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Polyvinylidene fluoride nanocomposite super hydrophilic membrane integrated with Polyaniline-Graphene oxide nano fillers for treatment of textile effluents

Hifza Nawaz^a, Muhammad Umar^b, Azeem Ullah^c, Humaira Razzaq^a, Khalid Mahmood Zia^d, Xuqing Liu^{b,*}

^a Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan; hafsanaawaz1122@gmail.com; humaira.razzaq@uow.edu.pk

^b Department of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, UK; muhammad.umar@manchester.ac.uk

^c Nano Fusion Technology Research Lab, Institute for Fiber Engineering (IFES), Interdisciplinary Cluster for Cutting Edge Research (ICCER), Shinshu University, Matsumoto, Nagano 390-8621, Japan; 08tex101@gmail.com

^d Department of Applied Chemistry, Government College University, Faisalabad 38030, Pakistan; drkmzia@gcuf.edu.pk

*Corresponding Author: xuqing.liu@manchester.ac.uk; Tel.: +44 (0) 161 306 4125

Abstract

Water pollution from the fashion industries containing dyes has become a major source of water pollution. These anthropogenic contaminated waters directly enter irrigation and drinking water systems, causing irreversible environmental damage to human health. Nanomembrane technology has attracted extensive attention to remove these toxic chemicals but new approaches are still required for improving removal efficiency and control the channel size. The work deals with the fabrication of a novel hybrid polyvinylidene fluoride (PVDF)-polyaniline (PANI) membrane with graphene oxide (GO). Incorporation of PANI-GO as a nanofiller has significantly improved antifouling properties and a solvent content of the fabricated membrane. Besides, pure water flux also increases from 112 to 454mLm⁻²h⁻¹ indicating the hydrophilic nature of the nanocomposite membrane. Among various compositions, the nanocomposites membrane with 0.1%w/v GO demonstrated a maximum of 98% dye rejection at 0.1MPa operating pressure. After multiple testing of the membrane, the flux recovery ratio reached about 94% and dyes rejection improved with the addition of PANI-GO. The removal efficiency of the composite membrane for Allura red is 98% and for methyl orange is 95%. Based on the above results the PVDF/PANI/GO membranes are recommended for practical use in wastewater treatment, particularly for anionic dyes removal from textile effluents.

Keywords: dyes, nano-filtration, membranes, phase inversion, antifouling, wastewater, textile industry

1 Introduction

Water is the basic need of every living organism present on earth. Humans require water for drinking, agriculture, washing, and other purposes. Freshwater present on earth is greatly affected by the pollution caused by different activities. This wastewater includes municipal wastewater, agricultural wastewater, and industrial wastewater. Industrial wastewater is more hazardous for the ecosystem because it includes dissolved salts, chemicals, and other organic and inorganic compounds along with insoluble particles [1]. Hazardous environmental pollution, health issues, and waste of water resources occur due to the direct discharge of wastewater. For the protection of our ecosystem, harmless treatments have great importance in removing the effluent from wastewater. Dyeing and printing processes in textile industries are major causes of surface water pollution, so this problem needs attention for a long time. The effluents from dyes and printing process into the rivers and streams create a lot of issues [2]. Water becomes unsuitable for domestic and industrial purposes due to an increase in the concentration of dyes and pigments. It also affects the transmittance of light which limits the growth of aquatic plants and reduces self-purification processes. Our aquatic ecosystem is also adversely affected by textile effluents [3]. Due to complex molecular structures of textile dyes, it's difficult to remove colors by conventional treatment methods (e.g. bleaching, ozonation, hydrogen peroxide/UV, and electrochemical techniques) [4]. They are stable to light, oxidizing agents, and aerobic digestion. Numerous new methods for elimination of dyes from textile effluents are exposed and they are more beneficial than the conventional treatment methods with the advancement of discipline and technology [5]. These include reverse osmosis (RO) [6], Ultra-filtration (UF) [7] and Nano-filtration (NF) [8]. Nowadays, ultrafiltration is more valuable because of its effective performance in the purification of pollutants from wastewater [9].

In the field of material sciences, Polyvinylidene fluoride (PVDF) ultrafiltration membranes have attained great attention due to their specific properties such as membrane-forming, antioxidation activity, excellent aging resistance [10], thermal stability, high mechanical strength, and good chemical resistance properties [11]. Hao Wu *et al* prepared modified PVDF/SiO₂ membranes by using the phase inversion method. Results showed that PVDF has good thermal stability, chemical resistance, high mechanical strength and improves the antifouling properties of the membrane with the addition of SiO₂ [12]. Alicia Kyoungjin *et al* developed modified PVDF/PDMS blend membranes for the removal of dyes. Results indicated that this membrane can be used for the treatment of negatively charged dyes [13]. But the hydrophobic nature of the PVDF makes it liable for contamination through the organic compound that decreases the water flux due to an increase of fouling within the membrane [14]. To overcome this problem several methods (chemical grafting, physical blending, surface modification, etc.) have been introduced to minimize the hydrophobic nature of the pure PVDF membrane. Physical blending is a widely used method due to superficial preparation through the phase inversion process. Ahmad *et al* prepared the blends membrane of Polysulfone and SiO₂ nanoparticles through the phase inversion method that has the highest pure water flux, large pore size, and the high antifouling properties [15]. Liu *et al* also prepared blended PVDF/Al₂O₃ membranes through phase inversion method. Results from SEM

analysis indicated that Al₂O₃ improve the surface of the composite membrane [16]. By using this method, various inorganic materials (Al₂O₃, ZrO₂, ZnO, Fe₂O₃, and TiO₂) were introduced in the PVDF membrane to improve their properties such as hydrophilicity, higher specific surface area, photocatalytic activity, bactericidal and self-cleaning, etc. Yuliwati *et al* prepared modified PVDF membranes by using the phase inversion method. Results showed that the pore size and hydrophilicity of the PVDF/TiO₂/LiCl membrane was affected by TiO₂ and monohydrate lithium chloride. The flux and permeability of the modified membrane was also improved [17]. Hamid *et al* prepared the composite membrane of Polysulfone and TiO₂ nanoparticles through phase inversion method for removal of humic acid. The composite membrane has the highest pure water flux and antifouling properties. Results show that this membrane can be used for 90% removal of humic acid [18]. The results indicated that high concentration of inorganic materials show negative effect on the elasticities and morphologies of pure PVDF filtration membranes. Due to this, it is important to identify such kind of (inorganic) materials that enhance the strength of membrane and also enhances hydrophilic properties of the pure PVDF membrane. Table 1 shows the polymer composite membranes of the previously reported works for removal of different contaminants from wastewater.

Table 1. Polymer membranes for wastewater treatment

Polymer membrane	Method of Preparation	Remarks	Membrane performance	Rate of Rejection	Reference
PVDF/LiCl	Phase inversion process	Flat-sheet unsupported membrane	Salt Removal	98%	[19]
PVDF/Acetone	Electrospinning	Nonwoven composite membrane	Separation of water-in-oil emulsion	90%	[20]
PVDF/TiO ₂ -PDA	Free radical polymerization	Flat-sheet hybrid membrane	Excellent antifouling properties	--	[21]
PVDF/H ₃ PO ₄	Electrospinning	Flat-sheet composite membranes	Desalination	91%	[22]
PVDF/TiO ₂ /PVP	Phase inversion via dry-jet wet spin method	Hollow fibre membrane	Degradation of dyes molecule	84%	[23]
PVDF/Cellulose/Ionic liquid	Electrospinning with surface coating	Superoleophobic composite membrane	Oil/water separation	91%	[24]
PVDF/PVDF-g-POEM	Atom transfer radical polymerization (ATRP)	Thin film nano composite membranes	Textile wastewater treatment	71%	[25]

PVDF/PAN/ PVA	Extrusion method	Tubular membrane	Photocatalyt ic degradation	--	[26]
PVDF-g-PVP	De-fluorination of double bond hydration with graft polymerization	Macro void hybrid membranes with high porosity Ultra-thin	oily wastewater treatment	94%	[27]
PVDF- TiO ₂ /Al ₂ O ₃	Phase inversion method	porous layer and asymmetric structure	Removal of heavy metals	89%	[28]

Graphene oxide is one of attractive (inorganic) materials due to its high surface area, hydrophilic nature, chemical inertness, electronic insulation properties, mechanical stability, and excellent tensile modulus. Wang *et al* prepared the poly(vinylidene fluoride) (PVDF)/GO composite membrane through phase inversion method which shows excellent hydrophilicity, high water flux and good antifouling properties [29]. GO is good for the preparation of organic-inorganic blended ultrafiltration membranes due to the presence of the carboxylic and hydroxyl groups in graphene oxide. Polyaniline (PANI) offered suitable substitutes for conventional hydrophilicity due to its special properties such as good adsorption, excellent steric hindrance, easy preparation, nontoxicity, and availability as active functional groups that have interactions with PVDF and GO during membrane casting.

To the best of our knowledge, this is the first attempt to synthesize the tri-component PANI/PVDF/GO composite nanofiltration membrane. Both PANI and GO will significantly improve the antifouling and dye rejection properties and demonstrate great prospects for textile wastewater treatment. Current research work is mainly focusing on the development of a composite membrane to efficiently remove dyes from wastewater. In this context, pristine PVDF and PANI/PVDF/GO composite nanofiltration membranes were manufactured by using phase inversion method. The developed membranes were tested by a series of characterization techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), Tensile strength, Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Thereafter, the prepared PVDF/PANI/GO membranes were used to investigate properties of the membrane such as porosity, shrinkage ratio, solvent content, pure water flux and retention efficiency of bovine serum albumin (BSA). The effect of GO and PANI on the structure, performance, and efficiency of the PVDF membrane was also characterized.

2 Experimental

2.1 Materials

Chemicals including poly (vinylidene fluoride) (PVDF) (-CH₂CF₂-) (Alfa Aesar), polyaniline emeraldine salt (PANI) (MW ~10000) (Sigma-Aldrich), N, N-Dimethyl formamide (DMF) (99.5%) (Wako), N, N-dimethylacetamide (DMAc) (97+%) (Wako), Sulphuric acid (H₂SO₄) (95-98%) (Wako), 1-propanol (C₃H₈O) (99.5%) (Wako), Hydrogen peroxide (H₂O₂) (30 – 35 %) (Wako), Potassium permanganate (KMnO₄) (99+%) (Sigma aldrich), Sodium hydroxide (NaOH) (98.5%) (Fischer scientific), Acetic Acid (CH₃COOH) (99+%) (Wako), Graphite powder (99.99%) (Sigma-Aldrich), Ethanol (C₂H₅OH) (99.5+%) (Wako), and Sodium Nitrate (NaNO₃) (99%) (Wako) were used as received.

2.2 Synthesis of graphene oxide (GO)

GO was prepared by chemical oxidation and physical exfoliation [30]. Briefly, 2 g of graphite powder was added to 46 ml of conc. H₂SO₄ under continuous stirring followed by the addition of 1 g NaNO₃ in 500ml beaker placed in an iced bath over a hot plate magnetic stirrer. Afterward, 6 g of KMnO₄ was added to the mixture under constant stirring and the temperature was raised to 20°C. The reaction mixture was left under stirring until a thick dark paste was obtained. The temperature of the hot plate was further raised to 90°C, while adding 100 ml of distill water to the reaction mixture. The reaction mixture was continuously stirred at 90°C under dropwise addition of 10 ml H₂O₂. Finally, a dark brown solution was obtained which was washed with distilled water to neutralize. The mixture was filtered, and the cake obtained was washed with 1:10 HCl for the removal of metal ions. The mixture was again washed with distilled water for the removal of acid traces and again filtered to get a solid cake. The filtered cake was dispersed in distilled water and ultra-sonicated to exfoliate the GO. The unexfoliated GO was removed by centrifugation at 3000 rpm for 20 min. The GO powder was obtained by drying the exfoliated GO in a vacuum oven overnight at 60°C.

2.3 Synthesis of PVDF-PANI-GO composite membranes

Composite membranes were fabricated by using the phase inversion method. PANI and GO were used as additives to increase the hydrophilicity and filtration properties of PVDF membranes. PVDF (12% w/v), PANI (3% w/v) and GO (0.05%, 0.1%, 0.5%, 1% w/v) were dissolved to DMF and the solution was stirred for 24 hours at 59 °C. The mixture was heated in a water bath at 40 °C under constant mechanical stirring in a covered beaker for 0.5 hours to swell the polymers. Then the temperature of the water bath was raised to 70°C and stirred for another 7 hours to completely dissolve the polymers. Solutions were kept at 50°C in an oven for at least 6 hours to get rid of any air bubble. The obtained clear solutions were cast on to a glass substrate through a hand coating device equipped with a doctor blade and it was immediately dipped in a coagulation bath containing deionized water at 25°C [31]. After the phase inversion process, the developed membranes were further held overnight in fresh distilled water to extract the remaining solvent entrapped in the prepared PVDF/PANI/GO composite membrane. Fig.1. gives the schematic for

the development of the membranes by the phase inversion method. The compositions and codes for different samples are listed in Table 2.

Table 2. Code of Pure PVDF, PVDF-PANI and PVDF-PANI-GO composite membranes.

Code	PVDF (w/v %)	PANI (w/v %)	GO (w/v %)	DMF (w/v %)	Total conc. (w/v %)
0P	12	3	0	85.0	100
PP	12	3	0	85.0	100
PG1	11.95	3	0.05	85.0	100
PG2	11.90	3	0.1	85.0	100
PG3	11.50	3	0.5	85.0	100
PG4	11.00	3	1	85.0	100

2.4 Characterization

Membranes were characterized by using XRD, FTIR, TGA, and SEM. Panalytical 3040/60 X'pert PRO diffract meter was used for XRD characterization and evaluation of structural properties of samples in the range of 0° to 80°. FTIR spectrum was obtained by 1000 Perkin Elmer in the range of 500-4000cm⁻¹, which was used for functional group analysis. TGA/DT Perkin-Elmer, USA was used for thermal gravimetric analysis i.e. the determination of the thermal stability of pristine and composite membranes. The surface morphology and cross-section of the PVDF/PANI/GO membranes and pure PVDF filtration membrane was analyzed by using FEG FEI SEM (Tescan Mira3 SC) with an accelerating voltage of 10 kV.

2.5 Membrane permeation performances

2.5.1 Porosity

A piece of the membrane was cut into a square of 1cm² and it was immersed in deionized water for one day [32]. The weight of the membrane was measured before and after wetting. The following formula was used for the calculation of porosity.

$$\text{Porosity \%} = \frac{W_2 - W_1 / \rho_w}{W_1 / \rho_w (W_2 - W_1) / \rho_w} \times 100 \quad (1)$$

W₁ and W₂ is the weight before and after wetting, and ρ_w is the water density.

2.5.2 Solvent content

A piece of the membrane was cut into a square of 1cm² and it was immersed in different organic solvents such as propanol, ethanol, water, and methanol for one day. The weight of the membrane was measured before and after wetting. The following formula was used for calculating solvent content [33].

$$\text{Solvent Content \%} = \frac{W_2 - W_1}{W_2} \times 100 \quad (2)$$

W₁ and W₂ is the weight before and after wetting respectively.

2.5.3 Shrinkage ratio

A piece of the membrane was cut into a square of 1cm². Vernier caliper and screw gauge were used to measure its length and thickness, then the membrane was immersed into water for 12 hours and its length and width were calculated again. The following formula was used for calculation [23].

$$\text{Shrinkage ratio \%} = \left[1 - \frac{(a \times b)}{(a_0 \times b_0)} \right] \times 100 \quad (3)$$

a₀ and b₀ are the length and width of the wet membrane (cm), while a and b are length & thickness of dry membrane in (cm) respectively.

2.5.4 Pure water flux

The vacuum filtration pump was used for the calculation of pure water flux. For permeation experiments, the membranes were immersed in water for one day. Trans-membrane pressure (0.1 MPa) was applied to developed membranes for 30 minutes. Pure water flux of the developed sample membranes was calculated at 25°C for every one-minute time interval. The following formula [34] was used for calculation of pure water flux;

$$\text{Pure Water Flux (J)} = \frac{Q}{At} \quad (4)$$

Symbols t for time, A for the membrane area in cm and Q for the amount of water that passes through a membrane in 1 minute (t) is used.

2.5.5 Antifouling property

For the calculation of antifouling property of the composite membrane bovine serum albumin (BSA) was used, which is one of the model proteins for the investigation of the antifouling nature of membranes. The aqueous solution of BSA (0.8 g L⁻¹) was used in a filtration cell that follows the initial pure water flux (J_{w1}) measurement. Filtration of the BSA solution was done by using the samples of membrane for 30 minutes at 0.1 MPa trans-membrane pressure. Then, the membrane was fouled and washed with water for 30 minutes, after which flux (J_{w2}) (L m⁻² h⁻¹) was calculated again [35]. Following formula was used for evaluation of the flux recovery ratio;

$$\text{FRR \%} = \frac{J_{w1}}{J_{w2}} \times 100 \quad (5)$$

Rejection (percent) of BSA [36] was calculated using the formula,

$$\% R = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (6)$$

C_p and C_f are the molarity of permeate and feeds BSA solution, respectively.

The molarity of feed and permeate BSA containing solution at λ_{max} = 280 nm was analyzed by the UV-VIS spectrophotometer.

2.5.6 Determination of dyes removal

The removal experiments of methyl orange (MO) and allura red (AR) was carried out under vacuum filtration. UV-VIS spectrophotometer (DR5000, Hach) was used to determine the removal of dyes in the sample solution. The concentration of dyes in the sample solution was detected by the maximum absorbance wavelength ($\lambda_{\max}$) in the UV-VIS spectrometer. Dye rejection was calculated by using the formula,

$$\% R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (9)$$

C_p and C_f are the molarity of permeate and feed of dye solutions, respectively. The calibration curve for methyl orange ($\lambda_{\max} = 464$ nm) and allura red ($\lambda_{\max} = 505$ nm) are given in Fig. 2. The solutions were analysed against standard fitted plots; ($y = -0.4247 + 9.716x$ for MO), and ($y = -0.7404 + 23.80x$ for allura red) to determine the percentage dye removal from the wastewater samples.

2.5.7 Adsorption study

The adsorption studies toward anionic dye were carried out by using MO as the model dye to determine the adsorption capacity of the PVDF/PANI/GO composite membrane. The experiments were conducted within a set of 150 mL flasks which contain PVDF/PANI/GO composite membrane (0.6g) and 50.0 mL solution of MO. The samples were kept in an isothermal water-bath for 90.0 minutes at the temp of 298 K. UV-VIS spectrophotometer (DR5000, Hach) was used to measure initial and remaining concentrations of MO. By dye adsorption experiments, we also determine the effect of different parameters such as time (0–25 hours), pH (4.5–9.5), and effect of dye concentration (MO) (25.0–200 mg/L).

The value of the adsorption (q_e) was measured by using following equation [37]:

$$\text{Adsorption } (q_e) = \frac{(C_o - C_e)V}{m} \quad (7)$$

The concentration of MO at initial and equilibrium point represented by C_o and C_e (mg/L), respectively; V is volume; and m is the mass of composite membrane. For pH-dependent experiments, 0.01M HNO₃ or 0.01M NaOH solutions were used to adjust the pH in the range (4.5–9.5) of the MO solution (100 mg/L) [38]. In kinetic adsorption experiments, 0.6g of PVDF/PANI/GO composite membranes were dipped into different concentrations of MO solution and taken out after certain time intervals.

For the adsorption isotherm experiments, PVDF/PANI/GO composite membranes were dipped into the solution of MO (100 mg/L). The same process was repeated at different temperatures (298 K, 308 K, and 318 K). The value of adsorption (q_t) after time t , was calculated using the following equation [39]:

$$\text{Absorption } (q_t) = \frac{(C_o - C_t)V}{m} \quad (8)$$

The concentration of MO at initial and equilibrium point represented by C_o and C_t (mg/L), respectively; V is volume, and m is the mass of the composite membrane. The detailed study with results and discussion was explained in supporting information.

3 Results and Discussion

3.1 SEM analysis of PVDF/PANI/GO composite membranes

The morphology of pure PVDF membrane and effect of PANI and GO on membranes surface was analyzed by scanning electron microscopy. Fig. 3 (1a-6a) shows SEM micrographs of pure PVDF and composite membrane's surface that contains PANI (hydrophilic polymer) and various concentrations of graphene oxide (PP, PG1, PG2, PG3, PG4). From the SEM images, it can be observed that there is an increase in roughness and asymmetry of composite membranes due to the addition of graphene oxide. This increase in asymmetry and roughness causes an increase in hydrophilicity and pure water flux of membrane. The enhancement in roughness can also be due to the nucleation and growth of polymer after incorporation of PANI. The surface of composite membranes also shows a 'pit-like' structure [40]. For geometric analysis of these membranes, structure of porous membrane has been regenerated through software (ImageJ) from SEM images of membrane [41]. The corresponding estimations of pores diameter and distributions of pores on these membrane's surfaces shown in Fig.3 (1b-6b). We can clearly see that in pure PVDF membrane number of pores are less but with addition of the filler (PANI and GO) content, the number of pores increased. The average diameter of pores also decreases with the addition of PANI and GO [42]. The pristine PVDF membrane has an average pore diameter of around 1.53 μm while pores in composite membranes (PP, PG1, PG2, PG3, and PG4) have an average diameter of about 0.78 μm , 0.34 μm , 0.09 μm , 0.03 μm and 0.01 μm respectively. The reduction in pore size is the result of complex structure formation due to good chemical interaction of the PVDF with filler content (PANI-GO).

A cross-sectional analysis of pure membranes was also performed by using SEM. Fig. 3 (1c-6c) shows cross-sectional images of pure PVDF and PVDF/PANI/GO composite membranes. All synthesized membranes have good miscibility of polymers and graphene oxide, so they do not show any phase separation. The cross-section of the membrane contains about 100 μm thickness with asymmetric morphology. SEM analysis of pure PVDF membrane (a) revealed asymmetric pores structure with a dense layer on top of the membrane. The dense layer on the upper side formed due to the faster phase inversion process of PVDF in the coagulation bath. With the introduction of fillers (PANI/GO) content, these membranes become more porous and uniform distribution of the pores can be seen within composite membranes. SEM analysis also represents that the number of pores increases with the addition of the filler content, but excessive GO may penetrate in the pores and reduced their amount. Fig. 3 (5c) and (6c) represent that filler (GO) content of 0.1% w/v is suitable but after that excessive GO can block the pores and reduce the pure water flux of (PG3, PG4) membranes [43].

3.2 Physicochemical analysis of the PVDF/PANI/GO composite membranes

XRD analysis in Fig. 4 (a) illustrates the diffractograms of the GO, Pure PVDF, PVDF/PANI and PVDF/PANI/GO composite membranes. It is expected that the graphite show two characteristic peaks at 26° and 55° corresponding to the lattice planes (002 and 004) [44]. After oxidation, these reported peaks shift towards smaller angles. The diffractogram of the GO which shows only (002) plane peak at 10°. The presence of the peak at 10° confirms the efficiency of the oxidation process due to an increase in the planar distance between graphene nanoplatelets upon the insertion of oxygen groups. Thus the peak at $2\theta = 10^\circ$ is an expected one for the oxygenated groups in the GO due to an increase in the interplanar distance [45]. The pure PVDF spectra show its characteristic α -phase crystalline peaks at 18.08° and 19.7° [46]. Polyaniline and GO are both amorphous and

hence will show similar effects individually as well as in combination [47]. The GO peak disappears in the composite membranes, which confirms the fine dispersion of the GO within the composite. As reported by Gascho *et al* that when GO was vacuum filtered the XRD pattern started to show peaks other than at 10° , due to partial restacking of the graphene oxide [45]. In composite membranes, the α -phase peaks at 18.08° disappear due to the crystal transformation of PVDF. Moreover, composite membranes exhibit a new diffraction peak at 20.5° , which corresponds to the (110) and (200) planes of β -phase. The formation of β -polymorph can be due to interaction between the carbonyl groups ($-\text{C}=\text{O}$) present in GO and the CF_2 segments in PVDF polymer. There is a similar pattern of XRD shown for different concentrations of graphene oxide but a very little shift in the position of hump can be observed with increasing concentration of graphene oxide.

The presence of β -phase in PVDF/PANI/GO nanocomposite membranes was further confirmed by FTIR analysis. Fig. 4 (b) shows the FT-IR spectra of pure PVDF and membranes blended with the PANI and GO at four different concentrations (0.05%, 0.1%, 0.5%, 1% w/v). There are some similar peaks in the spectra of all membranes relating to the characteristic peaks of PVDF; Peaks at the 612 cm^{-1} are assigned to CF_2 bending, 793 cm^{-1} correspond to CH_2 group and 976 cm^{-1} represent the out of plane deformation of the CH group. All these peaks represent the α -phase of the PVDF membrane. While the peaks at 1271 , 1077 , and 840 cm^{-1} represent β -phase of the composite membrane. The FT-IR spectra of membranes containing additives reveal an extra broad peak comparing with the pure PVDF membrane at around 1411 cm^{-1} for N-H bending, peaks at the 871 cm^{-1} are assigned to aromatic ring present in the polyaniline. The peaks at 1252 cm^{-1} correspond to the $-\text{C}-\text{N}$ stretching mode of the benzenoid ring. The transmittance peak at 2359 cm^{-1} was attributed to C-O carbonyl stretching in the GO skeleton. What's more, the absorption peak at 1180 cm^{-1} was attributed to the stretching vibration of CO groups. XRD and FTIR analysis represent that there is no significant difference between the different concentrations of GO in the composite membrane. It represents that each membrane has GO nanosheets which contain enough carbonyl group to nucleate the chain of PVDF into β -phase.

3.3 Thermal and mechanical stability of PVDF/PANI/GO composite membrane

The thermal behavior of the composite membrane was studied through Thermo Gravimetric Analysis (TGA). TGA of pure PVDF and PANI/PVDF/GO composite membranes with variable concentration of GO i.e. 0.05% w/v to 1% w/v are displayed in Table 3 and Fig. 5 (a). On heating the membranes from 35°C to 800°C , pure PVDF membrane and PVDF/PANI blend membrane show the considerable weight loss in comparison to the composite membranes with GO. Thermal decomposition of the composite increased from 398°C to 470°C [48]. This increase in temperature demonstrates the thermal stability of the composites. It establishes the fact that the thermal stability of the composites increases as the concentration of GO is increased from 0.05% w/v to 1% w/v. Also, as the concentration of GO increases, the interfacial interactions between the PVDF and PANI also enhances due to the presence of a functional group in graphene oxide.

Table 3. TGA calculated parameters of pure PVDF, PVDF/PANI and PVDF/PANI/GO composite membranes.

Codes	Td	Temperature at:			Residue %
		5% wt. loss	10% wt. Loss	Max. wt. Loss	
0P	398	366	409	494	10
PP	460	460	490	495	12
PG1	463	484	499	499	21
PG2	467	452	501	501	28
PG3	469	474	505	505	30
PG4	470	370	507	507	31

Tensile properties were analyzed to determine the mechanical properties of PVDF-PANI-GO composite membranes. These results represent that nanocomposite membranes were stronger, but they become more brittle than pure PVDF membrane due to the addition of GO (Fig. 5 (b)). Some more important factors that involved to describe these facts are; carbon nanomaterials (GO) entangle with the polymeric chains of PVDF and PANI and provide the additional binding site for the hybrid membrane and results in an excellent interaction between GO and polymer chains [49]. Due to this, Young's Modulus was increased from 32.12MPa to 90.03MPa with increasing the concentration of the GO. The tensile strength of composite membranes was also increased with the addition of GO nanosheets due to their large surface area, which is one of the significant factors to enhance the interaction with polymers. The good miscibility of GO with PANI and PVDF also contributes to increasing the mechanical properties of the PVDF/PANI/GO composite membrane. Tensile strength of polymer nanocomposite membranes increases with the addition of GO from 0.05%w/v to 0.1% w/v, but further increase in the concentration of GO from 0.1% w/v to 1% w/v causes enough brittleness in membranes to break them easily and thus reduces the tensile strength [50].

3.4 Membrane permeation properties of PVDF/PANI/GO composite membrane

The porosity of all different composite membranes was calculated by measuring their wet and dry weight with water density. The results of membrane porosity are summarized in Fig. 6 (a). Fig. 6 (a) illustrates that there is a continuous increase in the porosity of the PVDF/PANI/GO composite membrane with an increase in the concentration of GO from 0 to 0.1% w/v. This increase in porosity can be explained by the hydrophilic nature of GO content which results in increased porosity. But when the concentration of graphene is increased from 0.1% w/v to 1% w/v, the porosity decreased because the excess amount of graphene oxide may block the pores of the membrane. Porosity had also a great influence on the % shrinkage ratio. With an increase in

porosity, shrinkage ratio decreases because it increases the hydrophilicity of the membrane. The results for the % shrinkage ratio are also shown graphically in Fig. 6 (a). From Fig. 6 (a), it is clear that the % shrinkage ratio is decreased as the concentration of filler (GO) is increased. The shrinkage ratio is found less than 15% in these membranes and this ratio is found to be more effective.

For determination of the nature of the membranes, four different solvents were selected according to the polarity of the solvent. These solvents were arranged in decreasing order of polarity from water to Propanol. To check out the solvent absorption of the composite membrane, 1cm² of each composite membrane was dipped into the different solvents like water, ethanol, methanol, and propanol for 24 hours. The solvent content was calculated by the weight difference of the dry and wet membrane. It showed that water content increased with increasing the filler content (GO) due to this improved hydrophilicity of the composite membrane which may enhance the water permeability by attracting water molecules inside the membrane and facilitating them to pass through the membrane. After investigating the solvent content of these membranes, the results are given in Fig. 6 (b).

Pure water flux (PWF) was calculated before and after the addition of the hydrophilic additive at the pressure of 0.1MPa. The influence of the graphene oxide content on the performance of PVDF/PANI membranes has been illustrated in Fig. 6 (c). The pure water flux of PVDF/PANI/GO composite membrane increased dramatically with PANI content, the water flux also increases with the addition of graphene oxide (0.05 w/v to 1% w/v) but further increase in the concentration of graphene oxide causes blockage of pores of the membrane which results in a decrease of pure water flux [51].

3.5 Hydrophilic properties of PVDF/PANI/GO composite membrane

The hydrophilicity of the blend and composite membrane surface has been determined through the contact angle measurement. It plays a significant role in increasing the pure water flux and antifouling properties of the membrane. Hydrophilicity is better when the contact angle of the membrane is smaller. Furthermore, on the upper surface of the hydrophilic membrane, water from the compact layer repels the organic deposition on the membranes to improve their antifouling properties. Such an increase in hydrophilicity is beneficial to reduce membrane fouling, especially organic fouling. The hydrophilic and more wettable surface layer typically yields better water permeability and fouling resistance in water purification applications [52]. During the phase inversion method, graphene oxide migrates on the upper surface of the membrane and form it hydrophilic. This is supported by a decrease in contact angle of composite membranes then pure PVDF membrane.

Fig. 7 (a) illustrates that the contact angle decreased from 90° to 56° with the addition of the filler content (GO) which shows that the hydrophilicity of the membrane has been improved. PVDF is one of the hydrophobic matrix, which contributes to the hydrophobic nature of the pure PVDF membrane, but the addition of polyaniline induces the -NH group on the surface of the membrane which has the tendency for hydrogen binding and results in decreased contact angle and thus

improved hydrophilicity of the membrane [53]. GO nano-sheets contain large number of the –OH groups responsible for increased hydrophilicity of membrane [54]. Fig. 7 (b) represent the contact angle measurement after every four seconds to calculate the water permeation properties of synthesized membranes. These results show that GO content within the membrane decreases the age of drop and increases the pure water flux.

3.6 Performance of PVDF/PANI/GO composite membranes for removal of dye

3.6.1 Dye rejection and flux of composite membranes

Filtration properties of synthesized membrane were calculated by preparation of two type of dyes solutions with 100ppm concentration of allura red and methyl orange into the deionized water. Fig. 8 represent the dye rejection properties of pure PVDF (0P) and composite membranes (PP, PG1 and PG2). The dyes were passed through membranes with 0.1 MPa pressure. All membranes show dye rejection due to the sieving nature and adsorption behavior of porous membranes [55]. The molecular weight of dyes also affects the dye rejection rate, when we used the same membranes to calculate their performance, the rejection rate slightly increased with an increase in the molecular weight of dyes [56]. The dye rejection properties of PG3 and PG4 membranes cannot be evaluated because their high crystallinity and brittleness make them so fragile that they break on applying pressure of 0.1MPa. Fig. 8 (a) and (b) illustrates that the graphene oxide and polyaniline composite membrane has a higher percentage of dye rejection about 95% for methyl orange and 98% for allura red in comparison to the pure PVDF membrane. Composite membranes contain the smaller pore size than the hydrodynamic diameter of dyes molecules, so the sieving mechanism of membrane controls the flow of dyes through it. Moreover, the dye flux for pristine PVDF membrane is about 23 L m⁻² h⁻¹, while for composite membranes (PP, PG1, and PG2) flux is about 58, 62 and 65 L m⁻² h⁻¹ respectively. Fig. 8 also shows that the removal efficiency of membrane for AR was slightly better than MO due to the different structure and high molecular weight of allura red (496.42 g/mol) than methyl orange (327.33 g/mol) [57]. Fig. 8 (c) and (d) illustrates the UV analysis of the permeate solution of methyl orange and allura red from all membranes. As filler content (PANI-GO) was increased, the absorbance values of permeate solutions becomes low due to better ability of nanocomposite membranes to remove the dyes. For reproducibility, all experiments were conducted three times, and mean results were presented with standard deviation. Table 4 gives a comparison of the dye rejection rate and water flux of the previously reported work.

Table 4. Comparison of the dye rejection rate and water flux of the previously reported literature.

Filtration Membrane	Method of Preparation	Dye	Pure water flux (L m ⁻² h ⁻¹)	Contact angle	Rate of Dye Rejection (%)	References
Polypropylene /PVA	Dip coating method	Victoria blue (B)	118.73	62.43	91.2	[58]

PVC/ TiO2 /Al2O3	--	Erichrom e black T	165	86	>99	[59]
PES/PEG/PVP	One step electro spinning	Indigo carmine	212.80	--	96	[60]
Poly(p-phenylene sulfide /GO	Solution casting	Methylen e blue	325.65	54	94.2	[61]
PS/PES	Interfacial polymerization	Reactive dyes	35.43	--	90.9	[62]
PVDF/Tetrahydrofuran	Phase inversion free radical graft copolymerization	Methyl orange	171.80	75	80.3	[63]
PAN/ Chitosan		Crystal violet	229.82	84	89.04	[64]
Sulfated polyelectrolyte/ Chitosan	Solution casting	Reactive orange 16	110.32	72	90.9	[65]
Polyamide /carboxyl-functionalized graphene oxide	Interfacial polymerization	New Coccine	311.02	89.32	95	[66]
PVDF/PANI/ GO	Phase inversion	Methyl orange and Allura red	454	56.11	98	This Work

3.6.2 Effect of dyes concentration on membrane performance

Film Theory equation [67] proves that dyes concentration of feed solution has a significant effect on the performance of nanofiltration membranes. Five series of experiments were conducted to find out the effect of different concentrations (50,100, 200, 400, 800ppm) of dye (Methyl orange) on membrane flux and dye rejection. According to Fig. 9 (a), dye flux of pure PVDF and composite membranes were gradually declined with increasing the concentrations of dye (50 to 800ppm) in the feed solution. As the concentration of dye increases, dye molecules deposit and aggregate onto the surface of the membrane that causes polarization and increased osmotic pressure within the membranes [68]. Moreover, these aggregates might block the pores of the membrane surface by adsorption that cause membrane fouling. Therefore, the flux of 0P, PP, PG1, and PG2 were decreased by 25.1%, 18.9%, 16.1% and 10.2% respectively. PG2 showed a very slight decline in dye flux due to better antifouling properties of the composite membrane [69]. According to Fig. 9

(b), an increase in the concentration of dye in feed solution also has a significant effect on dye rejection. The dye removal efficiency of the composite membrane (PG2) was least affected and show a high rejection rate of about 98%.

3.7 Antifouling properties and BSA rejection of PVDF/PANI/GO composite membranes

The particles and solutes deposit on the surface of the membrane and into the pores of the membrane cause membrane fouling and decline in flux during the filtration process [70]. Although the membrane fouling is unavoidable, it can be decreased by adopting suitable strategies such as the use of hydrophilic material within the membrane. In this work, the addition of PANI and GO to the casting solution results in increase in hydrophilicity of membrane and decreases its fouling. Antifouling properties of membranes were evaluated by using BSA as the model fouling agent. The relative pure water flux (PWF) was calculated before and after the filtration of the BSA solution and reported as the flux recovery ratio [71]. Fig. 10(a) show that the pure PVDF membrane was not effective for BSA rejection (39%) due to its hydrophobic nature but with the addition of PANI (PP) and graphene oxide (PG1, PG2) rejection rate was increased to about 73%, 76%, 78% respectively [72].

To check the reusability and anti-fouling properties of membranes, dye wastewater (methyl orange solution) was used as a fouling agent. The contaminated membranes were washed with HCL solution for 30 minutes after every cycle to remove the fouling agent from the membrane surface and then their performance was investigated [73]. These antifouling testing were only performed on 0P, PP, PG1, and PG2 because PG3 and PG4 were not suitable for the filtration process due to their excessive brittleness. Fig. 10 (b) show that flux of all membranes was reduced with the passage of time due to the adsorption of dye molecules on membrane surface that cause pore blockage of the membrane. After cleaning through HCL for a half-hour, membranes show favorable recovery in dye flux of all membranes. Fig. 10 (c) represents that the flux recovery ratio of composite membranes (PP, PG1, and PG2) was higher as compared to the pure PVDF membrane after three cycles. Long term dye flux of membranes is shown in Fig. 10 (d). The flux of all membranes was declined with the passage of time but PG2 shows a less decline than other membranes. This is due to good hydrophilic properties of GO and PANI in composite membrane surface [74]. Such membranes repel the hydrophobic contaminants from their surface during the filtration process. So PG2 show excellent anti-fouling properties for practical applications.

3.8 Practical Implications of this study

Based on the results, PVDF/PANI/GO composite membranes have great potential for the treatment of textile effluents particularly dyes. They outperform the previously used nanofiltration membranes considering the water flux and dye rejection properties, indicative of superiority to deal with textile wastewater. In order to demonstrate the superiority of developed PVDF-PANI-GO composite membranes in real applications, the key results and significant parameters of these membranes were compared with commercially available PVDF membranes. The results demonstrate that the pure water flux of our novel membrane ($454 \text{ L m}^{-2} \text{ h}^{-1}$) is higher than commercial pure PVDF membrane ($252 \text{ L m}^{-2} \text{ h}^{-1}$) [75]. The commercially available PVDF membrane is only useful for microfiltration but our novel PVDF-PANI-GO membrane can also be

used for nanofiltration of pollutants due to their smaller pore size ($0.09\mu\text{m}$). The PVDF membrane is hydrophobic in nature with higher contact angle (118.3°), so organic contaminants can foul the surface of this membrane whereas the hydrophilic nature of the novel PVDF-PANI-GO composite membrane due to its lower contact angle (56.11°) illustrates its better antifouling properties [76]. The result of recycling tests also indicates that the developed nanocomposite membranes possess good long-term stability in the nanofiltration process. Therefore, these novel membranes provide a new route to remove dyes from textile wastewater. The performance of PVDF-PANI-GO composite membranes were found to be better than established technologies under same conditions (Table 4).

In future, focus could be to improve the dye removal capability of novel PVDF-PANI-GO composite membranes to make them more competitive. Further, these membranes could be coupled with biological treatment technologies to develop single integrated system in order to improve efficiency of effluents removal and reduce energy consumption. There is also a potential of collaboration with industrial partners to test real water samples and improve their reusability up to 3-5 years for scaling up and introduce it as a commercial product.

4 Conclusion

In this research article, we described the synthesis of GO by using modified Hummer's method and its integration in pure PVDF and the composite PVDF/PANI/GO membrane by using the phase inversion method. The optimized amount of GO for wastewater treatment membrane is 0.1% w/v, if we further increase the concentration of GO, membranes become brittle and reduce the number of pores in composite membrane. Considering the morphological and structural evidence of membranes, we reached the following conclusions;

1. PVDF based membrane containing PANI and GO have smaller shrinkage ratio and pore size with excessive roughness of membrane surface than pure PVDF membrane. This indicates that fillers improve the permeation properties of composite membranes.
2. The hydrophilicity of membranes enhances with the addition of GO and PANI. The contact angle decreased from 90.32° to 56.11° , which describes the presence of oxygenated and hydroxyl functional groups of graphene oxide on the surface of the composite membrane.
3. Pure water flux of composite membrane enhances from 112 to $454\text{ L m}^{-2}\text{ h}^{-1}$. Graphene oxide also improved the BSA rejection in the pure PVDF membrane from 38.6% to 78.32%.
4. Thermal and mechanical stability improves with the addition of 2D material in the pristine membrane. Degradation temperature was increased from 398°C to 470°C with the addition of GO and PANI in the PVDF membrane. The Young's Modulus and tensile strength of composite membranes also improved from 32 MPa to 90 MPa.
5. After multiple testing of the membrane, the flux recovery ratio reached about 94% and dyes rejection improved with the addition of GO and PANI content. The removal efficiency of the composite membrane for allura red is 98% and for methyl orange is 95%.

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Graphical Abstract