M-1	20	0.1	0	80
M-2	20	0.2	0	80
M-3	20	0.4	0	80
M-4	20	0.2	0.0108	80
M-5	20	0.2	0.054	80
M-6	20	0.2	0.27	80

and excess solution was wiped out by lightly wiping membrane surface. The coated membrane was then degassed at 80 °C to remove residual air bubbles and to facilitate the development of a sleek and uniform coating layer. Following the drying process at ambient temperature for 24 h, the membrane was obtained and ready to use. This dip-coating process helps to achieve the uniform deposition of g-C₃N₄ and functionalized g-C₃N₄ nanosheets on the surface of PSF membranes, which increased the PSF membrane performance for different filtration applications such as water purification and pervaporation.²⁴ The formulation of the casting solutions and the types of dip-coated membrane are demonstrated in Table 1.

Characterization

The structural characteristics of the fabricated membranes were studied by using SEM. Before conducting SEM analysis, membranes were carefully fractured at liquid nitrogen to obtain clear cross-sectional views and sputter-coated with a slender layer of gold to give good conductivity and imaging distinctions. The presence of functional groups to determine the chemical integrity of pristine and modified membranes Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet –6700, Thermo Fisher Scientific, USA) was used. The crystallinity of the membranes obtained was evaluated by X-ray diffraction (XRD) (PANalytical X'Pert, Malvern, UK). The surface characteristics such as the specific surface area and the pore volume of g-C₃N₄ and functionalized g-C₃N₄ was investigated by Brunauer-Emmett-Teller (BET). WCA angle was determined by using tensiometer to measure the hydrophilicity of the surface. The thermal stability of pure PSF membrane and the coated membranes in a temperature range from 30 to 800 °C with the aim of estimation of the decomposition temperature and thermal behaviour was examined by TGA. These analyses gave information on the influence of the membrane structure and thermal characteristics with the addition of g-C₃N₄ and its functionalized g-C₃N₄.

Membranes performance evaluation

A crossflow filtration cell (Sterlitech HP4750, USA) was used to evaluate the efficiency of membranes with an area of the membrane 0.0025 m² at a pressure of 6 bar. Pure water flux was determined using deionized water, while Cr(VI) rejection was evaluated using the Cr(VI)-containing aqueous industrial water matrix.

Using Eq. (1), the flux of pure water (J_w) was obtained by:

$$(J_w) = \frac{V}{A \times \Delta t} \quad (1)$$

Where (J_w) presents the pure water flux (L m⁻² h⁻¹), while V is the volume of the permeate (L). A is the effective surface area (m²) of the membrane and t is the permeation time (h).

Rejection efficiencies for Cr(VI) removal were performed using a Cr(VI)-containing aqueous industrial water matrix as the feed solution, provided by Briter Engineering Company Ltd Pakistan. The concentration of Cr(VI) in the feed and permeate was assessed using a UV-Vis spectrophotometer to measure the Cr(VI) content in both streams. The UV spectrometry method was employed to determine Cr(VI) concentration in the feed and permeate solutions, and the removal efficiency was calculated based on the difference in concentration between the feed and permeate.

The rejection percentage (R%) for Cr(VI) removal were calculated using Equation (2):

$$R (\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (2)$$

where C_f and C_p are the feed and permeate concentrations of solutes, respectively.

The gravimetric method was used to assess the membrane porosity, as expressed by Equation (3):

$$\text{Porosity } (\%) = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{A d \rho} \right) \quad (3)$$

In the above equation, W_{wet} and W_{dry} are the wet and dry weights of the membrane (g), while A is the membrane surface area (m²), d is the membrane thickness (m), and ρ is the water density (g m⁻³). This parameter provides additional insight into the internal pore structure and contributes to the comprehensive understanding of membrane performance.

Results and discussion

Characterization of the g-C₃N₄ and functionalized g-C₃N₄ particles

The BET study was performed to determine the specific surface area (SBET) and total pore volume of both g-C₃N₄ and functionalized (f-g-C₃N₄) particles. The results of the study are summarized in Table 2. The BET analysis was performed using N₂ adsorption-desorption at –195.800 °C on a TriStar II 3020 analyser. The samples were automatically degassed in two stages: 90 °C for 30 min followed by 150 °C for 240 min, with a ramp rate of 10 °C/min. The BET surface area was calculated in the relative pressure range of approximately P/P₀ = 0.03–0.30.

Pristine (g-C₃N₄) and functionalized (f-g-C₃N₄). Both N₂ adsorption-desorption isotherms of pristine g-C₃N₄ and PPD-functionalized g-C₃N₄ showed mesoporous-type adsorption with an apparent hysteresis loop, especially in the relative pressure range of 0.45–0.5. The nitrogen

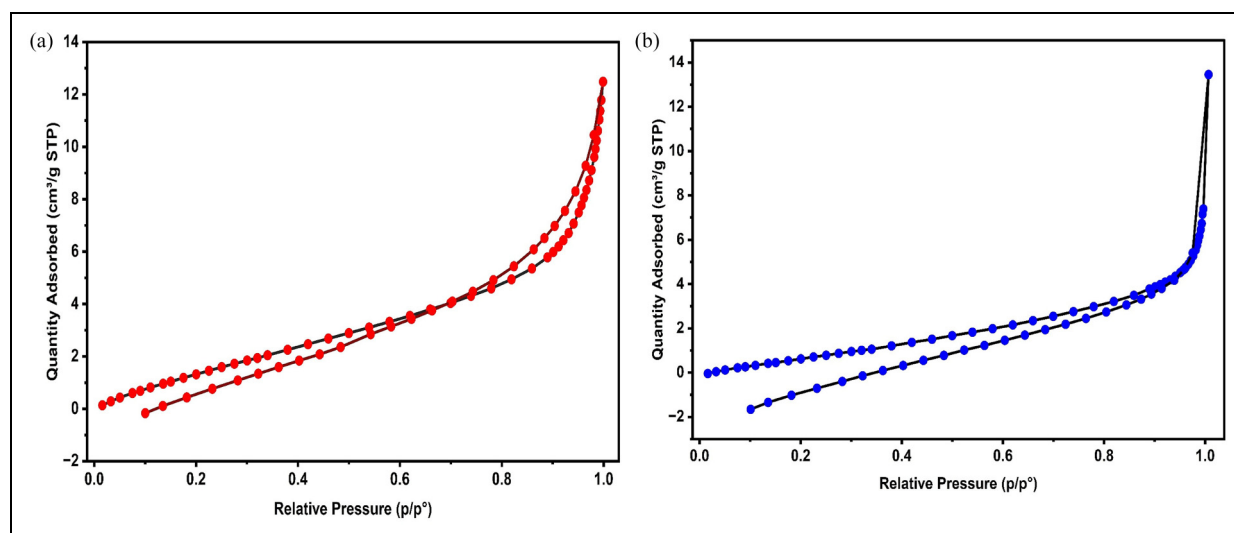
Table 2. Specific surface areas and total pore volume of g-C₃N₄ and f-g-C₃N₄ particles.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{(Langmuir)}}$ ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)
g-C ₃ N ₄	8.2118	1450.09	0.511
f-g-C ₃ N ₄	28.1058	1806.59	0.614

adsorption isotherm of BET-1 is linear and then increases sharply near $P/P_0 = 0.9$ – 1.0 . This behaviour can be attributed to the presence of mesopores and interparticle voids, which are typical of g-C₃N₄ nanosheets layered and aggregated structure. The relatively lower BET surface area of pristine g-C₃N₄, however, implies that there are some active surface sites that are not available because of nanosheet stacking and aggregation. Adopting the PPD functionalized g-C₃N₄ resulted in an improved adsorption–desorption profile and higher textural parameters in BET-2 than for the pristine g-C₃N₄. The BET surface area and pore volume of the PPD-g-C₃N₄ composite have increased after PPD functionalization, which indicates that the PPD functionalization process has opened the access of the g-C₃N₄ surface by increasing the surface voids and reducing nanosheet restacking. The modifications create additional active sites with increased nitrogen content and make larger pores available for water molecules and Cr(VI) species to access the active sites. The improved textural properties of PPD-functionalized g-C₃N₄ are directly related to membrane performance. The pore volume will enhance water transport through the modified membrane layer, and the high surface area will provide more adsorption/interaction sites for Cr(VI). Hence, the BET results agree with the improvement in membrane hydrophilicity, water flux and rejection of the PPD-functionalised g-C₃N₄/PSF membrane towards Cr(VI) ions. In modified g-C₃N₄ nanosheets, surface modification enhanced surface accessibility, dispersibility and overall functional performance has been reported (Figure 1).²⁵

Characterization of non-functionalized and functionalized composite nanofiltration membranes

The FTIR spectrum of the pristine PSF membrane (M0) had characteristic peaks at about 1584 cm^{-1} and 1488 cm^{-1} , which correspond to the stretching vibration of C=C in the aromatic rings, and a prominent peak at 1242 cm^{-1} , attributed to C–O–C asymmetric stretching vibration in the ether groups. The peaks are consistent with the characteristic PSF backbone and serve as a reference to assess the chemical changes after adding g-C₃N₄ and PPD-functionalized g-C₃N₄. When 0.2 g of g-C₃N₄ was added to the PSF membrane (M2), a significant enhancement in the intensity of the broad band (3100 – 3400 cm^{-1}) was seen. The band is assigned to the O–H/N–H stretching vibrations, primarily due to the terminal amino groups and N-rich sites of the g-C₃N₄ structure. The shift of this band is evidence of incorporation of extra polar functional groups within the membrane matrix which are more water molecule attractive to the membrane surface. Accordingly, this increase in surface hydrophilicity may decrease the resistance of water transport through the membrane and play a part in the increase of water flux, which is seen in the M2 membrane. The further changes in the M5 membrane functionalized with 0.054 mg of PPD and then dip-coated were seen in the region between 1200 and 1650 cm^{-1} . The higher intensities of the bands in this region can be attributed to the C–N, C=N, aromatic C–C, and N–H associated vibrations, which are the sum of the contributions from g-C₃N₄ and PPD. The peak at 1515 cm^{-1} is enhanced, suggesting the PPD has added aromatic and amine groups. The changes indicate the successful loading of PPD onto/into the PSF membrane matrix layer. The enhanced intensity of the FTIR bands in M5 and the minor shift in the peak positions indicate that higher FTIR bands can be formed by stronger interaction between PPD-functionalized g-C₃N₄ and PSF matrix, likely due to hydrogen bonding, dipole–dipole interactions, and π – π interactions. The FTIR band shifts and intensities changes are similar to those that have been linked to enhanced interfacial compatibility, increased polymer system polarity, increased dipole interaction, and more compact polymer-composite morphology

**Figure 1.** (a) BET-1 of g-C₃N₄ (b) BET-2 of functionalized g-C₃N₄ particles.

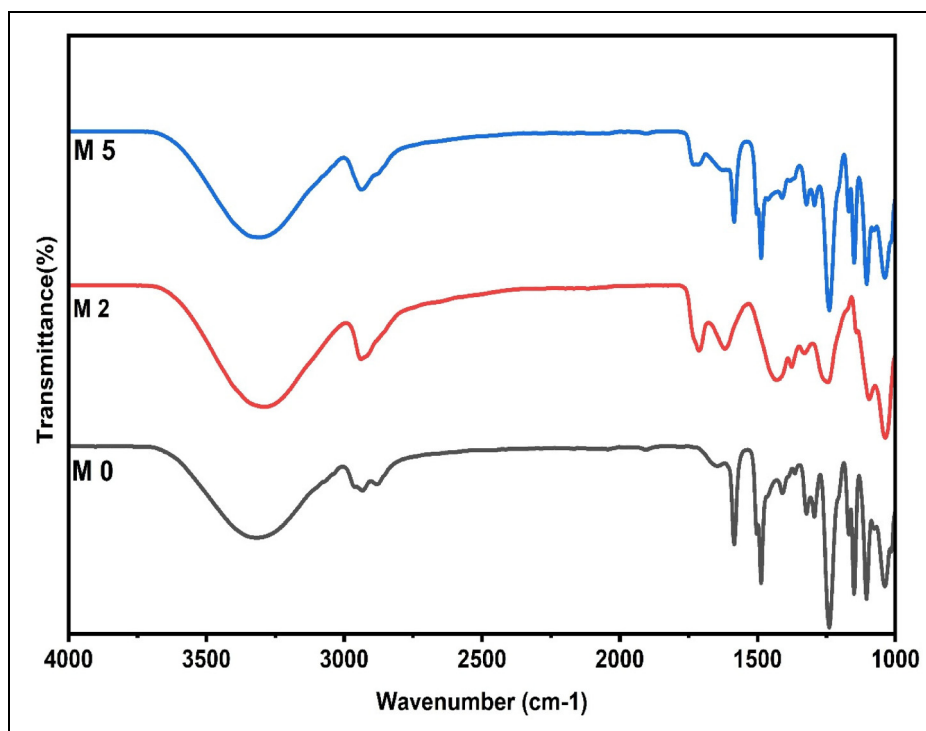


Figure 2. FTIR analysis of pristine M0, modified M2, and functionalized M5 PSF membranes.

in $g\text{-C}_3\text{N}_4$ /graphene-modified polymer systems.²⁶ The enhanced filler–polymer interaction can lead to better dispersion of the functionalized nanofiller and minimize the aggregation of nanosheets of $g\text{-C}_3\text{N}_4$. Surface modified $g\text{-C}_3\text{N}_4$ -based/Graphene systems are also reported to exhibit improved surface functionality, chemical stability and better functional performance.²⁷ Based on the FTIR results, it is concluded that the functionalization of PPD leads to an improvement in the performance of the membranes in two ways: it increases the hydrophilic polar groups which favour the transport of water molecules through the membrane, and it introduces nitrogen and amine groups which can provide sites for adsorption via electrostatic interactions, hydrogen bonding, and surface complexation with Cr(VI) species. Such effects lead to better flux and rejection of Cr(VI) for the M5 membrane (Figure 2).

The crystalline structure and phase orientation of pristine, modified and functionalized PSF membranes was assessed by XRD study and was depicted in Figure 3. As observed in the diffraction patterns, there are several diffraction peaks at 2-theta values of around 14.5° , 17.2° , 18.5° , and 21.6° in the diffraction patterns of the pristine PSF (M0) membrane. These peaks related to the characteristic SEMi-crystalline nature of the PSF polymer chain construction.²⁸ Upon incorporation of 0.2 g of $g\text{-C}_3\text{N}_4$ in membrane, M2, the main diffraction peaks of PSF were still visible, indicating that the polymer matrix does not lose its structural integrity. However, a little increase in the peak intensity and the exhibiting of minor peaks near the angle of the shoulder of the range corresponding to the (002) plane of $g\text{-C}_3\text{N}_4$ confirm the successful integration of the carbon nitride nanosheets in the membrane.²⁹ For the M5 membrane, in which it involves the functionalization with PPD, XRD record demonstrates a well-preserved crystalline profile. The

preservation of the sharp peak at 21.6° suggests that the long-range order of the PSF support is not disturbed by the dip-coating and amine functionalization. Furthermore, the small shifts or alterations in peak sharpness of both modified membranes (M2 and M5) with respect to M0 suggest an interaction between functional groups of PPD/ $g\text{-C}_3\text{N}_4$ and chains of PSF which can affect the mechanical stability and porosity of the membrane. This structural similarity with FTIR confirmed chemical changes that result in the successful fabrication of a robust and functionalized membrane surface suitable for improved water flux and separation performance (Figure 3).³⁰

TGA analysis was used to determine the thermal stability of the prepared membranes, revealing a distinct dependence on filler concentration and functionalization as demonstrated in Figure 4. A series of TGA were conducted on PSF membranes modified with varying amounts of $g\text{-C}_3\text{N}_4$ and PPD. Through the pure PSF membrane (M0), the typical curve of the thermal degradation is seen, and a major loss of weight was observed over the temperature range of about 400°C . When 0.1 g of $g\text{-C}_3\text{N}_4$ (M1) is incorporated, the thermal stability does not change significantly, and weight loss is also such as that of M0. But with a loading of 0.2 g (M2), some improvement of thermal stability is achieved, and the degradation rate decreases in the $450\text{--}500^\circ\text{C}$ zone, which is evidence of higher thermal degradation resistance. Additional incorporation of $g\text{-C}_3\text{N}_4$, to 0.4 g (M3) results in a minor reduction in thermal stability, presumably because of particle agglomeration. It is found that addition of PPD improves the thermal performance with M4 (0.0108 mg PPD) having slight change in weight loss as compared to M2. While M5 (0.054 mg PPD) exhibits the best performance, with the most gradual and controlled degradation curve, indicating optimal functionalization. Yet M6 (0.27 mg PPD) demonstrates a minor growth in

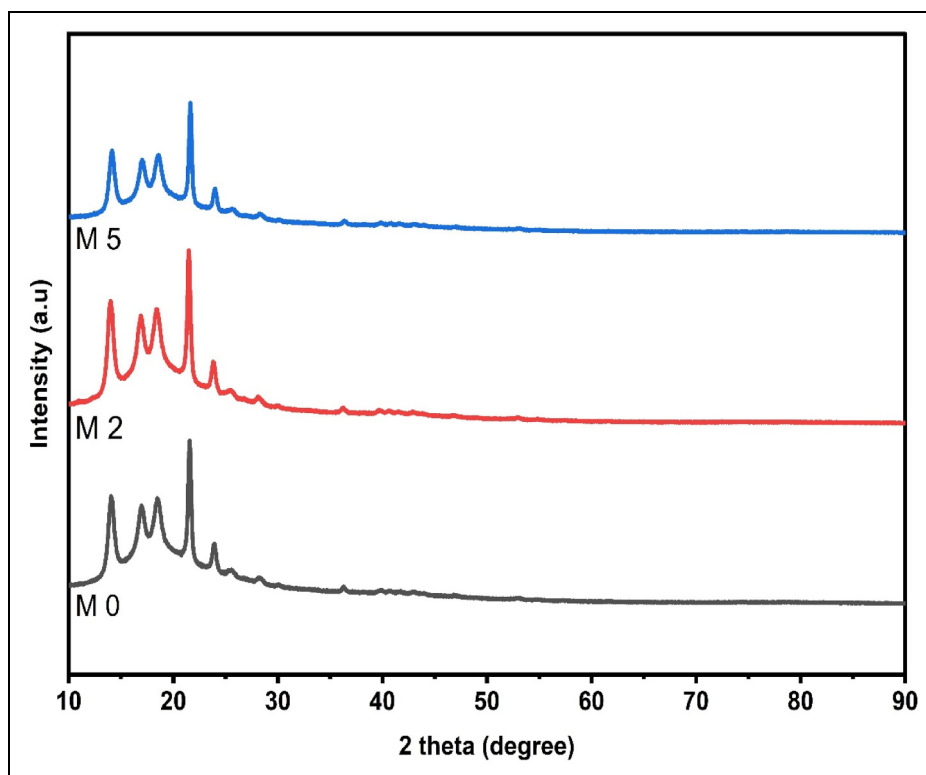


Figure 3. XRD analysis of pristine M0, modified M2, and functionalized M5 PSF membranes.

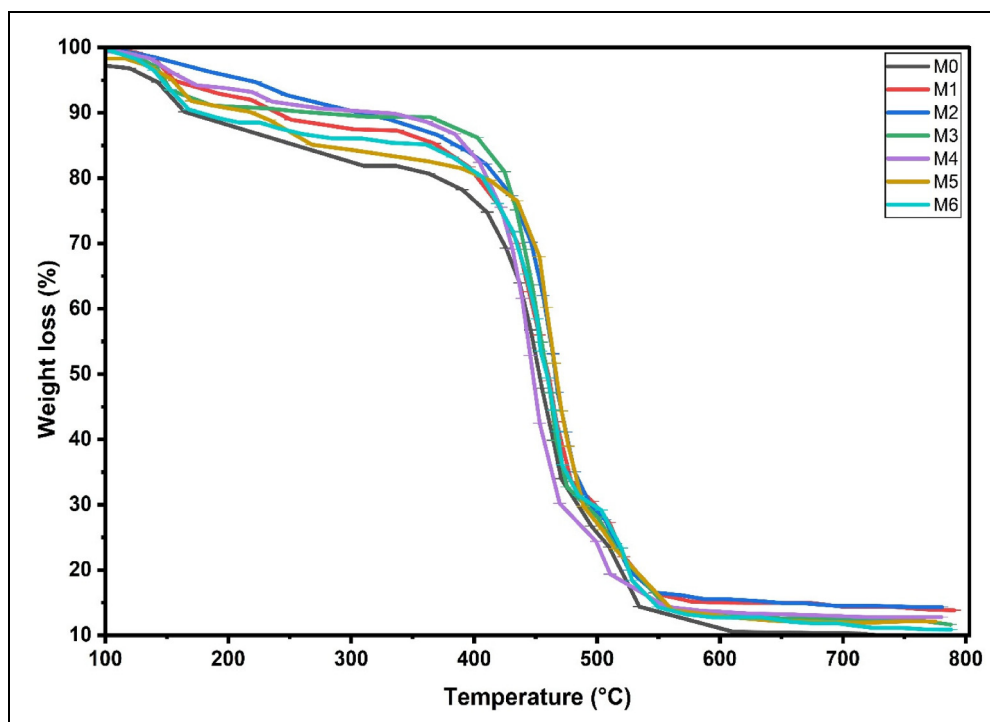


Figure 4. TGA of pristine M0, modified M1, M2 and M3, and functionalized M4, M5 and M6 PSF membranes.

weight loss implying that overworking the PPD functionalization has the adverse influence on the thermal stability of the membrane. In general, M2 (0.2 g $\text{g-C}_3\text{N}_4$) and M5 (0.2 g $\text{g-C}_3\text{N}_4$ functionalized with 0.054 mg PPD) have the best thermal stability with M2 being the best choice in $\text{g-C}_3\text{N}_4$ loading and M5 in functionalizing (Figure 4).³¹

Various PSF membranes modified with $\text{g-C}_3\text{N}_4$ and functionalized $\text{g-C}_3\text{N}_4$ were subjected to WCA measurements to examine their surface wettability and hydrophilicity which was illustrated in Figure 5. The WCA values, being significant, help determine the first point of contact of the membrane surface with water, which is a major factor for

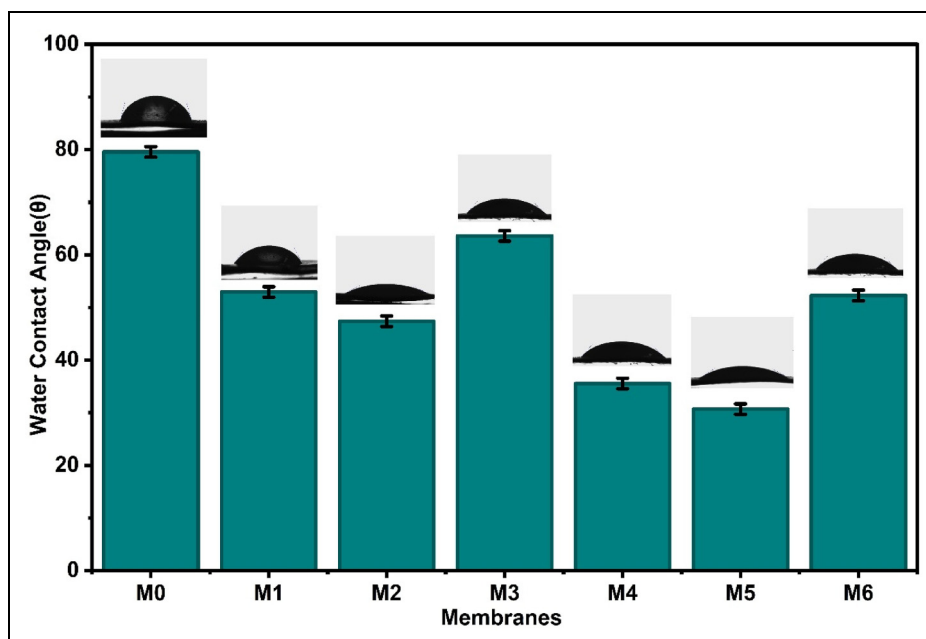


Figure 5. WCA of pristine M0, modified M1, M2 and M3, and functionalized M4, M5 and M6 PSF membranes.

filtration and other membrane processes. The pristine PSF membrane (M0) demonstrates the highest WCA (≥ 79 – 80°), confirming the comparatively hydrophobic nature of bare PSF. After dip-coating with 0.1 g $\text{g-C}_3\text{N}_4$ (M1), the contact angle decreases markedly to ≥ 52 – 54° , indicating a substantial increase in hydrophilicity due to the introduction of more wettable surface chemistry and increased surface energy. Increasing the dip-coating amount to 0.2 g (M2) further reduces the WCA to ≥ 47 – 48° , demonstrating the highest hydrophilicity among the non-functionalized coatings and supporting that 0.2 g $\text{g-C}_3\text{N}_4$ is the optimum loading for improving wettability and, consequently, membrane performance in water-based filtration.³² When the coating amount is increased further and dip coated on the PSF membrane, the trend does not necessarily keep improving. In M3 (0.4 g $\text{g-C}_3\text{N}_4$) dip coated on the PSF membrane, the WCA rises to ≥ 63 – 65° , meaning the surface becomes less hydrophilic than M2. This behaviour is line with the probability that excessive loading of $\text{g-C}_3\text{N}_4$ induces particle agglomeration and a less uniform coating layer, which in turn reduces the number of effective hydrophilic sites exposed to water. Therefore, although adding $\text{g-C}_3\text{N}_4$ generally improves wettability, the graph indicates that beyond the optimum condition (M2), further increase in loading can reduce the hydrophilicity improvement.³³ After fixing $\text{g-C}_3\text{N}_4$ at 0.2 g and introducing PPD functionalization, the WCA decreases further in M4–M5, then increases again in M6, clearly demonstrating an “optimum functionalization” effect. In M4 (0.0108 mg PPD), the WCA drops to ≥ 35 – 36° , indicating a strong increase in hydrophilicity compared with M2. The lowest WCA is obtained for M5 (0.054 mg PPD) at ≥ 30 – 31° , demonstrating the maximum hydrophilicity (best wettability) and supporting that 0.054 mg PPD is the optimum functionalization level for performance. However, when the PPD amount is increased to 0.27 mg (M6), the WCA increases back to ≥ 52 – 53° , implying reduced hydrophilicity relative to M5. This rise is commonly attributed to over-

functionalization causing a denser/less uniform surface layer or altering surface chemistry in a way that reduces the availability of hydrophilic sites for water interaction. Overall, the WCA results confirm that M2 is the optimum membrane within the non-functionalized $\text{g-C}_3\text{N}_4$ series, while M5 is the optimum membrane within the PPD-functionalized series, because both conditions correspond to the lowest contact angles (highest hydrophilicity) in their respective comparisons (Figure 5).³⁴

The cross-sectional SEM images demonstrate apparent morphological differences between the pristine, modified and functionalized membranes as demonstrated in Figure 6. The pristine PSF membrane (M0) has a typical asymmetric membrane structure with the relatively dense top selective layer and the porous sublayer with finger-like macrovoids extending downwards, which is typical of the phase inversion fabricated PSF membranes. Upon dip-coating with 0.1 g $\text{g-C}_3\text{N}_4$ in M1, the top layer demonstrates an increase in thickness and texture, indicating the successful deposition of a coating layer, while the underlying porous structure is not significantly altered. If the loading is increased to 0.2 g (M2) a more uniform and continuous top layer with better interfacial adhesion and less visible surface defects are produced. The coating demonstrates good dispersion and compactness with negligible agglomeration, indicating the optimal coverage and compatibility between $\text{g-C}_3\text{N}_4$ and the polymer matrix. However, if the loading is increased to 0.4 g (M3), the surface is comparatively rougher and less regular with indications of particle clustering and a less homogeneous coating layer. This observation implies that too much $\text{g-C}_3\text{N}_4$ can cause agglomeration and non-uniform deposition, and this can have a detrimental effect on membrane structural integrity and performance.³⁵ After fixing the content of $\text{g-C}_3\text{N}_4$ at 0.2 g and introducing PPD functionalization, further evolution of the structure is observed. In M4 (0.0108 mg PPD), the coating grows slightly denser and better bonded with the substrate compared to M2,

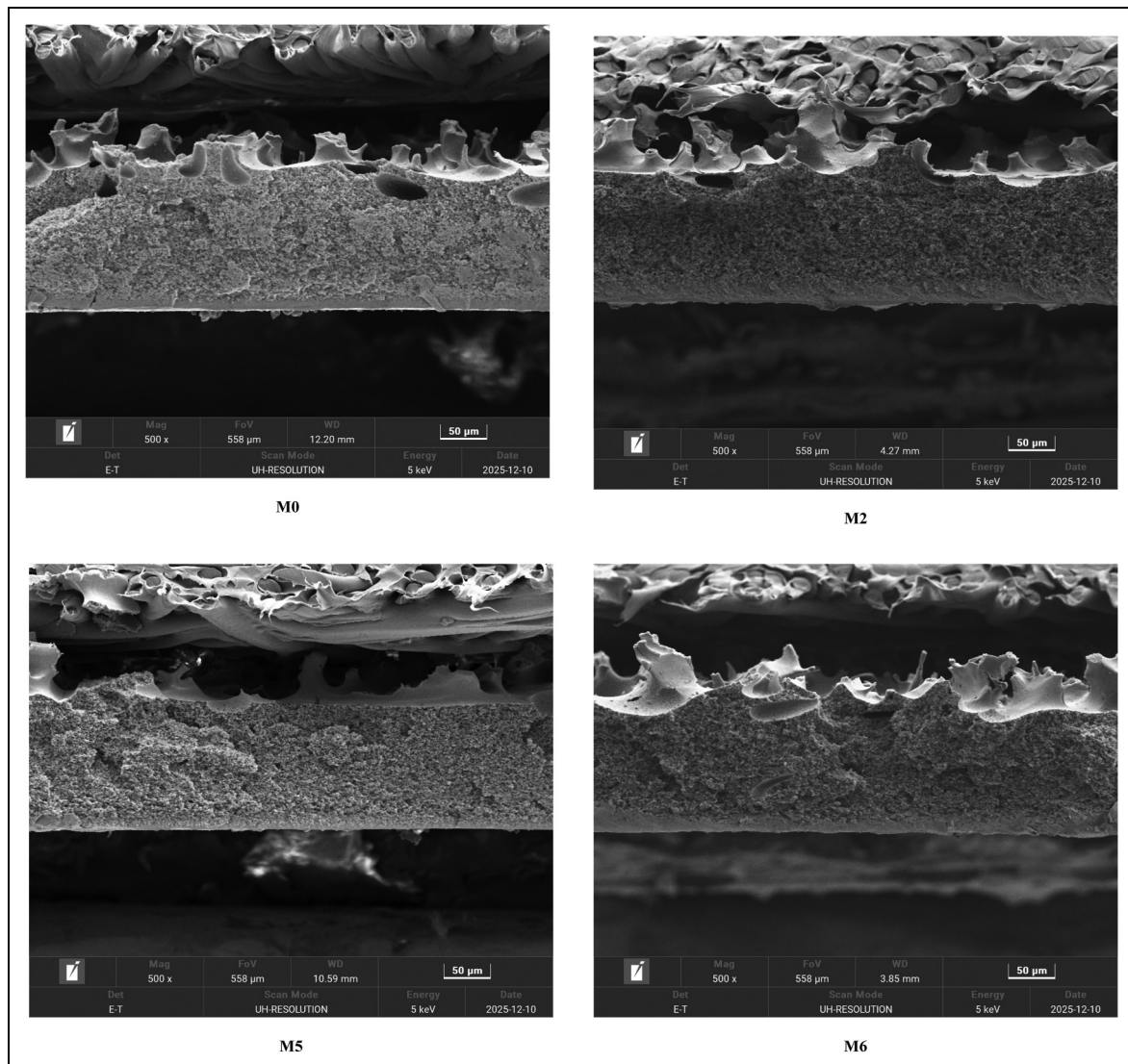


Figure 6. SEM of pristine M0, modified M2 and functionalized M5 and M6 PSF membranes.

however, some minor irregularities still exist. In M5 (0.054 mg PPD), the most uniform compact and relatively more uniform selective layer can be observed in the SEM image among all samples. The top layer seems continuous with interfacial bonding improved and little void formation while the substructure is mechanically stable. This indicates that 0.054 mg PPD offers the best functionalization that improves compatibility between $g-C_3N_4$ and the polymer surface and creates a structural stable membrane. On the contrary, in M6 (0.27 mg PPD), the surface again becomes less uniform with more roughness and the potential creation of microvoids, suggesting that over-functionalization could result in structural stress or over-deposition. Therefore, from the SEM findings, M2 has a comparatively more uniform coating compared to other membranes that do not have any functionalization. Similarly, M5 has been observed to have a relatively more continuous and dense structure compared to the functionalized membranes. However, these observations are qualitative and should not be interpreted as direct evidence of quantitative pore size modification. Since pore size distribution analysis was not conducted, changes in pore structure, pore interconnectivity, or pore-size narrowing cannot be conclusively confirmed from SEM images alone (Figure 6).³⁶

The porosity analysis demonstrates a nice structural transition of the membranes upon the rise of $g-C_3N_4$ loading and subsequent PPD functionalization as illustrated in Figure 7. The pristine PSF membrane (M0) has moderate porosity such as phase inversion fabricated asymmetric membranes. Upon dip-coating with a reduced amount of $g-C_3N_4$ (M1) a slightly higher value of porosity is observed which suggests that the incorporation of the nanomaterial leads to solvent-nonsolvent exchange and pore formation. When the loading is increased to intermediate level (M2), the porosity increases significantly and reaches highest value in non-functionalized series. This indicates the existence of an optimal concentration of $g-C_3N_4$ enhances the pore interconnectivity and structural openness because dispersion improvement and better polymer-filler interaction. However, when the loading is further increased (M3), porosity is decreased as compared to M2. This reduction can be explained by excessive filler aggregation, which may partly block pore channels or disturb the phase separation process, resulting in a less uniform internal structure. Similar behaviour has been reported in nanofiller modified membranes, where overloading interferes with pore formation.³⁷ After the $g-C_3N_4$ fix content at the best level and the introduction of the PPD functionalization,

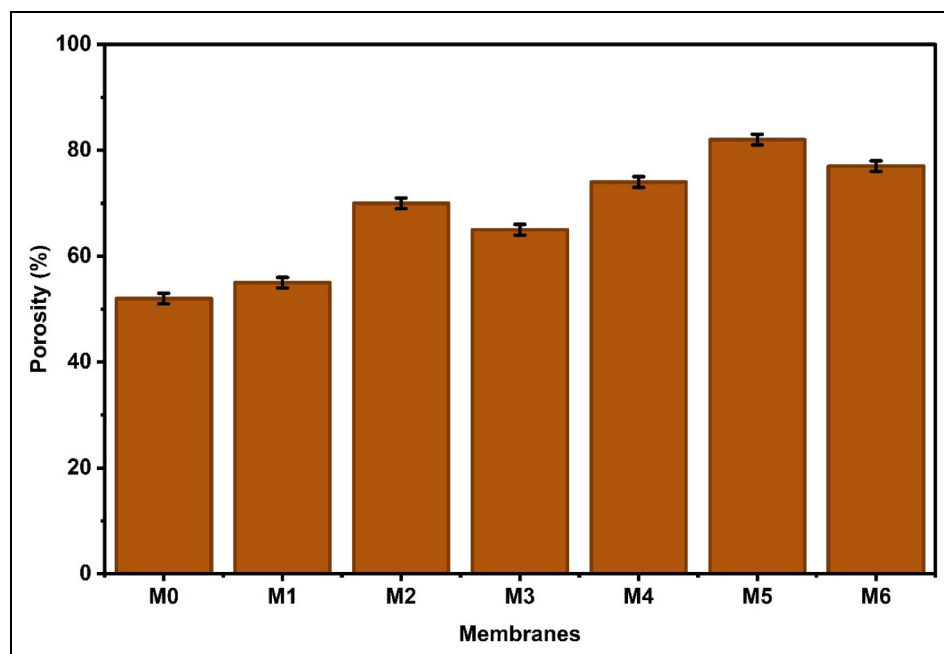


Figure 7. Porosity of pristine M0, modified M1, M2 and M3, and functionalized M4, M5 and M6 PSF membranes.

a further improvement of the porosity is obtained. With a slight amount of PPD (M4), the amount of porosity is increased compared to the membrane without functionalization, indicating better compatibility between the $g-C_3N_4$ and polymer matrix, which will lead to a more efficient phase inversion and pore formation. When the PPD concentration is boosted to the intermediate level (M5), the membrane demonstrates the greatest total porosity of all samples, thus proving that this is the level of functionalization which offers the best interfacial interaction and structural uniformity. However, when the PPD amount is further increased (M6), there is a tiny decline in the porosity in comparison with M5. This behaviour implies that the excessive functionalization may bring about densification effects or partial collapse of pores because of increase of content of organic materials in the matrix. Therefore, M2 is the optimum membrane in the non-functionalized $g-C_3N_4$ series and M5 is the optimum overall membrane in the functionalized series, which confirms that controlled filler loading is important for better efficiency (Figure 7).³⁸

Performance of the membranes

The prepared membranes separation performance was evaluated by testing pure water flux and Cr(VI) rejection efficiency to examine the permeability and selectivity features of the membranes.

Water permeation and rejection performance. The water flow rate through the modified membranes is clearly better after they've been treated with $g-C_3N_4$ and then PPD as shown in Figure 8. The pristine PSF membrane, M0, has the lowest water flow rate of $19.62 \text{ L m}^{-2} \text{ h}^{-1}$. This is just demonstrating us how well the base material can let water through. But when we add a layer of $g-C_3N_4$, about 0.1 g of it, to the membrane, M1, the water flow rate increases to around $27.89 \text{ L m}^{-2} \text{ h}^{-1}$. This tells us that the treatment has made the

membrane more hydrophilic, or water-friendly, and that the pores in the membrane are more accessible. Increasing the loading to 0.2 g (M2) results in significant flux improvement to almost $48.50 \text{ L m}^{-2} \text{ h}^{-1}$ indicating that this concentration provides best filler dispersion and improved water transport ways. However, when further loading to 0.4 g (M3) which flux is decreased $37.82 \text{ L m}^{-2} \text{ h}^{-1}$ approximately, which could be elucidated by filler aggregation and partial pore blockage for higher loading. Such behaviour commonly occurs with nanocomposite membranes with moderate filler loading enhances permeability and, if the filler loading is high, it reduces flow channels. After fixing the $g-C_3N_4$ content at 0.2 g and introducing PPD functionalization, a further improvement in flux is observed. M4 (0.0108 mg PPD) demonstrates an increase to around $42.48 \text{ L m}^{-2} \text{ h}^{-1}$, indicating enhanced interfacial compatibility and improved water affinity. The highest flux is achieved in M5 (0.054 mg PPD), reaching approximately $56.12 \text{ L m}^{-2} \text{ h}^{-1}$, confirming that this level of functionalization optimizes surface hydrophilicity and pore structure, thereby facilitating rapid water transport. When the PPD amount is further increased (M6, 0.27 mg), the flux decreases slightly to about $46.12 \text{ L m}^{-2} \text{ h}^{-1}$, suggesting that excessive functionalization may lead to partial densification or reduced effective pore size. Overall, M2 represents the optimum membrane within the non-functionalized series, while M5 demonstrates the highest overall permeability, highlighting the importance of controlled nanofiller loading and moderate functionalization in enhancing membrane performance (Figure 8).³⁹

The Cr(VI) rejection performance of prepared membranes demonstrates the obvious improvement with incorporation of $g-C_3N_4$ and then PPD functionalization as presented in Figure 8. The pristine membrane (M0) exhibits relatively low rejection (around mid-30% range) presenting poor flux, which is an indication of weak interaction of polymer surface with Cr(VI) species. After the introduction of the $g-C_3N_4$ (M1 and M2), the rejection is greatly enhanced and

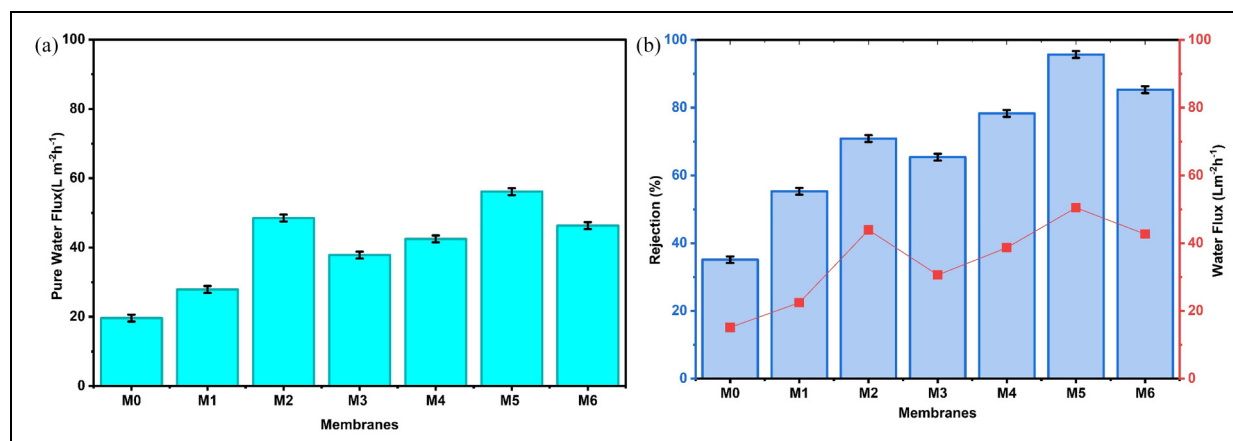


Figure 8. Membrane performance: (a) pure water flux (b) Cr(VI) rejection of the prepared membranes.

Table 3. Comparison of Cr(VI) removal performance of the present membrane with reported membrane systems.

Membrane system	Target pollutant	Flux/permeability	Rejection /Removal	References
Chitosan-enhanced UF membrane	Cr(VI)	9.3–12.5 L m ⁻² h ⁻¹	75%	41
PVDF/ZnO nanocomposite UF membrane	Cr(VI)	-	91.69%	42
CA/ZnO nanocomposite UF membrane	Cr(VI)	≈10 L m ⁻² h ⁻¹	94.77%	43
PSF/SiO ₂ /PDA membrane	Cr(VI)	13 L m ⁻² h ⁻¹	94%	44
PPD-g-C ₃ N ₄ /PSF	Cr(VI)	≈56 L m ⁻² h ⁻¹	≈95%	This study

exceeded 70% for M2 but also considerably for the water flux (above 40 L m⁻² h⁻¹). This suggests that optimized loading of g-C₃N₄ improves both the permeability and selectivity by increasing surface hydrophilicity and creating extra interaction sites for the Cr(VI) ions. However, when the loading is increased even more (M3) a slight decrease in rejection and flux is observed, indicating that too much filler content may cause aggregation or partial obstruction of the pores, which influences the transport behaviour. Such permeability-selectivity trade-offs are very common in nanocomposite membrane systems.⁴⁰ Further improvement is noticed after functionalization of the g-C₃N₄ with paraphenylenediamine. In M4, Cr(VI) rejection further increases and is almost 80%, with stable flux performance. The best overall performance is achieved in M5 for which rejection is around 95% and water flux is high (around 50 L m⁻² h⁻¹), demonstrating the best compromise between permeability and selectivity. However, when the concentration of PPD is raised further (M6), a small decrease in both rejection and flux is seen, which suggests that over-functionalization can cause surface densification. Overall, M2 is the optimum membrane in the series of non-functionalized membranes, while M5 has the best removal efficiency of Cr(VI) with good flux performance. Compared to their pure water flux, all membranes demonstrate a decline in water flux during Cr(VI) filtration which can be attributed to the higher osmotic pressure of the Cr(VI) feed solutions (Table 3).⁴⁰

Conclusions

This research has demonstrated that the introduction of g-C₃N₄ and the controlled functionalization of the material with PPD strongly affect the structural and separation properties of PSF membranes. Moderate loading of g-C₃N₄

enhances the membrane hydrophilicity, porosity, and permeability, and the extensive loading causes aggregation and loss of performance. Functionalization further improved Cr(VI) rejection, most likely due to the combined influence of enhanced hydrophilicity, improved porosity, uniform coating morphology, and modified surface chemistry. Among all prepared membranes, the membrane with the loading of 0.2 g g-C₃N₄ is the best condition in the non-functionalized series, while the membrane with the loading of 0.054 mg PPD exhibits the best performance with the highest chromium rejection and the highest water flux among all prepared membranes. The results confirm that careful optimization of the concentration of nanofillers and their level of functionalization is vital in achieving an effective balance between permeability and selectivity in advanced water treatment membranes. However, the proposed electrostatic interaction between Cr(VI) species and amine groups was not directly verified in this study; therefore, future work should include zeta potential analysis, pH-dependent rejection/adsorption studies, adsorption kinetics/isotherms, and post-filtration XPS analysis to confirm the removal mechanism.

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