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Surfactant modified graphene oxide laminates for filtration

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ABSTRACT

We have used a cationic surfactant cetyltrimethylammonium bromide (C16TAB) to increase the interlayer spacing between laminates in graphene oxide (GO) membranes for higher water flux. The addition of C16TAB to the GO membrane increased the permeability without compromising the ability to completely reject sucrose molecules. Species larger than sucrose can still permeate through modified GO membranes nearly with same rate as in the case of pure GO membranes. We speculate that interaction of C16TAB surfactant with sucrose molecules could be responsible for the selective rejection of sucrose. The selective rejection of sucrose, which is a common draw in forward osmosis (FO) process, suggests that surfactant modified GO membranes have the potential to improve the efficiency of the FO process.

1. Introduction

It is well-known that pristine graphene, which is a monoatomic layer of carbon atoms, is impermeable to any gases or solutions [1], while graphene oxide has recently shown huge potential for applications in filtration technology [2–14]. In the laminated form, graphene oxide layers are stacked together with an interlayer distance of ~0.86 nm, which is the path of mass transport when using it as a filtration membrane [15,16]. As the crystalline structure can be affected by water partial pressure, the interlayer spacing in graphene oxide expands to ~1.1 nm on hydration, resulting into an unimpeded flow of water [17]. It has been demonstrated that GO membrane shows fast transport of water molecules through nanocapillaries between the graphene layers separated by functional groups attached to graphene [1,18]. The permeability for GO based membranes is inversely proportional to the number of GO laminates or the membrane thickness, due to the increasing length of mean free path for water molecule, while salt rejection decreases proportionally with GO membrane thickness [19–23]. It has also been predicted by molecular dynamic simulation that interlayer spacing between GO laminates plays a crucial role in terms of water mobility and separation efficiency [21]. The expansion of interlayer spacing between GO laminates will increase water permeability, due to the decrease of interfacial slip effect.

By modifying the interlayer distance in GO laminates, we have provided a tailored path for water transport incorporating surfactant molecules between the two adjacent laminate layers in the GO membranes. This idea was backed-up with existing reports [24] suggesting that the structure and chemical properties of GO can be tuned by the addition of surfactants [25–27]. Surfactants, such as sodium cholate, dimethylaminoethyl methacrylate and polyamine, have been incorporated to GO laminates to enhance stabilization and fouling resistance respectively [28–30]. Recently, Jia et al. modified GO based membrane with dicarboxylic acids, diols and polyols via esterification reactions [22]. Although an adjustable interlayer spacing was achieved, the expansion of d spacing was still limited to less than 1.5 nm. Zambare et al. also functionalized GO membrane with polyamines to enhance its hydrophilicity for increasing water permeability and fouling resistance [31]. However, the effect of surfactant on membrane rejection and water flux was not studied explicitly in the past.

In this study, a cationic surfactant cetyltrimethylammonium bromide (C16TAB) was incorporated between GO sheets of the laminated membrane and the resulting material was tested as

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filtration membrane. The nanofiltration characteristics and water flux performance of the composite membrane were investigated and the role of C16TAB surfactants has been discussed. The characteristics of the modified GO membrane such as interlayer spacing and composition were also analyzed and discussed.

2. Experimental

Graphene oxide was synthesized by oxidizing natural graphite flakes using a modified Hummers' method with $KMnO_4$ to graphite ratio of 3 by weight [32]. The graphite oxide was exfoliated into monolayer flakes by sonication, followed by centrifugation to separate the monolayer graphene oxide. GO membranes were prepared by vacuum filtration of GO suspension in water through Millipore PVDF membrane with 0.22 μm pore size [15]. Modified GO (surfactant added) membranes were prepared using a similar method. However, prior to vacuum filtration, appropriate quantity of C16TAB was dispersed in the GO suspension, and the resulting material was filtered on a polymer based membrane template to obtain a GO laminated structure containing C16TAB (C16TAB-GO) with thickness of around 1 μm. Same amount of GO was used to prepare both (GO and C16TAB-GO) membranes with approximately 1 μm thickness and 2 cm in diameter.

Two experimental set-ups were conducted as shown in Fig. 1. A U-tube type module was used to test the permeation of solute species through graphene oxide membrane (Fig. 1a). In this setup, one side of the tube was filled with deionized water (permeate) while the other side was filled with aqueous solution of salts (feed). The driving force for solute species transporting through membrane is the concentration gradient, and to make sure water is only driven by osmotic pressure, the liquid level of feed and permeate was maintained equal constantly. Appropriate quantity (~10 ml) was taken out from feed and permeate compartments at regular intervals for quantitative chemical analysis. The GO membrane was also tested in a vacuum filtration setup shown in Fig. 1b. A vacuum pump (pressure ~0.5 bar) was used to provide hydraulic pressure as driving force for the water flow. The permeation rate was analyzed by in-situ measurement of the change in filtrate mass.

Water permeation rate was only measured for vacuum filtration (Fig. 1b), not the U-type module, due to the constant osmotic pressure changes induced by dilution. The solute permeates from set-up (a) and (b) were both quantitatively analyzed for solute passage. Ion chromatography was used for quantitate chemical analysis of anions, Inductively coupled plasma (ICP) mass spectrometry (SHIMADZU AA-6300) for cations, optical absorption spectroscopy (qualitative) for larger ions such as $(PTS)^{4-}$ of *pyrenetetrasulfonic acid tetrasodium salt* and $[Ru(bpy)_3]^{2+}$ of *Tris(bipyridine)ruthenium(II) dichloride*, and total organic carbon analysis for quantitative analysis organic molecules present in feed and permeate.

All membranes were hydrated from both sides using de-ionized water prior to the filtration experiment to ensure wide open interlayers across GO membranes. The chemical properties of the GO and the GO-C16TAB were characterized prior to the testing using Carbon–Hydrogen–Nitrogen (CHN) elemental analyzer (PERKINELMER 2400II) and energy-dispersive X-ray (EDX) spectroscopy respectively. The crystalline structure of GO and GO-C16TAB membranes was analyzed by X-ray diffraction (XRD) using Cu Kα radiation ($\lambda = 1.541$ Å) in the 2θ range of 2.0–75° with step size of 0.017° to measure the interlayer distance for both membranes. The operating tube current and voltage were 45 mA and 40 kV, respectively.

3. Results and discussion

Surfactant modified graphene oxide membranes were analyzed to understand the chemical composition using the techniques discussed above. According to our Energy Dispersive X-ray (EDAX) and Carbon–Hydrogen–Nitrogen (CHN) analysis of surfactant modified GO membranes, the weight percentage value for **c**arbon (C), **h**ydrogen (H), **n**itrogen (N) and **b**romine (Br) were 60.6%, 6.9%, 2.0% and 1.3% respectively. Using these measured values of C,H, N and the C to N ratio of 19:1 for surfactant (C16TAB) the C weight percent for surfactant was estimated as 31.9% while the remaining 28.7% (of total 60.6%) carbon is for graphene oxide.

These results suggested that the surfactant molecules were densely arranged in between two GO laminates to an extent that carbon content from surfactant is more than the carbon from the GO itself. Moreover, fourier transform infrared spectroscopy (FTIR) (Fig. 2) results indicate no existence of chemical bonding between

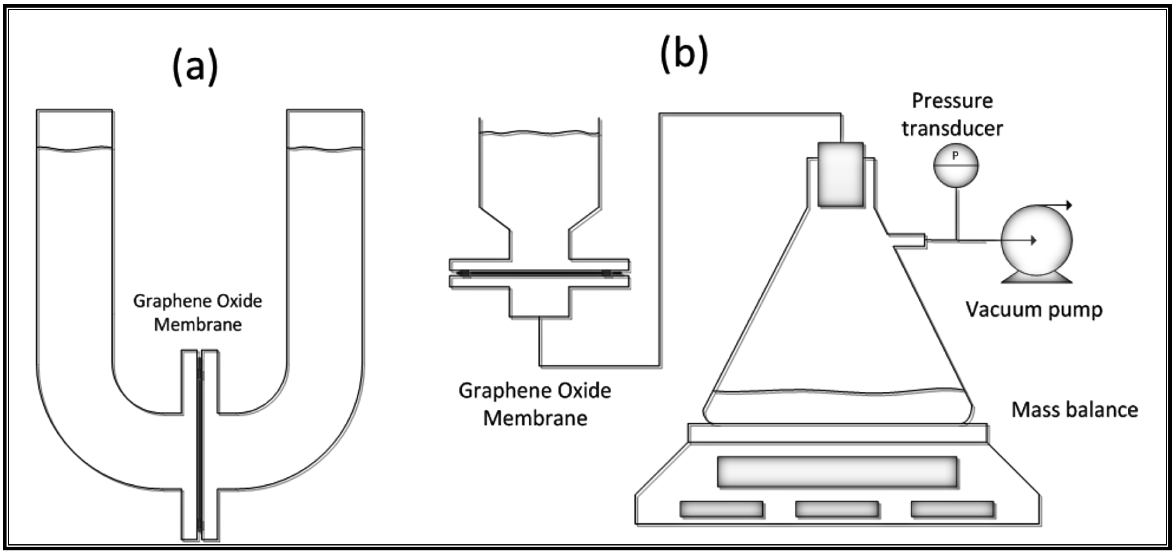

Fig. 1. Schematic of the experimental set-up used to test membrane performance: (a) for quantitative analysis of ionic and molecular permeation through GO based membrane and (b) for realizing practical method for water flux measurement.