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Selective molecular separation of lignin model compounds by reduced graphene oxide membranes from solvent-water mixture

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Abstract

Selective separation of lignin depolymerization products is key to fractionating and isolating high-value aromatic compounds from the depolymerization process. The primary aim of this study was to synthesis graphene oxide (GO) membranes for selective separations of lignin oligomeric units from polar organic solvent-water media. GO membranes were synthesized on a polymeric substrate by a shear assisted casting of aqueous GO dispersion using a wire-wound rod. Deposited GO was then reduced to different extents by controlled thermal incubation, and the impact on membrane performance was investigated. The extent of reduction of GO was established by extensive characterization with FTIR, XPS, Raman Spectroscopy, XRD, and contact angle measurements. Impressive performance with the rejection of over 70% for the model compound trimer BMP (2,6-bis[(2-hydroxy-5-methyl phenyl) methyl]-4-methylphenol) was achieved compared to only 20% rejection for the dimer GGE (guaiacylglycerol- β -guaiacyl ether) with isopropanol-water (90–10% by volume) as a solvent. This corresponds to an encouraging selective separation with selective permeation of dimer (GGE) 3.5 times higher compared to trimer (BMP). rGO membranes exhibited a stable performance over 84 h of operation at a shear rate of 1.1 Pa in a cross-flow mode of operation. Selective separation of GO can be effectively modulated by controlling the O/C ratio by the extent of reduction of GO; indeed, the retention of trimeric compounds increased with increasing GO reduction. The remarkable performance of GO membranes could enable energy-efficient fractionation of lignin oligomeric compounds from polar organic solvents.

1. Introduction

Lignocellulosic materials, the most abundant biopolymers, serve as a valuable source of energy and other value-added chemicals [1,2]. Lignocellulosic biomass consists of three

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Appendix A. Supplementary material

Flux vs Pressure plots, chromatogram showing rejection and separation of lignin model compounds, plots showing retentate concentration vs recovery, GO XRD. Etc. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.115865>.

types of biopolymers: cellulose, hemicellulose, and lignin. Among these biopolymers, lignins are the aromatic, water-insoluble polymers, which are a valuable source of aromatic compounds (such as vanillin) [3]. Refining lignins remains a subject of considerable research interest, which involves milestones such as efficient depolymerization and separation of products [4,5]. Technologies, such as hydrogenolysis and pyrolysis, have been effectively implemented for the deconstruction of lignins. However, homogeneous deconstruction of lignins with products of narrower molecular weight distribution remains a challenge [6]. As the products after the deconstruction of lignins have non-homogeneous molecular weight distributions, fractionation and purification of the product streams are vital to the recovery of high purity fine chemicals.

Lignin depolymerization by catalytic hydrogenolysis is realized in protic organic solvents, such as isopropanol-water mixtures [7]. The typical products of lignin depolymerization consist of monomers and oligomers [7]. The efficient use of lignins as a source of fine chemicals requires a highly selective process for separating components after the depolymerization step [8]. Membrane technologies have found applications in the recovery of value compounds [9]. Use of Organic Solvent Nanofiltration (OSN) membranes provides a non-thermal approach for the separation of organic molecules from solvents [10]. OSN membranes can retain organic molecules with molecular weights from 300 Da. Separation of lignin oligomeric compounds by commercial OSN membranes was successfully achieved by Werhan et al. [11]. Sultan et al. demonstrated the fractionation of lignin-derived oligomeric compounds using a cascade of OSN membranes with different molecular weight cutoff [12]. However, better selectivity (sharp molecular weight cutoff), higher permeance and long term stability of OSN membranes are essential for efficient application of OSN technology for separation of key components.

Among the next generation materials for nanofiltration membranes, graphene oxide (GO) has attracted considerable interest [13,14]. GO is an atomically thin sheet of carbon with domains of sp^2 and sp^3 hybridized carbon, and contains oxygenated functionalities [15]. GO membranes have received extensive attention in OSN applications owing to their exceptional stability in a wide range of solvents [16–18]. The ability of GO membranes to retain solutes around 1.2 nm makes them a suitable candidate for OSN applications [19,20]. Furthermore, the ultrathin coating of GO on a substrate yields membranes with higher solvent permeance [21]. Additionally, the use of existing commercial coating technologies, such as gravure printing, has helped realize the large-scale synthesis of GO membranes [22].

The nanostructure of GO is enriched with interlayer spacing between the GO sheets and inter edge defects [23,24]. The interlayer spacing constitutes a major route for transport through GO membranes and plays a vital role in determining the selectivity of the membranes [25]. The interlayer spacing of GO membranes depends on van der Waal's forces and electrostatic interactions between the deposited GO sheets [26]. The polarity of solvents is known to impact electrostatic interactions significantly, and a decrease in interlayer spacing is reported for solvents with lower dielectric constant (lower polarity) [16]. Additionally, the extent of reduction plays a vital role in determining the performance of the GO membranes. Reduction of GO, in essence, is the partial restoration of sp^2 carbon domains by removing oxygenated functionalities [27]. Lower interlayer spacing is observed

for GO with a higher extent of reduction owing to greater pi-pi stacking interactions between the restored sp^2 hybridized carbon domain on reduced GO [28]. GO membranes thus offer an opportunity to tune selectivity by modulating the extent of GO reduction [29]. Additionally, partial reduction of GO has also been found beneficial in imparting stability to the membrane by preventing delamination of deposited GO films [19]. Furthermore, GO membranes also offer the ability to tune charge interactions with solutes by incorporation of polyelectrolytes in the GO domain, which could be exploited in selectively controlling the transport of charged solutes through the membrane [30]. Excellent stability and the ability to optimize the separation performance of GO membranes, besides control over permeance by modulating the thickness of the GO layer, has made GO membranes a promising candidate for OSN applications.

In this study, the application of rGO membranes to selective separations of model lignin oligomeric compounds was investigated. The main aim of the study was to understand the rejection behavior of rGO membranes towards the separation of model phenolic dimers and trimers. The objectives of the study were: (1) Synthesis of stable rGO membranes with the controlled extent of GO reduction. (2) Quantify the impact of reduction on the chemical structure of GO and membrane performance. (3) Quantify the performance of rGO membranes towards the separation of model lignin oligomers using model phenolic dimer and trimer compounds (Fig. 1). To achieve the stated goals, stable GO membranes were fabricated on a microporous polymeric substrate using a wire-wound assisted casting approach, followed by controlled thermal reduction. Reduction of GO membranes was effectively employed for tuning separation performance of GO membranes towards the separation of trimers. Selective separation of model lignin dimer and trimer compounds by rGO membranes was also investigated. This understanding would facilitate the application of rGO membranes for separation and recovery of high-value lignin-derived oligomeric compounds.

2. Materials and methods

2.1. Materials

All chemicals used in the study were of reagent grade and were used with no further purification. Graphene oxide (Trade name: Graphenea Graphene oxide 4 mg/ml) was purchased from Graphenea, Inc. Sodium hydroxide (NaOH), potassium chloride (KCl), guaiacylglycerol- β -guaiacyloether (GGE, “dimer”) and 2,6-Bis[(2-hydroxy-5-methyl phenyl) methyl]-4-methylphenol (BMP, “trimer”) were purchased from VWR. Structures of the compounds are shown in Fig. 1. The PVDF substrate used in the study was PV200 membrane with an effective pore size of 44 ± 5 nm, obtained from Nanostone-Water Inc. Water used at all stages of the experiments was purified (final resistivity < 18.2 M Ω , TOC < 1 ppb) using a Purelab flex water purifier obtained from ELGA Lab water.

2.2. Membrane synthesis

rGO membranes were synthesized by casting an aqueous solution of GO on PVDF substrate using a wire-wound rod (Fig. 2a, b). Prior to membrane synthesis, membranes were thoroughly rinsed with water and air-dried. The casting was done using a wire-wound rod

with a wet film thickness of 7.7 μm . The deposition of GO on the substrate was controlled by using a GO stock solution of 4 mg/ml, depositing an estimated amount of 30 mg GO per m^2 of the substrate. After depositing the GO solution, the membranes were air-dried. Coating cycles were repeated 6 times, depositing a net amount of 180 mg GO per m^2 of the substrate (Fig. 1c). Finally, the substrate with coated with GO was incubated in an oven for different durations at 90 $^{\circ}\text{C}$. The resulting membranes are referred to as reduced GO (rGO) membranes, henceforth.

2.3. Characterization

The surface morphology of the graphene oxide membranes was studied with scanning electron microscopy (SEM-Hitachi 4300) and Atomic Force Microscopy (AFM). Cross-section samples of the membranes were analyzed using a focused ion beam (FIB, Helios Nanolab 660). Changes in the O/C ratio and C1s binding energy of GO during thermal incubation were measured by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Al K-alpha X-ray Photoelectron Spectrometer with a photon energy of 1486.6 eV). Each XPS spectrum was an average of ten scans. Functional groups on GO were probed using Fourier Transform Infrared Spectroscopy (FTIR, Agilent Cary 630 IR). The spectra were acquired in the Attenuated Total Reflectance mode at 8 cm^{-1} resolution. Contact angle measurements were done using a drop shape analyzer equipped with a high definition camera (Kruss DSA100) by the sessile drop technique. The interlayer spacing of GO was measured using an X-ray diffractometer (SIEMENS D500 with $\text{Al-K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, at an accelerating voltage of 40 kV and a current of 20 mA). Graphene oxide dispersion was analyzed for hydrodynamic radius by dynamic light scattering (Anton Paar, Litesizer 500). Pore size and porosity of the PVDF substrate and size of GO sheets from the AFM images were obtained by processing image with ImageJ software.

2.4. Performance evaluation

The performance of the GO membranes was initially evaluated by measuring the isopropanol-water (10:90 by vol.) mixture permeability. Permeability was measured by monitoring flux for pressure gradients of up to 10 bar in a dead-end mode of operation using a stainless steel stirred pressure cell (Sterlitech HP4750). Before evaluating the performance of the membrane, the membrane was stabilized by passing pure water through it at 3.3 bar for at least 24 h. The flux of the fluid was measured by recording the mass of permeate through the RS232 output of the weighing scale at a sampling rate of 60 min^{-1} .

The separation performance of the membrane was evaluated using model lignin oligomeric compounds. During measurements, 200 ml of either trimer (BMP, 0.33) or a mixture of the dimer (GGE, 0.23 mM) and the trimer was used. Trimer was not soluble in aqueous solutions. Increasing the solution pH has been reported beneficial in increasing the solubility of lignin in water [31]. Therefore, the trimer was initially treated with 1% v/v of (1 N) NaOH-IPA mixture to solubilize it and was then diluted with water to make an IPA-water solution. Permeate and retentate were sampled at regular intervals after passing the solution through rGO membranes. Rejection tests were conducted with rGO membranes with varying extent of GO reduction. Well-mixed conditions on the feed side were maintained by mixing

the solution using a magnetic stirrer rotated at 300 rpm. Rejection of the solute was defined as:

$$R = \left(1 - \frac{C_{per}}{C_{feed}} \right) \times 100 \quad (1)$$

where C_{per} is the concentration of permeate and C_{feed} is the concentration of feed solution.

2.5. Analysis of phenolic lignin model compounds

A High-Pressure Liquid Chromatograph (HPLC) equipped with a UV detector was used to analyze the lignin model compounds. A C-18 column was used for the separation. The mobile phase comprised 65% (by volume) acetonitrile and 35% water. The column was operated at 303 K and at a mobile phase flow rate of 1.4 ml/min. A UV wavelength of 274 nm was used for the analysis. A chromatogram of one of the feed solutions consisting of dimer and trimer is shown in the Supporting Information (Fig. S5).

Size of oligomers was estimated by performing DFT calculations. DFT method was used to optimize the ground-state structures of the Trimer (BMP) and the Dimer (GGE). The initial coordinates were taken from making the structures in GaussView 5. B3LYP functional was used in the DFT calculations [32,33]. We have used the 6–31G basis set as it was found to be enough to predict reliable structure [34–38]. The optimized geometries were local minima.

3. Results and discussions

The primary goal of the study was to synthesize GO membranes for the selective separation of dimeric and trimeric lignin-derived compounds from polar organic solvent media. In this study, the extent of reduction of GO was controlled by varying the thermal incubation duration, and the influence on the separation performance was monitored. The current section discusses the characterization of GO reduced to different degrees, as well as the rGO membranes, this being followed by a discussion of the influence of GO reduction on the performance of the membranes.

3.1. Characterizations of the fabricated reduced graphene oxide membranes

Shear assisted casting of GO on the PVDF microporous substrate was employed for the synthesis of GO membranes. Average lateral dimensions of the GO sheets, as determined by AFM, was 1.7 μm with a standard deviation 0.9 μm (Fig. S1a). Dynamic light scattering showed an average hydrodynamic diameter of 1.8 μm for the GO sheets (Fig. S1b). GO forms a nematic crystalline phase, owing to the high aspect ratio of the atomically thin GO sheets with large lateral dimensions [39]. Membranes synthesized by shear aligned GO sheets have yielded high performance in the nanofiltration regime [22]. Therefore, a wire-wound assisted casting of GO was employed in the membrane synthesis, as schematically represented in Fig. 2a and b. The thickness of the GO coating on the polymeric substrate was modulated by varying the concentration of GO in its aqueous dispersion and the number of coatings. A coating of 180 mg/m^2 GO on the PVDF substrate, achieved by employing six coating cycles using 4 mg/ml aqueous GO dispersion, resulted in good separation

performance. The GO coating on the substrate was stabilized by thermal reduction of the GO. Optical images of the GO membranes after the different durations of thermal incubation are shown in Fig. 2d–h. The color of the deposited GO coating changed from light brown to gray with increasing duration of the thermal incubation.

3.2. SEM and AFM imaging

The surface morphology of the membranes was studied using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Initially, the top surface of the membrane before and after the deposition of GO was imaged using SEM and AFM. PVDF substrate used for the synthesis of GO membranes had an average pore size of 102 nm with a standard deviation of 5 nm (Fig. S2). The porosity of the substrate was found to be around 15%. No pores were observed on the surface of the GO coated substrate, indicative of a defect-free coating (Fig. 3b). The surface of the GO membranes showed the presence of wrinkles, which are typically observed for these membranes [24]. The GO membranes appeared smoother than the substrate itself. AFM was used to quantify the change. Five independent samples were used to determine the average surface roughness of the rGO membrane (SI Fig. S3). A reduction in surface roughness from 130 nm for the substrate to 78 nm for GO membranes (Fig. 3e and f).

Cross-sections of the GO membranes were imaged to study the membrane morphology and to measure the thickness of the GO coating. Membranes were fractured after immersion in liquid nitrogen for 5 min, and the cross-section samples thus prepared were imaged using SEM, as shown in Fig. 3c. A thin coat of GO was seen on the surface. However, it was difficult to accurately determine the thickness of the GO layer owing to the blunt cross-section sample. Therefore, a cross-section of the sample was prepared by milling the surface using a gallium beam and was subsequently imaged by SEM, as shown in Fig. 3d. A protective coating of platinum was deposited on the membrane to prevent damage to the surface by the gallium beam. The membrane showed a GO layer thickness of 70 nm for a GO coating of 60 mg/m².

3.2.1. ATR FT-IR spectral analysis—Changes in oxygen-containing functionalities present on graphene oxide during thermal reduction were probed using infra-red spectroscopy, as shown in Fig. 4. GO deposited on a glass substrate was used for the characterization to obtain clear, distinguishable spectra with a minimal signal from the substrate. Graphene oxide showed the presence of hydroxyl (3250–3650 cm⁻¹), carboxylic acid OH (2500–3300 cm⁻¹) carbonyl (1690–1760 cm⁻¹), carboxyl (1650–1750 cm⁻¹), C = C (1500–1600 cm⁻¹) and ether and/or epoxide (1000–1280 cm⁻¹) groups, and the spectra are consistent with the literature [27]. Changes in functionalities of graphene oxide after different durations of thermal incubation were monitored. A significant decline in peak intensity corresponding to OH stretching was observed with increasing duration of thermal incubation. A decrease in the intensity corresponding to OH stretching suggested a loss of bulk water and dehydration by the loss of OH functionalities. Peak intensity corresponding to epoxy functionalities also declined significantly during thermal incubation of graphene oxide.

GO has domains of sp^3 and sp^2 hybridized carbon atoms. Sp^3 hybridized carbon atoms contain functionalities such as hydroxyls and epoxides. GO is hygroscopic in nature and sorbs water on the oxygen-containing functionalities [40]. Thermal incubation of GO at moderate temperature ($\sim 100^\circ\text{C}$) is expected to remove the bound moisture [41]. A decrease in the intensity of the hydroxyl and epoxy functionalities was anticipated during thermal incubation [42]. However, complete removal of hydroxyl functionalities from the GO sheets is estimated to require a temperature in excess of 650°C . In a study by Jeong et al., thermal incubation of GO was able to decrease the O/C ratio of GO from 0.39 to 0.1 after 10 h of annealing at 200°C [43].

Contact angles of the rGO membranes with water were also measured to investigate the impact of the extent of reduction of GO on the hydrophilicity of the membranes. The contact angle increased from 33° (as prepared) to 79° (22 h 90°C) to 83° (164 h 90°C) indicating a decrease in the hydrophilicity with increasing thermal incubation time again confirming the increased extent of GO reduction.

3.3. XPS analysis

Elemental composition and C1s binding energy were measured for GO at various stages of reduction using XPS. A gradual decline in the O/C ratio of GO was observed after thermal incubation at 90°C , as shown in Fig. 5a. O/C ratio of the membrane declined from 0.46 for non-incubated GO to 0.25 after 164 h of thermal incubation. This decreasing trend in the GO oxygen content signifies the increasing extent of GO reduction with time of thermal incubation. Binding energies associated with C1s electrons were also determined for GO membranes at various extents of reduction (Fig. 5b–f). The C1s spectra were deconvoluted into three peaks: C–C (284.7 eV), C–O (286.8 eV) and $\text{C}=\text{O}$ (288.5 eV). A notable decline in the peak intensity associated with C–O binding energy was observed with increasing duration of thermal incubation. This suggests a loss of epoxy and hydroxyl functionalities present on the basal plane of GO, and is consistent with the literature [43].

3.4. X-ray diffraction

The magnitude of the interlayer spacing between the deposited sheets of GO is determined by electrostatic forces and π - π stacking forces. With the increasing extent of reduction, the sp^2 domain on GO is restored to some extent, reinforcing the attractive forces between the deposited GO sheets and reducing the interlayer spacing. The spacing between the deposited sheets of GO can be determined using X-ray diffraction. X-ray diffractograms of GO show a sharp peak (D001) corresponding to the interlayer spacing between the GO sheets. In this study, the shift in the D001 peak was monitored to probe the changes in the interlayer spacing (Fig. 6; individual diffractograms are shown in the Supporting Information, Fig. S8). The interlayer spacing of GO in the dry state declined from $9.3\text{ \AA}$ to $8\text{ \AA}$ after 164 h of thermal incubation at 90°C . Transport of water and solutes through GO membranes occurs through the spacing between GO sheets and the structural defects present in the nano-porous domain of GO [23,25]. The separation performance of GO is determined by its interlayer spacing, and GO membranes possessing a higher degree of reduction have shown improved separation performance owing to higher steric hindrance to the transport of molecules [28].

3.5. Pure water and isopropanol-water mixture permeability

The impact of the extent of reduction on the performance of rGO membranes was initially tested by measuring the membrane permeability. rGO membranes reduced to different degrees exhibited a linear increase in flux with increasing operating pressure gradients, as shown in SI Fig. S4. rGO membrane permeability (viscosity corrected) declined with the increasing extent of GO reduction (Fig. 7). Also, it can be noted that 10% (by vol.) IPA in water didn't significantly change the permeability of the membrane. Change in O/C ratio of Graphene Oxide is also shown in Fig. 7, which could be used to quantify the membrane permeability. Molecular transport through rGO membranes occurs through the interlayer spacing/channels. The change in flux of the rGO membranes is likely to be influenced by several factors, such as interlayer spacing of GO, the thickness of the active layer, the hydrophilicity of the membrane, and surface roughness. In the case of flow-through nanochannels, the flux of solvent is proportional to the third power of the interlayer spacing, provided the boundary conditions are the same [23]. XRD characterization showed a decline in interlayer spacing with increasing extent of reduction, which can potentially impact the thickness of the rGO layer. Also, hydrophobicity of the GO increased with the increasing extent of reduction of GO. No significant change in the surface roughness of the membrane was observed. The membranes had an average roughness of 69 nm with a standard deviation of 18 nm. The decline in the permeability of the membrane can be attributed to a combination of a decrease in interlayer spacing and increase in membrane hydrophobicity.

3.6. Impact of GO reduction on retention of trimer

The separation performance of the rGO membranes was investigated by measuring the retention of the BMP trimer. GO membranes with different degrees of reduction were used in this study. The rejection was measured in a dead-end mode of operation, and concentrations in the permeate and retentate were monitored for the different degrees of reduction (SI Fig. S6). An increasing trend in the rejection of trimer was observed with increasing extent of GO reduction (Fig. 8a). Our attempts to measure trimer rejection by air-dried GO membranes were not successful, as the membrane permeability increased dramatically under stirred conditions. Air-dried GO membranes also exhibited poor separation performance. The increase in permeability and poor separation performance of air-dried GO membranes is likely due to delamination of the deposited GO layer under stirred conditions. GO membranes after partial reduction were stable under the stirred experimental conditions and exhibited good separation performance. After 36 h of reduction, rejection of the trimer reached a maximum of 70%. Further increase in the duration of thermal incubation didn't significantly increase the retention of the trimer. The improved rejection can be attributed to the narrower pore size of the membrane. Narrower pore size increases the steric hindrance for the transport of molecules through the membranes, improving the retention performance.

For rGO membrane with 108 h of thermal incubation, retention performance was also tested using pure isopropanol as solvent. Trimer retention by the membrane dropped to less than 10% for pure isopropanol as a solvent. The finding is consistent with our earlier reported study and with the literature [16,19]. A highly polar solvent, such as water, has a strong dipole-dipole interaction with the polar functionalities present on the oxidized domain of

GO and consequently, water tends to form a stable sorbate on the oxidized domain. Formation of a stable water sorbate in the nanoporous domain of GO has been attributed to the improved selectivity of the membrane.

Performance of the membranes was also investigated over an extended duration of operations up to 84 h under a cross-flow mode of operation. Two independently synthesized rGO membranes under thermal incubation for 40 h were tested in this study for the retention of 50 ppm trimer solution at 21 °C, 10 bars pressure gradient, and 1.1 Pa shear rate. Membranes exhibited constant retention of 74% for trimer during the experiment (Fig. 8b). The flux declined during the experiment, reaching a near steady state of 14 LMH after 84 h of operation. The effect of temperature on the retention of trimer was also investigated at temperatures of 12, 21 and 30 °C. No significant change in the retention of trimer was observed, with an average retention of 30% (S. Dev: 4%). Constant retention of trimer serves as an indication of the stability of rGO membranes in a cross-flow mode of operation, which mimics a near real-world application scenario.

3.7. Membrane performance towards model lignin oligomers separation

Further tests were conducted to investigate the selective separation of model lignin oligomers from a mixture. A mixture of dimer (0.23 mM) and trimer (0.33 mM) was used as a stock feed solution to test the separation performance of rGO membranes. Fig. 9a and b show the performance of the rGO membrane (incubated for 36 h) towards the rejection of dimer and trimer with increasing recovery. The concentrations of permeate and retentate measured during the run are shown in the Supporting Information (SI Fig. S7). The membrane had a constant rejection of 70% for the trimer and 20% rejection for the dimer, exhibiting a selectivity of 3.5 (Fig. 9a). A constant rejection throughout the entire investigated range of recovery indicates the rejection is governed by steric hindrance. A charge dominated retention mechanism is sensitive to the feed concentration and is expected to decline with increasing recovery. Steric hindrance experienced during transport of molecules through the narrow pores depends on the relative dimensions of the molecule (r_i) compared to the pores (r_p). The steric partitioning coefficients (Φ) for the compounds were estimated according to Equation (2) [44].

$$\Phi_i = \left(1 - \frac{r_i}{r_p}\right)^2 \quad (2)$$

rGO membrane incubated for 36 h showed an interlayer spacing of around 0.84 nm. It is well known that GO is highly hygroscopic, and has a tendency of adsorbing up to 3–4 layers of water molecules, increasing the effective interlayer spacing. In our earlier reported research, the interlayer spacing of the GO was found to swell up to 1.2 nm, established through extensive XRD characterization and size-exclusion studies [19]. The solutes tested in this study had molecular weights of 320 and 348 g/mol for the dimer and trimer, respectively. Density function theory calculations were performed to estimate the size of the molecules. Calculations yielded a size of 0.9 and 1.3 nm for the dimer and trimer, respectively. Using the estimated sizes of the molecules and interlayer spacing of 1.4 nm (in the swollen state), the steric hindrance partitioning coefficients for the dimer and trimers are

0.13 and 0.005, respectively. The lower partitioning coefficient for the dimer compared to the trimer serves as a metric for the lower steric hindrance for the transport of the dimer. This, in turn, is hypothesized to mediate the selective separation between the investigated molecules through the rGO membrane. It is worth mentioning that GO membranes structures are reported to likely contain pinhole defect, providing an unhindered path for transport of molecules [45]. The presence of pinholes is likely to reduce the retention of molecules by rGO membranes, and thus, adversely affect the selectivity.

Fig. 9b shows the flux of the corresponding solution measured during the study. The flux of the solution declined to 33% of its initial value during the experiment. This decline in flux is likely not due to the increased osmotic pressure gradient since the solution had a very low osmotic pressure compared to the operating pressure gradient. Another major reason for the decline in the flux is membrane fouling, which is also not believed to be a cause of declining flux in this case. We believe that the decrease in flux is due to reversible changes occurring in the microstructure of the rGO membranes. The red-colored solid line in Fig. 5b shows the steady-state flux of the IPA-water mixture without any solute, which is the same (within experimental error) as the steady-state flux observed in the rejection study. GO membranes are reported to undergo reversible compaction of microstructural defects under a pressure gradient, causing a reversible decline in flux [24]. Being aware of the fact, initially, only the IPA-water mixture (without solute) was passed through the reduced GO membrane. The membrane showed a steady-state flux of 9 LMH under a pressure gradient of 6.2 bar. The fact that the same steady-state flux was observed for the solvent mixture and solution suggests the decline in flux is a result of reversible changes occurring in the microstructure of the rGO membrane.

In a comprehensive study conducted by Sultan et al., authors screened 12 commercial polymeric nanofiltration membranes for fractionation of lignin-derived products [12]. Permeability of the membranes were observed in the range of 0.012 to 0.417 LMH/bar. For lignin-derived liquor, authors observed high retention of compounds with molecular weights above 1000 Da and lower to moderate retention of compounds with a molecular weight below 1000 Da. Authors successfully demonstrated the use of a cascade of membranes with different molecular weight cutoff for the fractionation of lignin-derived products. However, lower permeability and moderate retention of lower molecular weight compounds were found limiting factors towards the implementation of the technology. Owing to the exceptional and tunable performance of rGO membranes [20], efficient fractionation of lignin-derived products can be achieved.

However, filtration of lignin-derived liquor brings several challenges which need to be considered. Additional research to evaluate the impact of other depolymerization products from lignin on the selectivity of the rGO membrane is required. Furthermore, the formation of gel layer from the lignin-derived products on the surface of the membranes is reported to increase the resistance for the flow of solvents and solutes through the membrane. The impact of the gel layer during filtration of lignin-derived liquor on solvent flux and solute retentions need further evaluation.

4. Conclusion

GO membranes were synthesized on a commercial PVDF supporting platform by casting GO solution using a wire-wound rod. Reduction of the as-synthesized GO membrane was achieved by thermally incubating the membranes at 90 °C. Solvent-water permeability is highly dependent on O/C ratio of rGO, which can be controlled by thermal incubation. High rejection of over 70% for the phenolic lignin model compound, BMP, was achieved in IPA-water solution. Conversely, only 20% rejection was achieved with another lignin model, GGE, imparting a separation factor of 3.5. rGO membranes exhibited a stable performance for filtration conducted over 84 h at 1.1 Pa shear rate in a cross-flow mode of operation. Considering the neutral charges and molecule size of the model compounds used, we suggest that steric hindrance plays a crucial role in the excellent molecular rejection and separation performance of our membranes. We have also demonstrated the controlled reduction of GO membranes by varying thermal incubation time and investigated the influence of reduction degree on the structural changes (by O/C ratio) and rejection performance of the reduced GO membranes. The retention of trimer increased with the increasing extent of GO reduction. The increase in retention of trimer by the membrane was attributed to the higher steric hindrance to the transport of molecules by reduced GO membranes. This work gives more understanding of the possible impact of the extent of GO reduction towards the separation performance of rGO membranes. Finally, the impressive performance of the reduced GO membrane along with its improved stability compared to non-reduced GO membrane indicates its potential for industrial applications ranging from pharmaceutical area to the concentration of value-added chemicals.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations:

GO	graphene oxide
PVDF	polyvinylidene difluoride
GGE	guaiacylglycerol- β -guaiacyl ether
BMP	2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol
LMH	liter/m ² h
DIUF water	deionized ultrafiltered water

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Fig. 1.

The phenolic model compounds used in this study. Dimer: Guaiacylglycerol- β -guaiacylether (GGE), Trimer: 2,6-Bis[(2-hydroxy-5-methyl phenyl)methyl]-4-methylphenol (BMP).

Fig. 2. Schematic representation of rGO membrane synthesis by wire-wound rod (a, b) and optical image of air-dried GO membrane sample (c). Figures d, e, f, g, and h show the optical images of rGO membranes after different durations of thermal incubation.

Fig. 3. Surface and cross-section morphology of reduced Graphene Oxide membranes (60 mg/m^2). (a) Scanning Electron Microscopic image of polyvinylidene substrate (PV200 Nanostone Water Inc.) and (b) after coating GO on the membrane surface. (c and d) Cross-section of reduced Graphene Oxide membranes. (e and f) Surface morphology of substrate before and after the coating of graphene oxide determined using Atomic Force Microscopy.

Fig. 4. Fourier Transform Infrared spectra of reduced graphene oxide at various time intervals during thermal incubation at 90 °C.

Fig. 5. Change in oxygen content and C1s binding energy of reduced Graphene Oxide after different durations of thermal incubation at 90 °C as determined by X-ray photoelectron spectroscopy. Figure a shows the change in O/C ratio. Figures b, c, d, e and f show the change in C1s binding energy after thermal incubation for 0, 3, 22, 55 and 164 h, respectively.

Fig. 6.

Interlayer spacing of reduced Graphene Oxide laminates with varying degrees of reduction determined by X-ray diffraction. The extent of Graphene Oxide reduction was controlled by the duration (X-axis) of thermal incubation at 90 °C. Detailed spectra are provided in the supplementary information.

Fig. 7.

Comparison of water and isopropanol-water (10% v/v) mixture permeability (Viscosity corrected) of the reduced Graphene Oxide membranes with extent of Graphene Oxide reduction. The latter was controlled by the duration (X-axis) of thermal incubation at 90 °C. Reduced Graphene Oxide loading on substrate=300 mg dry GO/m². Membrane area=13.2 cm². T=22 °C, pH=6.2.

Fig. 8.

Retention of model lignin trimer (BMP) by reduced Graphene Oxide membranes (a) with different degrees of Graphene Oxide reduction. The extent of reduction was modulated by controlling the duration of thermal incubation (x-axis) at 90 °C. Retention was measured with 3.3 mM solution of trimer in IPA-water mixture (10:90), operated at 10 LMH permeate flux. (b) performance of rGO membranes (40 hrs, 90 °C) over an extended duration of operation under cross-flow mode. Rejection of 50 ppm trimer was measured to assess the stability of the membrane. Operating temperature: 21 °C, Pressure: 10 bars, shear rate: 1.1 Pa.

Fig. 9. Separation performance of the Graphene Oxide membrane evaluated using model lignin dimer and trimer. (a) Comparison of the rejection of the model dimer (GGE) and trimer (BMP) as a function of permeate recovery; (b) Permeate flux as a function of permeate recovery during a standard rejection run. Membrane area = 13.2 cm², GO content = 180 mg/m², T = 22 °C, pH = 8.7, Transmembrane Pressure: 6.2 bar.