



Enhanced organophilic separations with mixed matrix membranes of polymers of intrinsic microporosity and graphene-like fillers



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ABSTRACT

Organophilic mixed matrix membranes (MMMs) have been fabricated with the polymer of intrinsic microporosity PIM-1 and graphene oxide (GO) derivatives for the recovery of 1-butanol and ethanol from aqueous solutions via pervaporation (PV). Graphene oxide (GO) has been synthesized in solution through a modified Hummers' method, functionalized with alkylamines, and further reduced. The use of two alkylamines with chains of different lengths, octylamine (OA) and octadecylamine (ODA) –8 and 18 carbons, respectively - has been evaluated and the functionalized GO materials have been used as fillers in MMMs. The membranes have been prepared by casting-solvent evaporation of PIM-1/GO derivative solutions at room temperature, and a range of characterization techniques have been used to interpret their structure and relate it to their separation performance. Electron microscopy has been carried out to determine the morphology of the membranes and the dispersion of the functionalized GO flakes in the polymer matrix. Moreover, the membranes have been characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and contact angle. Separation of alcohol from two binary mixtures composed of ethanol (EtOH)/water and butanol (BtOH)/water, containing 5 wt% of alcohol, have been performed. Under these conditions, the incorporation of graphene-like fillers at relatively low concentrations shows an increase in average separation factor for butanol ($\beta_{\text{BtOH}/\text{H}_2\text{O}}$) from 13.5 for pure PIM-1 membranes to, in some cases, more than double for the MMMs; with the addition of 0.1 wt% of reduced amine-functionalized GO $\beta_{\text{BtOH}/\text{H}_2\text{O}}$ reaches 32.9 and 26.9 for the short-chain (OA) and the long-chain (ODA) alkylamines, respectively.

1. Introduction

Over the last few decades, global concern on climate change has led to a growth of public environmental awareness of the need to reduce greenhouse gases. In this context the scientific community is exploring alternative sustainable energy sources, such as biofuels, to replace conventional fossil fuels in sectors such as transportation. Bioethanol and biobutanol are particularly interesting although the latter, with higher energy density, lower volatility and lower flammability, is expected to attract greater attention [1,2]. Butanol and ethanol can be produced from biomass through the acetone-butanol-ethanol (ABE) fermentation process, typically at an average weight ratio of 3:6:1, respectively [3]. However, production costs are extremely high due to the amount of energy required to recover the alcohol from the broth.

The fermentation process leads to a concentration of less than 2% of bioalcohol that is typically purified by a series of conventional distillation columns; 60–80% of the operating costs of the whole biofuel production come just from the purification steps [5]. End-product inhibition caused by the alcohol toxicity on bacteria during the fermentation alongside the required aforementioned high energy-intensive separation processes are still critical issues that hinder a more rapid implementation of this technology. In order to solve this drawback an alternative approach to distillation where membranes can selectively recover the alcohol from the broth in situ has been proposed in recent years. This on-line alcohol separation process can be done via pervaporation (PV) and is mainly based on the affinity of the membranes for alcohol over water by preferential sorption, diffusion and desorption. PV is a reasonable alternative to distillation in terms of

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economic viability; the alcohol is the component that preferentially permeates through the membrane and is present at low concentration in the feed side of the membrane. However, a major limitation with regards to the butanol recovery via PV is the lack of membranes with higher butanol selectivity, higher permeation fluxes, and better thermal stability [4]. Vane published a review on PV for the recovery of biofuels from fermentation processes where energy efficiency, capital cost, integration design with the fermentor, and further purification of the biofuel (dehydration) via PV is discussed in detail [5].

Research on butanol and ethanol recovery via PV has focused on the use of organophilic membranes, including polydimethylsiloxane (PDMS) [1,6–8], poly[1-(trimethylsilyl)-1-propyne] (PTMSP) [9], polyether block amide (PEBA) [2,10], polytetrafluoroethylene (PTFE) [11], and mixed matrix membranes (MMMs) prepared with some of these polymers and a range of fillers [2,4,12–16]. A good number of materials have been proven to be promising fillers for the preparation of MMMs for alcohol recovery. For instance, the addition of metal organic frameworks (MOFs) within the polymer matrix aims to improve the overall performance of the membranes by reducing the swelling degree of the polymeric matrix as well as to favour the transport of a preferential compound through the membrane due to preferential sorption and diffusion [17]. However, improvements have been achieved for relatively high loadings of fillers, and compatibility between the inorganic filler and the organic phase, chain rigidification and pore obstruction are still critical issues limiting the preparation of defect-free membranes [13,15]. Other fillers including zeolitic imidazolate frameworks (ZIFs) (ZIF-90 [18], ZIF-71 [13], ZIF-7 [15]), zeolites (ZSM-5 [2,19], silicalite-1 [1,16]), and carbon nanotubes [4,20] have been used.

Furthermore, layered nanomaterials have been attracting attention over the past years in a number of membrane-based separations, due to their high aspect ratio, small thickness and high specific surface area [21,22]. Some layered nanomaterials used in the fabrication of MMMs include layered aluminophosphate (AIPO) [23], crystalline layered silicate AMH-3 [24], titanosilicate JDF-L1 [21], layered zeolite Nu-6(2) [25], and copper 1,4-benzenedicarboxylate (Cu BDC) MOF [26], and have likely paved the way for graphene use in this area. Since the discovery of graphene in 2003 by Novoselo, et al. [27], graphene became one of the most attractive 2D materials for multiple applications, with its chemical derivative graphene oxide (GO) revolutionising membrane-based separation processes. Cohen-Tanugi and Grossman demonstrated theoretically that a single-layer graphene membrane could be used for desalination purposes [28]. Moreover, Nair et al. showed experimentally that a defect-free GO membrane is permeable to water vapour, whereas it blocks the permeation of all gases including helium [29]. In addition, graphene and GO have been incorporated into polymers forming MMMs for various applications including gas separation [30–33] pervaporation (dehydration of isopropanol and ethanol) [34,35] and desalination [36,37].

A new class of polymers, so-called polymers of intrinsic microporosity (PIMs), have attracted widespread interest in fields such as gas separation [38–41], hydrogen storage [42], organic solvent filtration [43,44], and pervaporation [45–47]. PIM-1 is an organophilic polymer with intrinsic microporosity that is selective towards organic compounds. It is formed by a sequence of rings along its backbone and a spirocentre (i.e., a single tetrahedral C atom shared by two rings) which makes the chain twist and turn, resulting in a randomly contorted structure with limited rotational freedom; high free volume is created as a result of the poor molecular packing, which leads to higher permeability values as compared to conventional glassy polymers used for molecular separations [42]. Despite being a promising material, PIM-1 suffers from physical ageing which compromises its long-term stability [46]. Previous reports have shown that physical aging in glassy polymers is dependent on the membrane thickness, being much more rapid in thin films than in thicker films [48–50]. Moreover, PIM-1 polymer suffers from excessive swelling in the presence of alcohols

which can limit its performance in PV and organic solvent nanofiltration (OSN) [44].

A wide range of fillers have also been used in combination with PIMs to improve their separation performance including silicalite 1 [51], silica nanoparticles [40,52,53], MOFs [39,54,55], carbon nanotubes [56] and few-layered graphene [57]. A theoretical study reported by Gonciaruk et al. [58] shows that the incorporation of graphene into PIM-1 affects the packing and can potentially prevent the swelling of the membrane, hence enhancing its performance. This improvement might be due to the parallel alignment of the PIM-1 chain fragments with the graphene sheets that lead to a decrease in their mobility and therefore to a decrease in swelling. The same study also predicts a good interfacial compatibility between the polymer and graphene sheets, which in turn might facilitate the dispersion of graphene in the polymeric solution. Consequently, driven by these results, in this experimental work a range of graphene oxide (GO) derivatives have been incorporated into PIM-1 membranes to study their performance for ethanol and butanol separation from aqueous solutions via pervaporation. In order to obtain a homogeneous and well dispersed phase in the polymer matrix, exfoliated GO flakes have been alkylamine-functionalized and further reduced. The effect of loading and length of alkylamine chains on the membrane morphology, wettability and separation performance have been examined.

2. Experimental

2.1. Materials

Graphite was purchased from NGS Naturegraphit GmbH (Germany). N,N-dimethyl formamide (DMAc), tetrafluoroterephthalonitrile (TFTPN), sulphuric acid, 1-butanol, ethanol, octadecylamine (ODA), octylamine (OA), dichloromethane (DCM) and chloroform were purchased from Sigma Aldrich (UK). Potassium permanganate and 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) were acquired from Aesar (UK). Ammonia was procured from Acros Organics (United Kingdom). TTSBI was dissolved in methanol and precipitated in DCM before use. TFTPN was purified through sublimation at 150 °C and then collected without vacuum. All the other chemicals were used as obtained without any purification.

2.2. Preparation of graphene-based materials

2.2.1. Graphene oxide (GO)

GO was prepared through the modified Hummers' method described by Rourke et al. [59]. In summary, potassium nitrate, KNO₃, (4.5 g) was dissolved in concentrated sulphuric acid, H₂SO₄, (169 mL). Natural flake graphite (5 g) was added under continuous stirring for 2 h. The mixture was cooled down and kept cold by means of an ice bath while 22.5 g potassium permanganate, KMnO₄, was added over 70 min. The mixture was left to stir for 3 days and was left thereafter for 4 more days without stirring. After that, 550 mL 5 wt% H₂SO₄ in water was added in approximately 1 h and left to stir for 3 more hours. Hydrogen peroxide (15 g, 30% vol.) was added drop by drop with considerable effervescence and stirred for 24 h. 550 mL of 3 wt% H₂SO₄/0.5 wt% H₂O₂ was added and the mixture was stirred for 3 days. The previous mixture was further centrifuged at 8000 rpm for 20 min and the supernatant was discarded. The pellet, a thick dark yellow liquid, was then dispersed with 500 mL of 3 wt% H₂SO₄/0.5 wt% H₂O₂ and shaken in order to fully disperse the pellets. This last step was repeated twelve times until a characteristic glittery colour was not visible. After that, the mixture was washed 5 times with DI water –500 mL of DI water was added in each washing cycle. GO was further dried under vacuum at room temperature.

2.2.2. Alkylamine-functionalized graphene oxide

Alkylamine-functionalized graphene oxides were synthesized based

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