Original article

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Polysulfone nanofiltration membranes enriched with functionalized graphene oxide for dye removal from wastewater

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Abstract: Composite-nanofiltration membranes based on polysulfone (PSU) and functionalized graphene oxide (f-GO) were prepared for dye removal from aqueous media. Graphene oxide (GO) was introduced to enhance the performance of these membranes. GO was functionalized using an aminated heterocyclic compound, namely 6-amino-4-(4-nitrophenyl)-3-methyl-4-phenyl-4,7-dihydro-1H-pyrazolo-[3,4-b]pyridine-5-carbonitrile. The f-GO was incorporated into the PSU membrane matrix in different weight ratios (0.25, 0.5, 1, 2 and 4 wt %). Characterizing the produced membranes with scanning electron microscope, Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) and X-ray diffraction indicated the well dispersion of f-GO in the membrane matrix. The obtained membranes were applied to remove Congo red and methylene blue, as typical anionic and cationic dyes respectively from water. The modified membranes showed superior efficiency in terms of water flux and dye rejection upon being compared with the control membrane. The composite membranes loaded with f-GO exhibited promising dye removal efficiency for both dyes.

Keywords: dye removal; graphene oxide; heterocyclic compound; nanofiltration membrane; polysulfone.

1 Introduction

Fresh water shortage and the decline of water quality form an obstacle against the continuous progress of humans. This

led to a demand for finding out suitable water treatment technology to relieve this situation [1–3]. Dyes result as byproducts from paper and textile industries configuring pollutants. These dyes form a burden on environment and human health if they are not discharged efficiently. Traditional methods to remove dyes and heavy metal ions from wastewater comprise adsorption and photocatalysis [4, 5]. Recently, membrane approach is favored as a convenient method for getting rid of settling dyes in wastewater. Among the high efficient membrane separation technologies [6–8], we can mention nanofiltration (NF) membranes. They can be determined in a pressure-driven membrane with low molecular weight cutoff. The latter has attracted a significant attention ascribed to its unique fractionation and separation for multi-ions, heavy metals, dyes and sugars [9–11]. Advances in the design and synthesis of NF membranes with improved retention, flux and cost-effectiveness will have tremendous impact in several fields such as water treatment, selective chemical separation and drug delivery. Conventional polymeric NF membranes possess restricted chemical resistance. Meanwhile, ceramic membranes are not cost-effective ones.

Polysulfone (PSU) is among the commonly used membrane materials. This merit can be correlated to its good mechanical, thermal and chemical stabilities. It is employed to manufacture porous membranes from microfiltration (MF) to NF. PSU exhibits superior film-forming properties [12]. PSU was investigated in the presence of clay nanoparticles for ultrafiltration application. The aforementioned nanoparticles enhanced the antifouling and flux recovery for the prepared membranes [13]. Eugenol and zinc oxide were introduced to PSU membrane. They improved the ultrafiltration properties of the prepared membrane beside its antifouling and antibacterial ones as well [14]. Quaternized graphene supported in reinforcing PSU-based membranes for alkaline fuel cell [15]. Among the polymer-based membranes, some are known to be hydrophobic due to the nature of the used polymer. These membranes are contaminated easily with dyes and pollutants during wastewater treatment [9]. Hence, the dye molecules may stack on the surface of the

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membrane. This leads to plugging the pores of the membrane. In this case, the separation activity and the durability of the membrane diminish. Thereafter, new materials are desired to improve the antifouling properties and hydrophobicity of these membranes. Inorganic nanoparticles have been investigated for such purpose [16]. Introducing nanoparticles into the membrane matrix during the phase inversion process increases the hydrophilicity and the antifouling behavior of the membrane. Titanium dioxide nanoparticles were employed to produce membranes with photocatalytic activities [17].

Graphene is a monolayer of atoms in a two-dimensional honeycomb sp^2 carbon lattice. It is an exciting multifunctional material. It possesses a combination of strong mechanical properties, chemical inertness and extremely large surface area [18, 19]. Membranes prepared from graphene show privilege. They are chemically inert like ceramic membranes. Moreover, they are able to form films using graphene/graphene oxide (GO) fluid phase dispersions like polymers. Researches are focusing on progressing the transport properties of graphene-based membranes such as high permeability and high selectivity for both liquids and gases [20, 21]. GO was used to enhance the performance of a forward osmosis membrane. GO assisted in improving the properties of enhanced PSU anion exchange membranes [22]. Nanofibrous membranes of PSU showed acceptable antibacterial activities [14]. Graphene and/or GO are favored to be functionalized for extending their efficiencies [6, 18, 23]. Functionalized graphene oxide (f-GO) retains more stability and compatibility when introduced to polymers than their pristine analogs. Functionalization takes place through grafting functional groups on the surface of graphene. GO is able to attract functional groups. It can act as a beneficial molecule for adsorption. This results from allocating various active sites onto its surface. GO was explored as an effective adsorbent for getting rid of heavy metal ions and organic contaminants [24]. Heterocyclic compounds are among the appropriate materials for such functionalization. Fused heterocyclic compounds such as pyrazolo-pyridines, pyrano-pyrazoles and pyrazolo-pyrido-pyrimidines exhibited convenient biological properties such as bactericidal and fungicidal efficiencies [25, 26]. Much attention has been drawn to develop new approaches for synthesizing many categories of these heterocycles enriched with nitrogen [27, 28]. Some of the multicomponent reactions to prepare pyrazolo-pyrido-pyrimidines depend on using amino pyrazole or amino-pyrimidine as starting materials with various catalysts [29–31].

The efficiency of a filtration membrane is recognized by water flux and (salt or dye) rejection. Reaching high

water flux and rejection are considered as major challenges which contribute in determining the efficacy of any membrane. It is important to improve each property of the previously mentioned ones individually without affecting the other negatively. Some studies did not investigate the flux and rejection behaviors distinctly. Moreover, it was important to monitor the alteration in the performance of the prepared membranes towards removing either anionic or cationic dyes with different surface charges. This work aims to prepare polymeric membranes based on PSU and enhanced with f-GO. The functionalization takes place by adhering a heterocyclic compound loaded with nitrogen onto the surface of GO. These membranes can be employed in nanofiltration applications for water treatment. It was interesting to investigate the efficiency of these membranes towards dye removal of anionic and cationic dyes from water through water flux and dye rejection. Hence, we selected Congo red and methylene blue as model dyes for anionic and cationic dyes.

2 Materials and methods

2.1 Materials

PSU (Udel P-3500) was kindly supplied from Solvay Advanced Polymers. Graphite, *N,N*-dimethylformamide (DMF, 99.8%), *p*-nitrobenzaldehyde, malononitrile, ammonium acetate, Congo red and methylene blue were purchased from Sigma Aldrich. Ethanol was purchased from El-Gomhoria chemicals company, Egypt.

2.2 Methods

2.2.1 Preparation of graphene oxide: GO was prepared according to modified Hummer's method [32]. This procedure involves oxidizing graphite flakes chemically to produce graphite oxide. A known weight of the prepared graphite oxide was exfoliated via sonication in DMF to obtain GO sheets. The sonication took place in a sonication bath for 8 h.

2.2.2 Synthesis of the heterocyclic compound 6-amino-4-(4-nitrophenyl)-3-methyl-4-phenyl-4,7-dihydro-1H-pyrazolo-[3,4-b]pyridine-5-carbonitrile: A solution of 3-methyl-1,4-dihydropyrazol-5-one (pyrazolone) [33] (0.98 g, 0.01 mol), *p*-nitrobenzaldehyde (0.01 mol) and malononitrile (0.66 g, 0.01 mol) was prepared in ethanol. Ammonium acetate (0.98 gm, 2% excess) was added to the solution and then heated under reflux for 5 h. The solvent was evaporated under vacuum, and the remaining solid was crystallized from ethanol. Yellow crystals mp. 276–277 °C (Yield, 95%); Ms (*m/z*, %): 296 (M^+ , 1%); 280 ($M^+ - NH_2$, 9%). IR (KBr). ν cm^{-1} : 3450 (NH); 3330 (NH); 3090 (CH, aromatic); 2965 (CH_3); 2210 (CN); 1605 (NO_2). 1H NMR (270 MHz, DMSO- d_6 , TMS): 2.10 (s, 3H, CH); 4.98 (s, 1H, CH); 7.10 (s, 2H, NH) 7.37–7.40 (d, 2H, aromatic protons); 8.11–8.10 (m, 3H, 2 aromatic protons and NH); 11.41 (br, 1H, NH). ^{13}C NMR (270 MHz,

DMSO- d_6), δ 9.70 (CH); 35.45 (C4); 55.50 (C5); 96.45 (C8); 121.53 (CN); 124.94, 125.13, 129.89, 130.06, 136.94, 147.42 (aromatic carbons); 153.13 (C3); 155.71 (C9); 160.10 (C6). Anal. Calcd. for $C_{14}H_{12}N_6O_2$: C, 58.85%; H, 4.23%; Cl, 12.41%; N, 24.51%. Found: C, 58.70%; H, 4.11%; Cl, 12.21%; N, 24.30%.

2.2.3 Functionalization of graphene oxide with the heterocyclic compound: The dispersed GO nanosheets were kept in DMF. The synthesized heterocyclic compound was added to the GO solution under stirring and heating at 80 °C for 4 h. The solution was centrifuged at 4000 rpm for 30 min. The supernatant was removed. The precipitate was washed several times using DMF and dried in an oven.

2.2.4 Preparation of composite NF membrane: The NF membranes were prepared using phase inversion technique as reported in literature [34, 35]. The f-GO was dispersed in DMF under vigorous stirring and sonication. PSU (1.8 g) was added to this solution with magnetic stirring for about 24 h at 25 °C. The f-GO ratio was varied to be (0.25, 0.5, 1, 2 and 4 wt % with respect to PSU). The solution was sonicated once more in a sonicator to assure the complete dispersion of the functionalized GO in the polymer solution. The produced composite solution was casted on a glass plate with the aid of casting knife with gape height 200 μ m. The casted solution with the glass plate was immersed into coagulation water bath without evaporation. The composite membrane was separated from the glass and kept in water and stored in a fridge.

2.2.5 Evaluating the performance of nanocomposite membrane in removing Congo red or methylene blue dyes: The nanocomposite membranes were evaluated using homemade dead-end filtration system with effective surface area of 14 cm². Each membrane was connected to a nitrogen gas cylinder as a source of applying pressure. The filtration cell was filled with Congo red or methylene blue dyes with different concentrations then filtered at different pressures. The concentrations of the dyes were measured before and after filtration using UV-vis spectroscopy at 498 and 668 nm for Congo red and methylene blue, respectively. Figure 1 represents a schematic diagram for preparing the membranes and applying them in dye removal from water. The water flux (J) and dye rejection (R) were evaluated using the following equation:

$$J = V/A \cdot t$$

$$R = [1 - (C_{\text{perm}}/C_{\text{feed}})] \cdot 100$$

where A is the active surface area of membrane (m²). V is the permeated volume (L) and t is the time of filtration (h). C_{permeate} and C_{feed} are the dye concentrations in permeate and feed respectively.

2.3 Instrumentation

Melting points were determined on an electrothermal apparatus (Buchi 535, Switzerland) in an open capillary tube. FTIR spectra expressed in (cm⁻¹) were recorded in KBr pellets on a PA-9721 IR spectrophotometer. ¹H NMR & ¹³C NMR spectra were obtained on a Varian EM-390 (270 and 500 MHz) spectrometer in DMSO- d_6 as solvent. Tetramethylsilane (TMS) was used as an internal reference, and chemical shifts (δ) are expressed in ppm. Mass spectra were recorded on Kratos (75e-v) Ms equipment. Elemental analyses were carried out by the micro-analytical unit at the National Research Centre, Giza, Egypt. The surface morphology of the nanocomposite membranes was examined via high resolution scanning electron microscope (SEM) (QUANTA FEG 250 ESEM). Energy dispersive X-ray spectroscopy was performed by (EDX; AMETEK, Mahwah, NJ) analysis at an acceleration voltage of 15 kV. Transmission electron micrographs (TEM) of the nanoparticle particles were taken using a JEOL JEM-2100 (JEOL, Japan). The prepared nanocomposite membranes were examined using X-ray diffraction (XRD), Philips X'Pert MPD diffractometer at room temperature for evaluation of their crystallinity. The surface composition of GO was determined by X-ray photoelectron spectroscopy (XPS). A monochromatic Al K α (energy 1486.6 eV) radiation at 50 W, a 2.5 nm sampling depth was employed. The take-off angle was 45°. The analyzed surface area was neutralized by an ion gun. The survey scans were followed by regional scans for each investigated atomic element.

3 Results and discussion

3.1 Investigating the synthesized 6-amino-4-(4-nitrophenyl)-3-methyl-4-phenyl-4,7-dihydro-1H-pyrazolo-[3,4-b]pyridine-5-carbonitrile

A mixture of 5-methyl-2,4-dihydro-3H-pyrazol-3-one (Structure 1), malononitrile and *p*-nitrobenzaldehyde was heated in ethanol-containing ammonium acetate under reflux. The resultant is the corresponding 6-aminopyrazolo [3,4-*b*]pyridine-5-carbonitrile (structure 2) as shown in Figure 2. The reaction proceeded *via* the formation of the benzylidene adducts at first. This was followed by the

Figure 1: Schematic diagram for applying the prepared membranes in dye removal from aqueous media.

addition of malononitrile and cyclization via loss of water. It was explained previously [36] that the formed adduct may undergo aromatization via loss of hydrogen to produce Structure 2. The ^1H NMR spectrum of the all synthesized adducts revealed the presence of hydrogen proton at C_4 at δ 4.6 and NH_2 δ 7.10. This elucidated Structure 2 and supported the formation of an adduct structure (Figure 2). ^{13}C NMR showed a δ 9.70 (CH); 35.45 (C_4); 55.50 (C_5); 96.45 (C_8); and 121.53 (CN).

Nitrogen heterocyclic compounds are characterized by their high bioactivities as antibacterial [25, 37], antiviral [26] and anticancer agents [30, 36]. They compose robust hydrogen bonds with other compounds. PSU contains oxygen and sulfur atoms. Hence, this facilitates the step of building up strong hydrogen bond with our synthesized compound 2. From this point, we can employ the synthesized heterocyclic compound 2 in f-GO with increasing its stability and efficiency in the prepared PSU membranes.

3.2 Characterization of GO

SEM was used to demonstrate the surface morphology of GO. It is observed in Figure 3A that GO exhibits a lamellar-structure for propagating sheets. Random layers appear as a result of the oxidized graphite. Transmission electron microscopy (TEM) was employed to identify the structure of GO. Figure 3B shows a lamellar-like structure for GO sheets. The transparency of GO varies according to the overlapping of some sheets. Light regions denote a slight number of GO sheets and become darker upon more as sheets overlay. Upon checking the formation of GO, XRD confirmed that the examined sample is the oxidized graphite. The measured XRD pattern of GO in Figure 3C displays a diffraction peak at about $2\theta = 10.9^\circ$ with a d -spacing of 8.11 Å. This confirms that the graphite flakes were successfully oxidized using modified Hummer's method. If graphite had been existing in the sample, a diffraction peak of 2θ between 25° and 30° would have appeared as an evidence [19]; but this is not the case here. XPS was used to explore the elemental composition of GO. In Figure 4, The XPS spectra show an elemental ratio of carbon to oxygen

(C:O) of 68:32. GO generally shows characteristic peaks referring to C_{1s} and O_{1s} at 284.5 and 532.8 eV respectively. It is noticed in the corresponding figure that three peaks split at ~ 285 , 287.8 and 288.63 eV. They refer to carbon atoms in different functional groups [38]. They comprise the first peak that refers to sp^2 C=C and sp^3 C-C that appear at 285 eV. Moreover, C-O and C-O-C at 287.8 and O=C-OH at 288.6 eV. The O_{1s} peak appears at 533 eV. The XPS results confirm the formation of GO in the investigated sample.

The FTIR spectra of GO and the f-GO are shown in Figure 5. GO represents multiple signs of oxygenated functional groups. They are obvious in the structure. A broad band appears denoting carboxylic functional group associated with hydroxyl group (OH stretching) with a maxima at 3436 cm^{-1} [22]. Some characteristic peaks denoting certain groups are noticed for: C=C at 1639 cm^{-1} , carboxy C-O at 1402 cm^{-1} , C-OH at 1272 cm^{-1} and alkoxy C-O at 1053 cm^{-1} . After f-GO with the heterocyclic compound, some changes in the FTIR bands can be noticed. A peak is observed at 3429 cm^{-1} (stretching) for primary N-H. A medium N-H bending is noticed at 1646 cm^{-1} and a medium stretching peak is noticed at 1021 referring to C-N group [36].

Energy dispersive EDX was employed to confirm the existence of GO and f-GO as well. EDX analysis of GO and f-GO are shown in Figure 5B and C, respectively. The EDX spectrum of GO represents carbon and oxygen peaks at 0.27 and 0.52 keV. An elevated peak for carbon is observed due to the higher carbon content (67.84%) than oxygen (32.16%) in GO sample. After f-GO, a new peak arose. It is a characteristic one for nitrogen appearing at 0.39 keV. This peak originated in GO after the functionalization process with the heterocyclic compound enriched with nitrogen. The peak intensities for f-GO changed to become (67.37%), (29.62%) and (3.01%) for carbon, oxygen and nitrogen consecutively.

3.3 Characterization of nanocomposite NF membranes

The morphology for the fractured surface of PSU membrane is shown in Figure 6A. It comprises a porous

Figure 2: The synthesis of the heterocyclic compound to functionalize graphene oxide.

Figure 3: (A) SEM of graphene oxide, (B) TEM of graphene oxide, (C) XRD of graphene oxide.

Figure 4: XPS of graphene oxide.

Figure 5: (A) FTIR of graphene oxide (GO) and functionalized graphene oxide (f-GO), (B) EDX of GO, (C) EDX of f-GO.

composition with a finger-like structure. The micrograph displays an asymmetric texture for the membrane. Some pores expand uniformly through the whole sample. The existence of pores is considered as a characteristic feature for the prepared membrane. These pores extend from the top to the bottom of the sample. This formation accounts

for solute retention or permeation. The presence of some voids in the bottom supplies the membrane with a mechanical support. Wider finger-like structure in the bottom of the sample allows higher permeation than smaller finger-like texture. Figure 6B provides a micrograph for the PSU membrane loaded with f-GO. It presents a branched

network construction. GO seems to be embedded in the polymeric substrate showing light spots in the matrix. Some pores are obvious inside the matrix. Permeation may not take place easily when the PSU membrane is tested in an aqueous medium containing some solutes [12]. It may be referred to repulsive forces between PSU and water. This will be followed by accumulating the solute at the interface. Hence, a certain pressure has to be exerted to facilitate the transfer process. Upon introducing f-GO, the modified membrane gains a hydrophilic character. This facilitates the permeation process even at lower pressures.

The XRD patterns for the blank and composite membranes are presented in Figure 7. The diffraction patterns of PSU membrane has a broad diffraction peak with a maxima at 18.5° , which is matching with previous literature [39–41]. A relatively broad peak for f-GO appears at $2\theta = 9.7^\circ$. This value goes in accordance with that of GO shown in Figure 3C. The shift and broadening in the peak may be correlated to the functionalization of GO with the heterocyclic compound. After introducing f-GO to PSU, the intensity of the characteristic peak for PSU decreased. Moreover, a broad band is noticed at $2\theta = 8.1^\circ$. It originated as a result of the presence of f-GO with the heterocyclic compound. Variations in the lattice parameters contribute in shifting XRD peaks. The broadening in the peak may be due to the abundance of oxygen containing functional groups on the GO layers. Moreover, the presence of pendant heterocyclic components has a role in demonstrating less ordered lamellar-structure [42, 43].

3.4 Investigating the performance of the prepared NF membranes

Formerly, various techniques were followed to get rid of synthetic dyes [11, 44–46]. In the present study, NF approach is utilized for dye removal from water by means of polymeric-based membranes. The performance of composite membranes in the rejection of Congo red or methylene blue dyes was illustrated in Figure 8A and B

Figure 7: XRD of polysulfone, f-GO and polysulfone loaded with f-GO.

respectively. The aforementioned dyes were chosen as models for anionic and cationic dyes respectively. It is observed that upon loading the f-GO to the PSU membrane, the water flux increased. Increasing the content of f-GO increased the permeate flux till it reached 2% concentration of GO in the membranes. The improvement in the permeation of the membranes may be correlated to the hydrophilic nature of GO. The latter bears a number of various functional groups as OH and COOH. Furthermore, employing f-GO in the membrane influenced the water flux which seemed to decrease upon increasing its content in the membrane. The decrease in permeate flux may be due to the blocking of the pores of the membrane upon increasing the GO layers sheets. The membranes exhibited a promising dye rejection performance for both dyes. The Congo red rejection values exceeded 99% through the whole tested membranes. Meanwhile, for methylene blue we found that the rejection value increased from 95 to 99% for the membrane loaded with f-GO of 2% by weight. The rejection behavior of the composite membranes was

Figure 6: SEM of (A) polysulfone (PSU) membrane, (B) PSU membrane loaded with f-GO.

Figure 8: Effect of f-GO loadings in polysulfone membranes to filtrate dyes with (25 ppm) concentration for (A) Congo red or (B) methylene blue at 4 bar.

Figure 9: Effect of different dye concentrations for (A) Congo red or (B) methylene blue on the filtration behavior of polysulfone membrane loaded with (2%) f-GO at 4 bar.

Figure 10: Effect of the applied pressure on the performance of polysulfone membrane loaded with f-GO (2%) at dye concentration of 25 ppm for (A) Congo red or (B) methylene blue.

enhanced upon introducing f-GO. The increment of rejection may be due to the lamellar-structure of GO that exhibited a high separation performance. Figure 8 showed that rejection of Congo red was higher than methylene blue. This behavior may be correlated to the higher molecular weight and molecular size of Congo red than that of methylene blue.

The dye removal performance of a filtration membrane depends on the operation conditions. They comprise dye concentration, applied pressure and time. Hence, various dye concentrations can be filtered through the membrane. For the investigated membranes, the water flux and dye rejection were recorded every 30 min for about 6 h. The obtained results showed steady water flux over the testing time interval with a slight decrease in flux. This may be due to the accumulation of the rejected dye molecules on the

membrane surface. Figure 9A and B displayed the dye rejection for the composite membrane with different dye concentrations. It is noticed that the increase in the dye concentration led to a decrease in rejection and permeation flux. This may be due to the increment in the solution viscosity besides the raise in the concentration polarization onto the membrane surface as well. At a certain level, the dyes molecules may block the membrane pores. All these possible factors may cause an increase in the membrane resistance for permeation with lowering the water flux. The obtained results were in accordance with previously reported in literature [47, 48].

Figure 10 showed the effect of pressure on the membrane performance. It can be seen that by increasing the applied pressure, the water flux increased with a slight decline in the dye rejection. The higher the pressure is, the

higher the driving force on water is allowed to pass through the membrane overcoming the membrane resistance [49]. It is worthy to state that with increasing the pressure, the rejection of contaminants increased to a certain limit then declined. The rejection behavior Congo red dye (Figure 10A) showed higher than that of methylene blue dye (Figure 10B). This may be due to the relatively smaller molecular weight and molecular size of methylene blue dye. The latter tends to pass easier through the membrane at a high applied pressure. Hence, the membrane resistance merely decreases. A high water flux originates with an increment in dye permeation, leading to a decline in the dye rejection.

4 Conclusion

Polymer-based NF membranes composed of PSU and f-GO were prepared. The f-GO was performed by using aminated heterocyclic compound, namely, 6-amino-4-(4-nitrophenyl)-3-methyl-4-phenyl-4,7-dihydro-1H-pyrazolo-[3,4-b]pyridine-5-carbonitrile prior to introducing it to PSU solution. The f-GO conducted to be more stable upon being loaded to PSU membrane. Loading f-GO onto the membrane matrix enhanced both water flux and dye rejection at relatively low pressure. The dye rejection behavior for both Congo red and methylene blue dyes was higher than 99%. The presence of f-f-GO demonstrated a promising environmental activity by which it provides the membrane a promising dye removal efficiency. This work extends a new approach for producing a novel composite membrane with a highly hydrophilic character. It exhibits a high performance in textile waste water treatment.

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