Graphene oxide membranes for effective removal of humic acid

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2-Dimensional materials-based membranes have been considered as promising candidates for water purification. Here, we report that graphene oxide (GO) membrane can reject aquatic humic acid (HA) up to 94.2% in a 2-bar pressurized filtration process. In-depth analysis indicated that the filtration performances such as water flux and rejection rate depend on the thickness and physical structure of the membranes. The experimental study reveals that the GO membrane with a mass loading of 0.58 mg/cm², which is approximately equivalent to 3 μm thickness, is required to reach the rejection rate of HA at 94% using 2 bar pressurized filtration method. We further confirmed the membranes’ integrity by over 98% rejection of methylene blue (MB). For practicality, we tested our membrane in tubular form by coating GO on PVDF hollow fibres, which presented similar rejection performances using vacuum filtration method while maintaining the water flux around 100 L m⁻² h⁻¹ bar⁻¹.

Introduction

Graphene oxide (GO) has emerged as a promising membrane material for water purification [1–4], organic solvent nanofiltration [5–7], gas separation [8, 9] and energy storage [10, 11] due to its unique layer-by-layer laminated structure composed of nano-capillaries [2, 4, 12, 13]. GO consists of a single layer of sp²-hybridized carbon lattice and oxygen-containing functional groups on the surface [14, 15]. It is generally considered that epoxy and –OH functional groups are mainly distributed to the basal planes of GO flakes and the –COOH groups are attached to the edges, providing a negative charge surface of GO flakes in water [16]. The abundant functionalities provide the hydrophilic nature for water transport as well as interlayer spacings between flakes for molecular sieving [4, 17, 18]. It has been reported that the nano-capillaries between two adjacent flakes are approximately 8 Å in diameter [13, 19, 20].

The GO membranes have exhibited high separation performance with ultrafast permeance. For instance, Huang et al. reported the enhanced ionic sieving by reduced GO membranes [21], which was later proved by Qi et al. with over 80% rejection of sodium chloride salt (NaCl, feed concentration = 1 M) with relatively high water permeance (200 L m⁻² h⁻¹ bar⁻¹) [22]. In addition, hybrid GO/graphene layered membranes were employed to remove ionic dyes (>96%) from an aqueous solution [18]. It also represented remarkable performance (>99.9%) for similar dye removal in organic solvents nanofiltration (OSN), reported by Qian et al. [6]. Despite the promising outcome for removing ionic pollutants, other challenges still exist. Typically for municipal water treatment, one critical challenge is removing dissolved natural organic matter (NOMs). NOMs consist of different hydrophobic and hydrophilic substances, making them difficult to be removed from water. Amongst different substances, humic acid (HA) is the major component of NOM [23, 24]. HA is considered as a complex component consisting of molecules with varying molecular diameters ranging from 1.2 nm (12 Å) up to 1 μm. Typical HA particles have an
average molecular diameter of ~400 nm [25] and most molecules are larger than 5 nm [26]. Such large HA molecules contain alkyl groups, aromatic units with reactive carboxylic groups (−COOH) and hydroxyl (−OH) groups [27] which makes HA molecules mostly negatively charged in water. GO membranes have emerged as an efficient tool for rejecting HA due to their properties for molecular sieving. A few studies have been reported about the high rejection of HA (60% [28] and 90% [29]) via the GO membrane-based separation technique using 10 mg/L of feed concentration. To achieve more effective HA removal using GO membranes for industrial applications, it is crucial to find the best trade-off between membrane permeance and rejection [30], which are highly related to the membrane thickness.

Herein, we designed the purification technique employing GO layers coated on commercially available polyvinylidene fluoride (PVDF) substrate. The membrane exhibited the removal of HA (feed concentration 15 mg/L) up to 94.2% under pressurized filtration (2 bar). In this research, we also report a thorough study on the influence of the membrane thickness, determined by mass loading of GO for membrane fabrication on the filtration performance, together with a theoretical presentation on the interlayer structure of GO membrane. Hence, the current work may provide an opportunity to use GO membrane for aquatic HA removal in industries and expand the knowledge on the laminate structure-dependent sieving mechanism.

### Results and discussion

GO membranes were prepared by coating GO flakes on porous PVDF templates. Here, it is worth mentioning that the mean area of GO flakes used for membrane preparation in this study is ~0.25 μm² [2], which was calculated based on the SEM images as we previously reported [31], and this is smaller than the typical size (~1 μm²) of GO flakes [9, 17]. Smaller flakes, in general, result in a greater number of pinhole defects but allow high water permeation [12, 32]. The morphological study was firstly conducted by scanning electron microscopy (SEM), which indicated that the PVDF-based GO membrane reveals the typical nano wrinkle structure due to the existence of the GO layer [Fig. 1(a)]. The unique laminated structure of GO membranes was determined by a cross-sectional image [Fig. 1(b)] [4, 12, 33]. Figure 1(c) shows an overview of PVDF hollow fibre used as a template for GO membranes and a laminated structure of GO layers on hollow fibre substrate is also seen in [Fig. 1(d)].

The GO mass loading of all membranes was calculated according to Eq. 1 (Experimental section). The GO mass loading vs membrane thickness measured using SEM is shown in Table 1.

However, determining the thickness of GO membranes thinner than 1 μm may induce a higher chance of inaccuracy. Hence, further discussion is presented by using GO mass loading instead.

As mentioned, the oxygen-containing functionalities on GO sheets contribute to the hydrophilic nature of the membrane. This is because hydrogen bonds can form between partially negatively charged oxygen atoms and water molecules, resulting in a highly hydrophilic surface. The surface contact angle measurements were conducted to confirm the surface hydrophilicity. The decrease in average contact angle was observed after coating the GO membranes on PVDF substrate. It shows that the measured average contact angle between the pure water droplet and the PVDF surface was 68.82°, however, significantly decreased to 28.19° after the attachment of GO [Fig. 2(a) and (b)]. The results show the hydrophilic nature of GO and suggest the higher hydrophilic performance of the GO membrane than that of the PVDF substrate.

The membranes’ crystallographic structure and swelling effect were studied via X-ray diffraction (XRD), as depicted in Fig. 3(a). It was observed that a membrane in a dehydrated state has 0.8 nm of d-spacing (red spectrum 2θ = 11.05°), which changed to 1.42 nm once the membrane was soaked in water for 4 h. It can be seen by comparing the width of two peaks, in which a broader peak of the dehydrated membrane represents the heterogeneous distribution of spacings in a dry state. Once the membrane is hydrated, the localized water molecules tend to expand the interlayer spacings, known as the swelling effect [20]. The limited capacity of water species between laminates suggests that the interlayer spacings become more homogeneous with a narrower distribution. It is highlighted here that the interlayer spacing could further increase as more water molecules are located inside the nano-capillaries if the membrane is kept soaking in water. However, the expansion of interlayers may be maintained at a particular level by introducing external pressure as reported [19].

Chemical characterizations for GO membranes were further conducted by Fourier-transform infrared spectroscopy (FT-IR) as shown in Fig. 3(b). The PVDF substrate itself only presents carbon–hydrogen and different phase carbon–fluoride bonds as previously reported [34, 35]. After coating with GO, the spectrum was observed with several strong peaks representing the existence of abundant chemical moieties after tethering GO membrane on PVDF: O–H groups at ~3350 cm⁻¹, C = O from carbonyl and carbonyl groups at ~1700 cm⁻¹, sp²-hybridized C = C at ~1600 cm⁻¹, C–O–C from epoxy/ether groups at ~1200 cm⁻¹, and C-O associated to alkoy/alkoxide ~1037 cm⁻¹ [36–38]. The lack of functional compositions of PVDF in this spectrum proved the efficient coverage of substrate with GO membrane. Furthermore, the strong peak of O–H groups indicates the hydrophilic nature of GO membranes, which is
in agreement with the contact angle measurements discussed above and is shown in Fig. 2.

After confirming the physical and chemical structures, the membrane performance was determined by water flux and rejection rate measurements. The water flux and rejection rates calculations are based on Eqs. 2 and 3. Our membranes offered the highest water flux value of 5 L m⁻² h⁻¹ bar⁻¹. For a clear understanding of the correlation between water flux and GO mass loading, another experiment was designed using a set of membranes with different amounts of GO: 0.14 mg/cm², 0.29 mg/cm² and 0.58 mg/cm². As expected, a significant decrease in water flux with increasing thickness of GO was observed [Fig. 4(a)]. This could be explained by the inner laminate structure of the GO membrane, as it strongly influences the water transportation pathway. Typically, water molecules enter through the pores (flake to flake lateral distance) on the membrane surface and then travel through the inner layers of the GO laminates through interlayer distance. This indicates that more layers offer a more extended pathway of water molecules, reducing the water flux as discussed in the literature [32, 39].

In contrast with the trend of water flux, the efficiency of HA (feed concentration 15 mg/L) removal was enhanced upon increasing the thickness (mass loading) of the GO membrane. Specifically, the rejection rate was 11.2% for 0.07 mg/cm² of GO membrane, followed by a continuous rise to 94.2% once the GO mass loading reached 0.58 mg/cm² [Fig. 4(b)]. The concentration of HA was determined by using liquid chromatography equipped with organic carbon and nitrogen detection.

| GO mass loading (mg/cm²) | 0.07 | 0.14 | 0.29 | 0.58 |
|--------------------------|------|------|------|------|
| Membrane thickness (µm)  | ~0.3 | ~0.7 | ~1.4 | ~2.8 |

Figure 1: Surface analysis of GO membranes: Morphological analysis of flat GO membrane via SEM (a) top view with GO wrinkles, (b) cross-section view of sample with GO mass loading of 0.58 mg/cm² (c) hollow fibre tube overview, (d) cross-section view of GO on PVDF hollow fibre.

Table 1: The relationship between GO mass loading and the estimated membrane thickness.
(LC-OCD), which provides both organic carbon detection (OCD) and fixed wavelength UV-detection (UVD). The HA peak at the retention time ~ 60 min [40] disappears on the permeate side of the membrane with the highest GO mass loading [Fig. 4(c)]. To clarify here is that the other two peaks at ~ 8 min and ~ 100 min do not correspond to HA and are probably due to low molecular weight impurities as their existence was also observed in the water sample, as shown in Fig. 6(a) (Experimental Section). It has to be highlighted here that during the HA concentration measurement using the LC-OCD method, samples were first filtered through a 0.45-µm PES filter before passing through the liquid chromatography size-exclusion column (SEC). Therefore, the observed rejection performance of GO membranes was studied based on HA particles smaller than 0.45 µm [40].

To confirm the integrity of GO membranes, we tested the membranes for methylene blue (MB) rejection using a series of GO membranes with mass loading ranging from 0.03 mg/cm² to 0.58 mg/cm². According to the UV–vis absorbance curve shown in Fig. 4(d), the rejection of MB starts from ~ 45% when the mass loading of the GO membrane is only 0.03 mg/cm² (thickness ~ 150 nm). However, the rejection performance of GO membranes significantly improved as the membrane mass loading/thickness increased. Typically, a rejection of > 98% was obtained when the thickness was increased to approximately 1 µm by using a mass loading of 0.14 mg/cm² for membrane

Figure 2: Surface performances of GO membranes: Contact angle measurement of (a) PVDF substrate and (b) flat GO membrane on PVDF.

Figure 3: Structural characterization: (a) X-ray diffraction plots showing d-spacing of GO membrane (b) Typical FT-IR spectrum showing the presence of functional groups in GO membranes.
preparation. The significant decrease in MB concentration from feed to permeate of membranes with increasing GO mass loading was all determined by UV–vis spectra [Fig. 4(d)]. The observed rejection of MB confirms the integrity of GO membranes at different mass loading/thickness.

According to the typical size-exclusion principle, the molecules larger than the membrane's pore size should be rejected [4, 6, 18, 41]. It was reported that only molecules/ions with a hydrated diameter smaller than 9 Å could pass through the GO membrane [42]. Considering the large, hydrated diameters of HA (~ 12 Å) [43] and MB (~ 14 Å) [44], the observed rejection can be attributed to the size-exclusion mechanism [2]. This hypothesis is also supported by the rejection (~ 94%) of HA which was detected in the molecular range of 0.1 kDa to 10 kDa [40], and the majority of such molecules are larger than 5 nm as shown in the previous articles [25]; however, the particles smaller than ~ 9 Å may pass through the membrane which is reflected by permeation of 6% HA. Additionally, it is worth mentioning here that the adsorption of a small amount of HA on the GO membrane is inevitable. Previous reports indicate that a membrane with 2 mg of GO, particularly 0.14 mg/cm² mass loading in our case, should adsorb approximately 0.02 mg of HA in a neutral environment (pH ~ 7) [45], which is ~ 13% of 10 mL HA feed solution. However, our membrane shows ~ 40% rejection, which is higher than the expected amount of adsorbed HA. This further confirms the size-exclusion mechanism of GO membranes.

Furthermore, the relatively low removal of HA and MB was observed at lower GO mass loading. This suggests a vital role of pinholes between adjacent GO flakes in rejection. Pihole defects may provide a much easier pathway for water transport and its formation occurs in the case of thin membranes [12]. HA and MB molecules might also pass through the pinhole defects.
with higher priority because of more available mass transport pathways.

The experiments presented above provided crucial information on efficient membrane selectivity for HA removal using flat membranes. To test the performance of our GO membranes in practical conditions for industrial application [46, 47], we used tubular membranes prepared by using the method described in the experimental section. Our reproducible experimental results demonstrate the over 94% HA rejection using a hollow fibre system. The hollow fibre filtration tests provide a promising outcome in terms of filtration performance compared with that of the flat membrane with significant higher water flux (~ 100 L m⁻² h⁻¹ bar⁻¹) using larger volumes of water [19]. It is highlighted here that the hollow fibre membranes show much higher water flux than that of flat membranes, which may be due to different fabrication and filtration methods. Previous research indicated that the speed of water transport might be more related to the microstructure between GO laminate [12]. Vacuum filtration provides less pressure than pressurized filtration (2 bar), leading to a looser inner microstructure which may contribute to more potential tortuous pathways for water transportation.

Conclusion

The performance of the GO membrane on filtration may vary depending on processing parameters and defects. This study provides information on the connection between the GO membrane's mass loading/thickness and pore structure. Our results indicate the GO membrane's solid performance for HA removal by exhibiting 94.2% rejection (with high feed concentration = 15 mg/L) under 2 bar pressurized filtration system. Our size-exclusion-based separation performance was confirmed by completely removing methylene blue (MB). Furthermore, the performance of GO membranes was demonstrated in an industrial application like hollow fibre vacuum filtration set-up with water flux of ~ 100 L m⁻² h⁻¹ bar⁻¹ while maintaining a similar rejection performance.

Calculation of GO mass loading

The mass loading was calculated using Eq. 1, considering the effective area of PVDF substrate (13.84 cm²) coated with GO. The following equation shows the example calculation for a 0.58 mg/cm² membrane.

\[
\text{GO mass loading} = \frac{\text{Mass of GO added}}{\text{Effective area of substrate}} = \frac{8 \text{ mg}}{13.84 \text{ cm}^2} = 0.58 \text{ mg/cm}^2
\]  

Membrane fabrication

GO solution is supplied by Nisina Materials Japan. The obtained GO solution was then dispersed in de-ionized (DI) water at the 1 mg/mL stock concentration, and then sonication for 2 h. The flat membranes were fabricated in dead-end filtration cells (Sterlitech HP 4750). PVDF (Sterlitech, 0.2 µm pore size) templates were washed thoroughly by filtering with DI water before adding the desired amount of GO suspension from the diluted stock solution. We used a dead-end cell with constant feed pressure ~ 2 bar using argon gas as illustrated in Fig. 4(a) to obtain uniform GO membranes [19] as shown in Fig. 4(b); the fabrication process typically lasts for over 48 h, including membrane drying before performances tests. Furthermore, Fig. 5(c) and (d) illustrates the experimental design used to fabricate tubular membranes of GO on PVDF hollow fibres. Unlike flat membrane synthesis, tubular GO membranes [48] were prepared using a set of PVDF hollow fibres in a sealed stainless steel homemade container. The desired amount of diluted GO stock solution was used for membrane preparation under constant pressure vacuum filtration, followed by 48 h of drying under the same pressure.

Characterization techniques

GO membranes were characterized by a range of analytical techniques. The scanning electron microscopy (SEM) (model FEI Nova NanoSEM 230, FE-SEM) was applied to study the surface and cross-sectional structure of GO membrane. The surface hydrophilicity was analysed using Contact Angle Goniometer from Ossila U.K. The chemical structure of GO membrane was studied using Fourier-transform infrared spectroscopy (FT-IR) (PerkinElmer, Spectrum Two). X-ray diffraction (XRD) (PANalytical Empyrean 1 Thin-Film XRD) was used to determine the interlayer spacing (d-spacing) of the GO membranes. HA concentration was determined by the liquid chromatography equipped with organic carbon and nitrogen detection (LC-OCD) (detection limit 0.005 mg/L). The LC-OCD was equipped with a 0.45-µm porosity PES filter, followed by a weak cation exchange size-exclusion chromatography column (SEC) with a detection range of molecular weight from 0.1 kDa to 10 kDa, a fixed wavelength (254 nm) UV detector (UVD) and organic carbon (OC) detector [40, 49].
UV–vis spectrophotometer (PerkinElmer Lambda 365) was used to determine the concentration of methylene blue ($\lambda = 668$ nm) [50]. Before each sample measurement, de-ionized (DI) water was recorded as the background spectrum to avoid any absorption of water and cuvette.

**Calculation of water flux and rejection rate**

Water flux was calculated according to Eq. 2.

$$J_w = \frac{Q}{AP\Delta t},$$  

(2)

where $J_w$ represents water flux in the unit of L m$^{-2}$ h$^{-1}$ bar$^{-1}$ (LMH/bar), $Q$ is the volume of permeate, $A$ is the effective area of membrane (13.84 cm$^2$), $P$ is the filtration pressure and $\Delta t$ is the filtration duration.

The rejection rate was calculated according to Eq. 3.

$$R = 1 - \frac{C_p}{C_F},$$  

(3)

where $R$ is the rejection rate, $C_p$ is the solute concentration in the feed and $C_F$ is the solute concentration in permeate.

**Performance of GO membranes**

The filtration performance of GO membrane was determined by water flux and rejection analyses. In this study, all flat membranes were tested using the dead-end filtration cell (Sterlitech HP 4750) at 2 bar pressure. Each membrane assembled inside the dead-end cell was treated with slow addition of the 50 mL HA solution. After filtration, 10 mL of HA solution was collected from both feeds (solution inside the dead-end cell) and permeate sides. The volume change on the permeate side was continuously recorded every 10 s using a computer-controlled mass balance during the water filtration process. Then, the samples were analysed by the LC-OCD to determine the HA concentration. Each experiment was repeated twice to study the reproducibility of membrane performance. The membranes were further tested with DI water as feed for baseline determination, and the permeate was analysed using the LC-OCD method [obtained spectrum shown in Fig. 6(a)]. Tubular membranes were tested for water flux and HA removal using constant vacuum pressure [48]. The volume change on the permeate side was continuously recorded using the same computer-controlled mass balance during the water filtration process. Permeate solution was collected and analysed using the LC-OCD method.
The same filtration technique was applied for MB filtration (feed concentration = 10 mg/L). The concentration of MB in feed and permeate was then calculated according to the maximum absorption measured by the UV–vis spectrophotometer. The maximum absorption peak of MB was scanned in the wavelength range from 300 to 800 nm and was detected within the visible light region (\(\lambda = 668\) nm), which is in agreement with literatures [50]. The employed standard curve of MB at a range of concentrations, 10 mg/L, 5 mg/L, 2.5 mg/L, 1.25 mg/L, 0.625 mg/L, 0.312 mg/L and 0.156 mg/L, is illustrated in Fig. 6(b).

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**Author contributions**

XR: Investigation, characterization, data analysis, writing—original draft, writing—review and editing. DJ: Characterization, data analysis. XW: characterization, data analysis, investigation. HB: Writing—review and editing. RD: Supervision, writing—review and editing. TF: Writing—review and editing. YYK: Supporting—original draft, writing—review and editing. RJ: Conceptualization, supervision, writing—review and editing, resources.

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**Data availability**

All data and materials generated or analysed during this study are included in this published article.

**Declarations**

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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