Membrane technology has played a dynamic role in various industrial separation processes, including wastewater treatment, desalination, gas separation, organic nanofiltration, etc. However, they showed limited use in water desalination due to their lower stability and separation efficiency. In this work, a class of two-dimensional (2D) GO lamellar membranes have been prepared with controlled pores for efficient and fast separation of ions and dye molecules. The GO membranes are functionalized with a star-like 6-armed poly(ethylene oxide) using the simple amidation route under mild conditions. The as-prepared covalently cross-linked networks are chemically steady in aqueous medium and show remarkable selectivity (~100%) for several probe molecules and 10–100 higher permeance than those of the reported GO-based membranes. Further, such membranes are also used for salt separation and show more than 80% rejection for Pb²⁺ and Ni²⁺ salts. Moreover, a 1360 nm-thick membrane shows >99% rejection for NaCl with a good water permeance of up to 120 L m⁻² h⁻¹ bar⁻¹. Additionally, these membranes are stable for more than 20 days under different conditions.

1. INTRODUCTION

Membrane technology has played a dynamic role in various industrial separation processes, including wastewater treatment, gas purification, hemodialysis, catalysis, bioprocessing, and petrochemical-based separations. Nanofiltration (NF) is one of the mature and energy-efficient technologies for separation/purification of small ions and molecules in commercial applications. The conventional polymeric membranes have low chemical resistance. Inorganic and ceramic-based membranes are difficult to produce in large-scale fabrication processes due to complicated procedures. In addition, these membranes are more fragile and expensive than polymeric membranes. Therefore, it is highly desired to develop new-type NF membranes with high durability, high solvent permeance, good stability in harsh conditions, and excellent separation efficiency by a simple fabrication process.

Recently, graphene oxide (GO) has drawn much attention for separation technology because GO nanosheets can be modified and fabricated into laminates by simple chemical methods. Especially, the recently developed water electrolytic oxidation methods open up the possibility for continuous production of GO nanosheets with a low cost. To date, GO has been widely investigated as ionic and molecular separation membranes in aqueous media with high efficiency. GO nanosheets having two-dimensional (2D) nanochannels in between may be employed as 2D passages for small ions and molecules, allowing and restricting species based on their size. The GO nanosheets are a complex structure of hydrophobic and hydrophilic domains and have carboxyl (−COOH) groups on their edges and hydroxyl (−OH) and epoxyl (C−O−C) groups on their basal planes. Due to their hydrophilic nature, the GO membranes can be easily swelled in water and humidity during the filtration process and resulting membrane re-exfoliated and delaminated, which hinders their practical applications in an aqueous solution. Therefore, further investigation is needed to explore the utilization of GO lamellar membranes in water environment without sacrificing their permeability, selectivity, and stability. To date, GO-based NF membranes with uniform 2D capillaries exhibit ~100% separation of small molecules in water. However, selectivity against small ions and stability is a big challenge for the scientific community.

Herein, a new generation of GO-based lamellar membranes with controlled pore size has been fabricated for NF applications. The PEGylated GO (PGO)-based membranes have been prepared by covalently introducing six-armed PEO molecules onto the surface of GO nanosheets using a simple method.
amidation process. As-prepared PGO membranes with a thickness of 250 ± 10 nm are used to separate small ions and dyes and show remarkably high rejection (>99%) for several probe molecules. The higher rejection of these membranes is attributed to the π−π stacking and hydrophobic interaction between PGO and probe ions or molecules. Further, PGO membranes show 10−100 times higher rejection (>99%) for several probe molecules. The higher rejection of these membranes, as-prepared PGO membranes with a thickness of 250 nm are used to separate small ions and dyes and show remarkably high rejection (>99%) for several probe molecules. The higher rejection of these membranes is attributed to the π−π stacking and hydrophobic interaction between PGO and probe ions or molecules. Further, PGO membranes show 10−100 times higher rejection (>99%) for several probe molecules.

2. EXPERIMENTAL SECTION

2.1. Synthesis of GO Nanosheets. The modified Hummers method was used to prepare GO sheets. The GO sheets were prepared by mixing 4.0 g of graphite powder with 98.0 mL of concentrated sulfuric acid and slowly adding 2.5 g of NaNO₃ with continuous magnetic stirring in a water bath. The resultant mixture was left for 30 min for further mixing. After that 1.5 g of KMnO₄ was added slowly and the reaction temperature kept below 5 °C and then 0 °C by adding ice into the water bath. Firstly, the resulting mixture was stirred for 80 min at 0 °C, then for another 2 h at 35 °C. After that, 90 mL of deionized water (DI) water was added to the reaction mixture slowly to avoid overheating. Then, further 400 mL of DI water and 7 mL of H₂O₂ (37%) were added with continuous stirring for 20 min to get a graphite oxide suspension. The as-obtained suspension was washed with 5% HCl aqueous solution three times and subjected to dialysis for 10 days to eliminate the impurities for neutral pH. Then, centrifugation was done at a speed of 6000 rpm for 20 min to remove multilayered sheets and visible particles. Further, GO was exfoliated into the GO suspension with the help of tip sonication (280 W). Finally, the as-prepared GO suspension was freeze dried and used for fabrication of the laminates.

2.2. Modification (Pegylation) of GO. As for pegylation of GO nanosheets, 5.0 mL of as-prepared GO dispersions was diluted two times and then sonicated for 1 h continuously in a water bath until the solution became clear. Added 1.0 g of Chloroacetic acid (CH₂Cl-COOH) and 1.2 g of NaOH to the clear GO solution and sonicated for further 3 h to convert hydroxyl functional groups of GO to carboxyl groups through acetic acid moieties conjugation (called as GO−COOH). Further, the carboxylated—GO (GO−COOH) was neutralized and then purified by filtration and rinsing. In addition, the optical density of GO−COOH was maintained up to 0.4 at 808 nm by diluting it with water. At this stage, 2.0 mg−1 of the 6-arm poly(ethylene oxide) was added to the GO−COOH dispersion and sonicated for 10 min. After that, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) was added twice and left overnight to complete the reaction followed by quenching with mercaptoethanol (Fluka Incl.). The final PEGylated GO (PGO) product was separated at 45,000 rpm in 2× phosphate-buffered saline, and the rest of the aggregates were discarded.

2.3. Fabrication of PGO Membranes. The PGO blend (0.25 g) was dispersed in DI water (50 mL) with the help of tip sonication until a clear dispersion was obtained. The blend with variable volume (20, 40, 60, 80 mL) was filtered through a nylon support membrane in a vacuum filtration assembly to obtain PGO-based lamellar membranes with variable thicknesses. In addition, pristine GO-based laminates were prepared by the same process for comparison.

2.4. Membranes’ Characterization. Scanning electron microscopy ((SEM), Nova Nano SEM 430, 15/10/5 kV) was used for structural characterization of both GO and PGO membranes, while the chemical compositions of the membranes were determined with X-ray photoelectron spectroscopy (XPS) (ESCALAB250 XPS, 500 μm spot size, 150 W). The calibration of all spectra was done at an adventitious carbon binding energy (264.6 eV). Fourier-transform infrared spectroscopy (FTIR) (Nicolet 6700 FTIR) was employed for confirmation of the PGO membranes. The D-MAX/2400 XRD diffractometer was used to obtain the X-ray diffraction (XRD) patterns, utilizing Cu Kα radiation having a wavelength of 0.154 nm. The interlayer distance (d-spacing) of membranes was calculated by employing the Bruker DektakXT Profiler. The hydrophilic and hydrophobic properties of the membranes were measured with a contact-angle goniometer. The surface charge of the GO-based membranes was measured with the help of a ζ-potential meter (model: ζ-sizer, Malven, U.K.) in the range of 4−10. The salt separation and rejection of other probe molecules were confirmed by an ionic conductivity meter (Mettler Toledo, M400) and ultraviolet–visible (UV–vis) spectrometer (Varian Cary 50), respectively.

2.5. Permeance and Separation Performance of the Membranes. Dead-end filtration and vacuum filtering methods were used to measure the membrane’s permeance and selectivity using 14.51 cm² as the effective area at room temperature and 1.0 bar pressure. The separation properties such as permeability and rejection of the DI water and feed solution were measured against 250 mL volume of each solution. The permeability (J) and rejection (R) were calculated according to eqs 1 and 2, respectively.

$$J = \frac{V}{A \Delta t \varphi}$$

(1)

$$R = A - \frac{C_p}{C_i} \times 100\%$$

(2)

where V (L) is the volume of DI water, P (bar) is the pressure used for filtration, Δt (h) is the time for permeation, A (cm²) is the area of membrane used for filtration, and C_p and C_i are the concentration of the permeate and feed solutions, respectively.

2.6. Stability Tests. The stability of the as-fabricated membranes was tested under static conditions after slicing them into pieces of 1.5 × 1.5 cm². Then the membranes were dipped in several pH solutions, such as pure water, aqueous NaOH, and aqueous HCl with pH 7, 12, and 2, respectively, keeping steady room temperatures, and their stability was tested at various times.

2.7. Degree of Swelling. The swelling ratio (D) of the pristine GO and PGO membranes was measured at room temperature with the help of eq 3. As-prepared membranes were put into DI water for 24 h and after that, the membranes were dried at room temperature further for 24 h. In both cases the weight of both membranes should be measured.

$$D = \frac{W_2 - W_1}{W_1}$$

(3)

Here W₁ is the weight of the original membrane, while W₂ is the weight of the dry membrane after treatment.
3. RESULTS AND DISCUSSION

3.1. Preparation of Membranes and Structural Characterization. The monolayer GO was prepared according to the reported method with thickness ∼1 nm and lateral size 0.6 to 1.5 μm (Supporting Figure S1). Before fabrication of the membrane, GO was sonicated with 6-armed poly(ethylene oxide) and EDC in the appropriate amounts for 2 h at room temperature. The obtained mixture was further stirred continuously overnight at room temperature. The dialysis (M.W. cutoff = 14 kDa) was performed with DI water for 10 days to purify GO-PEO from unbound 6-armed PEO against DI water. The change of color from brown (Figure 1a) to black (Figure 1b) indicated successful cross-linking between GO sheets and PEO. A homemade dead-end filtration cell was used to filter the blend (PGO) through the nylon substrate. The concentration and volume of GO and 6-armed PEO in the dispersion controlled the thickness of the membrane. Figure 2c represents the clear surface morphology with the regular and uniform structure of the PGO lamellar membrane. The PGO membrane showed a porous layered structure (Figure 1d) compared to the pristine GO membrane with a tight-layered structure (Figure 1e).

The 6-armed PEO is rich with oxygen-containing functional groups (Supporting Figure S2). XPS was used to identify the chemical composition of the PGO lamellar membrane. The XPS spectra obtained showed similarity with that previously reported, containing four components, i.e., carbon atoms in carboxyl, hydroxyl, carbonyl, and epoxy. The PEO is rich with oxygen-containing functional groups; the O/C atomic ratio has decreased after modification, from 0.44 (pristine GO membrane) to 0.31 (PGO membrane). These results confirmed that during the intercalation process the GO gets reduced, which is obvious with the above-mentioned color change. The PGO membrane showed a reduction in the peak intensity of the functional groups of oxygen (Figure 1g), which is typically similar to the C 1s XPS spectra of rGO membranes.

The XRD pattern of PGO and GO membranes was obtained (Figure 1h). The pristine GO membrane shows a single diffraction peak at a 2θ of 11.6°; attributed to an interlayer distance of 0.76 nm, due to the presence of trapped water and oxygen-bearing functionalities. In contrast, the wet PGO membrane shows a strong diffraction peak at a 2θ of ~10.11, assigned to an interlayer distance of 0.88 nm. The enhanced interlayer distance implies the presence of PEO molecules inserted between the GO sheets in the PGO membranes.

Figure 1. Structural characterization of GO-based lamellar membranes. (a, b) Pristine GO and PGO dispersion. (c) Surface morphology of PGO membranes. (d, e) Cross-sectional SEM studies of PGO (d) and pristine GO (e) membranes, respectively. (f, g) C 1s XPS spectra of pristine GO and PGO lamellar membranes, respectively. (h) XRD patterns of GO-based membranes.

Figure 2. Stability and hydrophilic properties of GO-based lamellar membranes. (a, b) Digital photos of a water droplet on the surface of PGO (a) and GO (b) membranes. (c–k) Stability of GO-based membranes. Stability of pristine GOMs (c, f, i) and PGO membranes (d, e, g, h, j, k) at pH ~7, ~2.2, and 12. Each image shows the time spent on the respective solution.

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Further, the PGO membrane showed a strong peak at a $2\theta$ of $\sim 10.6$, attributed to an interlayer spacing of 0.83 nm in the dry state. These molecules have a high number of functional groups containing oxygen groups, making them good hydrophilic molecules due to the weak van der Waals forces and hydrogen bonding between the GO sheets. Moreover, the appearance of a small peak around 21.4$^\circ$ in the PGO membrane corresponds to the narrowed interlayer distances of neighboring GO sheets. This distance narrowing is caused by attractive forces or interaction by the removal of the oxygen-containing functional groups during the reduction process. The above characterizations suggest that the PGO membrane has a unique layered structure with alternating GO membrane-like domains and rGO membrane-like domains. In this structure, the GO membrane-like domains are cross-linked by PEO molecules with rich polar functional groups and have a large interlayer spacing, which provide sufficient hydrophilic sites to capture the water molecules; the rGO membrane-like domains have nearly no oxygen functional groups, a small interlayer spacing, and are hydrophobic, similar to the capillary action in carbon nanotubes, which can permit rapid water permeation through practically frictionless flow.

Further, the cross-linking between GO and PEO was identified by FTIR studies (Supporting Figure S3). The GO membrane showed bands at $\sim 3441$ and $1747$ cm$^{-1}$ corresponding to the stretching vibration of the O$^-$$H$ and C$\equiv$O moieties in carbonyl and carboxyl groups. Additionally, the band at 1651 cm$^{-1}$ is attributed to C$\equiv$C and the bands at $\sim 1390$ and $\sim 1039$ cm$^{-1}$ are attributed to C$-$O. The spectrum of the PGO membrane showed almost the same functionality. The PGO membrane showed a strong band at 1747 cm$^{-1}$, which corresponds to the stretching vibration of $-C-\equiv O$ and $-C-O$ moieties in the ester group ($-O-C\equiv O$). The increased peak intensity showed that the residual $-COOH$ groups of PGO have covalently bonded with the $-OH$ group of the PEG molecule, leading to more ester groups. In addition, the strong band at 1640 cm$^{-1}$ observed in the PGO membrane is attributed to C$\equiv$C functional groups.

3.2. Hydrophilicity and Stability Studies. Hydrophilicity is the prerequisite for separation of membranes in aqueous solutions. The hydrophilicity of GO and PGO membranes was measured at 33% of humidity and 23 $^\circ$C. As shown in Figure 2a,b, the PGO membrane (contact angle, $\sim 46^\circ$) showed much better hydrophilicity than the pristine GO membrane (contact angle, $\sim 53^\circ$). As expected, the pristine GO membranes absorbed water and got swelled, compromising the cycling stability and permeability. The water uptake of water by PGO and GO (50 wt %) membranes was then evaluated as per the equilibrium weight swelling ratio (ESR). The lesser swelling PGO (ESR, $\sim 1.3$) than that of the pristine GO membrane (ESR, $\sim 2.4$) indicated that the GO sheets’ high water flux, and improved separation efficiency and stability.

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movement in the membrane gets reduced due to cross-linking of PEG-NH$_2$ and GO membrane-like domains (Supporting Table S1). These results indicate that the GO membrane-like domains and cross-linking of PEG-NH$_2$ molecules greatly suppress the movement of GO sheets in the membranes.

As mentioned before, because of the presence of oxygen, GO sheets get separated in solutions, causing pure GO membranes to be damaged. As a result, long-term stability is required for the applications of GO membranes in the solution phase, which can be achieved by modifying GO with hydrophilic functional groups and was carried out by conjugating PEO groups onto the GO. Therefore, the stability of GO and PGO membranes in different conditions was investigated (Figure 2). After 5 days, the GO membranes in the water get disintegrated, similar to those previously reported (Figure 2c). In contrast, the PGO membranes tend to be more stable and, even after 30 days, retain their original structure (Figure 2d,e). Further, the long-term stability study of PGO membranes was also carried out; the membranes were stable for up to 60 days in water. However, PGO membranes show stability for up to 30 days in acidic solution (pH = 2.2, Figure 2g,h) and basic medium (pH = 12, Figure 2j,k) as compared to pristine GO membranes (Figure 2f,i) and previously reported modified membranes of GO. The delamination of the GO membranes was done without stirring or shaking after 2–5 days, while no visible structural change was observed for PGO membranes even after 20 days, as shown in Figure 2g.

4. SEPARATION PERFORMANCE OF MEMBRANES

The water permeance properties of pristine GO and PGO-based membranes were measured. The pristine GO-based membrane (280 ± 10 nm) exhibits a water permeance of up to 65 ± 5 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. Meanwhile, the as-prepared 250 nm-thick PGO membrane shows almost 8–10 times higher water permeance (~670 ± 5 L m$^{-2}$ h$^{-1}$ bar$^{-1}$) than the pristine GO-based membrane with similar thickness as shown in Figure 3a and Table 1. Further, the water permeability of PGO membranes with variable thicknesses was evaluated (Figure 3a). Upon increasing the thickness of PGO-based membranes up to 1330 ± 10 nm, the water permeance decreased several times. This is possibly due to the multiple layers of the PGO blend. When the thickness of the PGO increased, some of the defects within the membranes/sheets are filled by upper and lower layers. Therefore, water passes through the thicker layer of the membranes and the overall flow decreases.

Further, we measured the separation efficiency of GO and PGO membranes using probe molecules with variable sizes and molecular weights including Congo Red (CR), methylene blue (MB), Brilliant Blue G (BBG), rhodamine B (RB), tannic acid (TA), ferricyanide (FC), serum albumin (SBA), and TMPyP ($5,10,15,20$-Tetrakis(1-methyl-4-pyridinio)-porphyrin)tetra($p$-toluenesulfonate)). Table 2 summarizes the separation performance of pristine GO and PGO-based membranes for different probe molecules or ions. The size, shape, and charge of the probe molecules or ions are important factors for separation performance. The 250 ± 10 nm-thick PGO membrane completely rejects the positively charged BBG (2.3 nm × 1.8 nm) dye with a water permeance of 190 ± 5 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ (Figure 3b) compared to pristine GO-based membranes (Table 2). It shows that our as-prepared PGO membranes are cationic in nature and therefore can effectively repel the cationic dyes and show good efficiency for the positive dye. The zeta potential studies also confirmed the cationic selective nature of PGO membranes at different pH values, as shown in Supporting Figure S4. The water permeance is 10–20 times higher than that of the GO membranes reported so far. The large size of the BBG molecule is one of the factors for the higher rejection. The rejection rate is 90 ± 2% for the small dye molecule CR (1.9 nm × 1.3 nm) (Figure 3b). The separation efficiency of the PGO membrane also depends on the charge properties of the dye molecules; electrostatic interactions allow the more positively charged molecules to be taken up by the membranes. As a result, the PGO membranes show a high rejection rate of ~100% for positively charged dyes such as MLB and RB. The UV/vis absorption studies further confirm the excellent rejection of the membrane against the feed solution before and after filtration (Supporting Figure S5). In addition to the above factors, the high rejection of dye molecules is also possible due to the hydrophobic interaction between PGO and the probe molecules. The dye molecules have mostly a benzene ring with hydrophobic domain and therefore they can interact with PGO membranes easily. This type of interaction is very common for the GO and CNTs-based membrane for dye separation; however, polymeric-based NF membranes have no ability to reject dye molecules with similar pore size capacities. Studies showed that the hydrophilic interaction in polymeric membranes can cause the adsorption of the solute on the surface of membrane, which is not suitable for long-term separation. As for our membranes, we tried to remove the adsorption effect by collecting the permeate after stabilizing the feed solution. Further, the PGO membrane shows less rejection (55%) toward the smaller molecule FC (0.9 × 0.9 nm) as shown in Figure 3b and Table 2.

Therefore, we can confirm here that our PGO membranes have the maximum number of nanochannels with a dimension of ~1 nm and the size distribution is relatively small. Next, biomolecules such as BSA, TA, and TMPyP with large size were used to assess the size selectivity (Figure 3b). The larger molecules such as BSA, TA, and TMPyP show 100% rejection (Figure 3b and Supporting Figure S6). From these results, it is confirmed that the pore size of the PGO membrane plays an important role in separation application. These PGO membranes show a good balance of permeance and rejection than pristine GO and reported GO-based membranes (Supporting Table S2), which is several magnitudes higher compared to the reported GO-based NF membranes. However, it is found that the permeance is reduced approximately 10–50% compared to the pure solvent permeance (Figure 3c), which is possibly due to the blockage of nanochannels by the solute molecules. We believe that as-prepared PGO membranes with outstanding separation performance should have a great potential for various separation applications in future.

Table 1. DI Water Permeance of GO-Based Membranes with Various Thicknesses at Room Temperature

| thickness (nm) | pristine GO membrane’s permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$) | PGO membrane’s permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$) |
|----------------|---------------------------------------------------------------|--------------------------------------------------------|
| 280 ± 10       | 65 ± 5                                                        | 670 ± 5                                                |
| 550 ± 10       | 30 ± 5                                                        | 575 ± 5                                                |
| 890 ± 10       | 12 ± 2                                                        | 490 ± 5                                                |
| 1360 ± 10      | 5 ± 1                                                         | 320 ± 5                                                |

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Table 2. Separation Various Probe Molecules through Pristine GO and PGO Layered Membranes at Room Temperature

| probe molecules/ions | molecular weight (g/mol) | analyte charge | conc. | size of molecules or ions (width and diameter (nm)) | GOMs (280 ± 10 nm) | PGOMs (250 ± 10 nm) |
|----------------------|--------------------------|----------------|-------|-------------------------------------------------|---------------------|---------------------|
|                      |                          |                |       | permeance | rej. | permeance | rej. | permeance | rej. |
| FC                   | 212.0                    | –              | 1.0 mM| 0.9 × 0.9 | 42 ± 5 | 40 ± 5 | 580 ± 10 | 55 ± 5 |
| MLB                  | 373.0                    | +              | 50 μM | 1.5 × 0.63 | 12 ± 2 | 97 ± 1 | 325 ± 10 | 100 |
| RB                   | 479.0                    | +              | 50 μM | 1.7 × 1.3 | 10 ± 2 | 98 ± 1 | 276 ± 10 | 100 |
| CR                   | 696.7                    | –              | 50 μM | 1.9 × 1.3 | 17 ± 2 | 90 ± 5 | 445 ± 10 | 90 ± 2 |
| BBG                  | 854.0                    | –              | 50 μM | 2.3 × 1.8 | 8 ± 2 | 99 ± 1 | 245 ± 5 | 100 |
| TMPyP                | 1363.6                   | N              | 1.0 mM| 1.7 × 1.7 | 7 ± 2 | 100 | 210 ± 5 | 100 |
| TA                   | 1701.2                   | N              | 1.0 mM| 2.3 × 3.0 | 5 ± 1 | 100 | 220 ± 5 | 100 |
| BSA                  | ~67 kDa                  | –              | 1.0 mM| 14 × 4 | 5 ± 1 | 100 | 185 ± 5 | 100 |

*GOMs, GO-based membranes; BBG, Brilliant Blue G; CR, Congo Red; Conc., concentration; FC, ferricyanide; MLB, methylene blue; Perm, permeance; RB, rhodamine B; Rej, rejection; TA, tannic acid; TMPyP, 5,10,15,20-Tertakis(1-methyl-4-pyridinio)porphyrin tetra(p-toluenesulfonate); SBA, serum albumin. Permeance measured in L m⁻² h⁻¹ bar⁻¹ and rejection measured in %.

Further, we tried to separate the MLB dye using different concentrations (20, 30, 50, 75, and 100 μM), as shown in Table S3. As the concentration of the MLB dye increases, the membrane fouling increases and rejection decreases. Moreover, MLB dye of concentration 50 μM was used for separation up to 24 h continuously, as shown in Table S4. As the time increased, the fouling ratio significantly increased and the permeance drastically decreased. Our PGO membrane became completely blocked after 8 h, which is possibly due to blockage of the nanochannels.

Additionally, we evaluated the desalination properties of both pristine GO and PGO membranes to measure the different salt ions such as NaCl, MgCl₂, Ni(NO₃)₂, and Pb(NO₃)₂ from water at pressure 0.95 bar as shown in Figure 4a,b. The 280 nm-thick pristine GO membrane shows ~65% rejection for large ions such as Ni(NO₃)₂ and Pb(NO₃)₂, as reported in the literature. Similarly, such membrane also shows very less rejection (~35%) for NaCl ions due to the smaller ion size, as shown in Figure 4a, while as-prepared PGO membranes with almost similar thickness exhibit better rejection: ~93 and ~95% for Ni²⁺ and Pb²⁺ salt ions, respectively (Figure 4b). The higher rejection of these ions is possibly due to the Donnan exclusion effect. According to Donnan exclusion theory, the valences of ions, followed by the order of Z co-ions or Z counter-ions, determine the rejection rate (Z refers to the valence). The PGO membranes are cationic selective membranes, and therefore repel cationic ions such as Ni²⁺, Pb²⁺ etc and show high rejection for ions. Additionally, these counter-ions can easily bind to a part of the surface charge, weakening the repulsive force and increasing the divergent ion rejection. The salt rejection obtained for the PGO membrane was in the order NaCl < MgCl₂ < Ni(NO₃)₂ < Pb(NO₃)₂, as shown in Figure 4b. Further, pristine GO and PGO membranes with different thicknesses were used to measure the rejection of 1.0 mM of NaCl as shown in Figure 4c,d. As we increase the thickness of the PGO membranes, the rejection is increased while permeance decreases several times. The 1330 nm-thick PGO membrane shows ~100% rejection for NaCl compared to the pristine GO membrane with similar thickness (Table 3).
Table 3. Separation of NaCl (1.0 mM) through Layered GO and PGO Membranes with Different Thicknesses at Room Temperature

| thickness (nm) | pristine GO membranes (280 ± 10 nm) | PGO membranes (250 ± 10 nm) |
|---------------|-------------------------------------|----------------------------|
|               | permeances  | efficiency | permeances  | efficiency |
| 280 ± 10      | 40 ± 2      | 35 ± 2     | 250 ± 10    | 560 ± 5    |
| 550 ± 10      | 17 ± 3      | 76 ± 2     | 520 ± 10    | 475 ± 5    |
| 890 ± 10      | 8 ± 2       | 88 ± 2     | 800 ± 10    | 290 ± 5    |
| 1360 ± 10     | 2 ± 1       | 97 ± 1     | 1330 ± 10   | 120 ± 5    |

5. CONCLUSIONS

In summary, we have fabricated a class of layered PGO-based membranes with controlled pores to achieve the desired separation and permeability for several probe molecules. The membranes were prepared by introducing the 6-armed PEO into the surface of the GO nanosheets using the simple amicronization process. The newly developed 250 nm-thick layered PGO membrane showed remarkably high rejection (>90%) for several ions and molecules. Besides this, the layered PGO membrane also showed good separation (>70%) for small ions such as NaCl, MgCl₂, Pb(NO₃)₂, and Ni(NO₃)₂ salts. In addition, such membranes are very stable under different conditions compared to pristine GO and reported membranes. We hope these membranes will have a bright future in many potential applications in biomedical and pharmaceutical separation processes, including blood purification, plasma separation, and blood oxygenation, and a wide range of nanofiltration applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.2c03907.

Detail AFM analysis, FTIR studies, z-potential, swelling data and separation of probe molecules at different conditions (PDF)

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