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Polyamine functionalized graphene oxide polysulfone mixed matrix membranes with improved hydrophilicity and anti-fouling properties

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HIGHLIGHTS

- Graphene oxide covalently functionalized with polyamines to obtain fGO
- fGO blended in polysulfone lowers water contact angle of the membranes.
- 3-Fold higher flux without significant change in BSA rejection in fGO membranes
- Over 90% flux recovery after BSA filtration on simple flushing
- Over 15% higher tensile strength obtained for fGO membranes

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ABSTRACT

Polyamine functionalized graphene oxide (fGO) based polysulfone mixed matrix membranes with enhanced hydrophilicity, permeability and antifouling properties were synthesized. The effect of chain length of the amine in fGO on the performance of the mixed matrix polysulfone membranes was studied using three different polyamines, ethylenediamine, diethylenetriamine, and triethylenetetramine. Synthesized membranes were characterized for water contact angle, tensile strength, SEM, AFM, EDS, overall porosity, water permeability, fouling resistance, etc. fGO based polysulfone membranes showed higher porosity and permeability, improved structural and mechanical properties, and better anti-fouling potential with high flux recovery after bovine serum albumin (BSA) filtration with little change in BSA rejection. Polysulfone membranes containing 1 wt.% ethylenediamine functionalized graphene oxide and 5 wt.% polyethylene glycol (PEG-600) additives, displayed remarkably high pure water flux of 170.5 LMH/bar, a 3-fold increase over corresponding control membrane, in addition to substantially higher BSA rejection and higher normalized recovered flux after fouling.

1. Introduction

Polysulfone membranes are widely used for ultrafiltration due to their superior thermal and mechanical properties and chemical resistance. However, polysulfone membranes are susceptible to fouling, especially due to proteins, which is a major factor limiting membrane performance during applications such as concentration of proteins and cell/protein separations. Fouling in ultrafiltration is due to the adsorption of colloidal particles and dissolved solids on the membrane surface and inside the membrane pores, which results in pore narrowing, pore blocking and cake formation [1–3]. Membrane smoothness, hydrophilicity, hydrogen bonding, van der Waals forces between solute and membrane surface, and electrostatic interactions due to the surface charge on solute and membrane surface are important factors affecting protein fouling in membranes [4–6]. Membrane fouling can be reduced by increasing hydrophilicity of the membrane surface and pores, resulting in strong attraction between the water molecules and the membrane surface forming a protective water layer, preventing the adhesion of foulants [7]. Smooth surface also decreases the deposition of foulants in the troughs on the membrane surface, improving fouling resistance [8]. Viscosity of the polymer solution and casting shear rate influence the smoothness of membrane surface. Higher viscosity polymer solution hinders de-mixing of solvent and non-solvent, inducing the formation of smaller surface pores giving a smoother surface and improving fouling resistance [9,10]. Surface chemistry of the membranes also plays a significant role in decreasing the fouling potential. Membranes have been modified using several methods such as chemical functionalization of polymers, blending additives, antifouling coatings, surface grafting, and surface modification to enhance membrane hydrophilicity and antifouling properties [3,7,11–15].

Improvement in the membrane performance and protein fouling resistance has been reported in the mixed matrix membranes synthesized

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by incorporating inorganic nanoparticles and carbon based nanomaterials in the polymer dope solution and has been reviewed recently [16]. Graphene and graphene oxide (GO) are versatile materials and have found applications due to their great mechanical stiffness, good electronic properties, high thermal conductivity, biocompatibility, and high specific surface area. GO biocompatibility towards enzymes has been mixed. Good biocompatibility has been reported for glucose oxidase, but a decrease in activity was observed for catalase enzymes [17,18], while, PEGylated GO has been, in fact, found to enhance the stability of trypsin [19]. GO-polyetherimide membranes exhibited enhanced biocompatibility during in vitro blood dialysis [20]. GO-BSA adsorption studies indicated that GO showed low affinity towards BSA adsorption [21]. Graphene based mixed matrix membranes showed higher permeance and better selectivity for water desalination [22]. GO is a partially oxidized form of intercalated graphite having covalently attached oxygen-containing functional groups such as hydroxyl, epoxy and carboxyl [23–25]. Oxygen-containing functional groups present on GO led to enhanced hydrophilicity, improved thermal and mechanical properties and salt rejection in polysulfone membranes [26,27]. Blending GO in polysulfone solutions has been demonstrated to increase rate of exchange of solvent and non-solvent during phase inversion. This results in the formation of larger pores as well as changes in sub-layer of membranes giving smooth surface and relatively uniform pores [27]. GO-polysulfone composite membranes have been reported for waste water treatment with higher dye removal capacity and for separation of powdered milk solution giving better antifouling properties [10,28]. Performance of the membranes with GO additives, however, was found to be critically dependent on homogeneous dispersion of GO in the membrane matrix [27,29].

The presence of large number of oxygen-containing functional groups on surface of GO offers reactive sites, which enable facile functionalization of GO. Isocyanate functionalized GO showed improved hydrophilicity in polysulfone ultrafiltration membranes and good fouling resistance compared to unmodified GO membranes [8]. Incorporation of amine-functionalized GO in polyimide membranes improved selectivity for CO_2 for gas separations [30], while polyethylenimine modified polyamide reverse osmosis membrane showed high antifouling property against positively charged foulants [31].

Herein, we report a promising strategy for improving hydrophilicity, mechanical strength and fouling resistance by blending of amine-functionalized graphene oxide (fGO) in polysulfone mixed matrix membranes. Three different types of amine-functionalized GO were synthesized by the coupling of ethylenediamine (EDA), diethylenetriamine (DETA), and triethylenetetramine (TETA) on carboxylic groups in GO. Membranes were synthesized in absence and in presence of pore-forming agent, polyethylene glycol (PEG-600), and characterized for structural and permeability properties. Amine functionalization of GO increases the dipolar character of the nanoparticles which alters the kinetics of phase inversion of fGO/polysulfone solutions. Synthesized membranes exhibit improved transport, rejection and fouling properties. Investigation of antifouling properties of membranes was carried out using bovine serum albumin (BSA) as a foulant.

2. Experimental

2.1. Materials

Polysulfone (Udel 1700, Solvay Chemicals) was used as the membrane material. N-methyl-2-pyrrolidone (NMP, SD Fine Chemicals, Mumbai) was used as solvent to prepare the casting solution. Natural graphite powder, (325 mesh, Alfa Aesar) was used for the synthesis of graphene oxide (GO). Nitric acid (HNO_3), sulfuric acid (H_2SO_4), and potassium permanganate ($KMnO_4$), purchased from SD Fine Chemicals, Mumbai, were used to oxidize natural graphite to graphene oxide for exfoliation. Ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), 1-ethyl-3,(3-dimethylaminopropyl) carbodiimide (EDCI), N-hydroxysuccinimide (NHS) and dimethyl formamide (DMF) (SD Fine Chemicals, Mumbai) were used for amine functionalization of graphene oxide (fGO). Poly(ethyleneglycol) (PEG-600, average molecular weight of 600 g/mol, SD Fine Chemicals, Mumbai) was used as pore forming agent. 1000 ppm solution of BSA (molecular weight: 66 kDa, HiMedia, Mumbai), used in anti-fouling studies, was made in phosphate buffer saline (PBS, pH = 7.4) solution. Deionized (DI) water was used as non-solvent for coagulation bath, for flushing, etc.

2.2. Synthesis and functionalization of GO

GO was synthesized according to modified Hummers method [23,32]. Amine functionalization of GO was performed by coupling of either ethylenediamine, diethylenetriamine, triethylenetetramine to the carboxyl groups of GO using EDCI and NHS as coupling agents [33]. 30 mg GO was dispersed in 50 mL DMF under ultrasonication for 1.5 h and the solution was cooled to 0 °C. Further 6 mmol of EDCI and 6 mmol NHS were added and the mixture was stirred for next 3 h at 0 °C. The mixture was then allowed to reach room temperature. 12 mmol of amine was added dropwise to the reaction mixture under constant stirring. fGO separated from the reaction mixture by vacuum filtration, was washed first with DI water and then with acetone, and was subsequently dried at room temperature under vacuum. Various amine functionalized GO that were synthesized are listed in Table 1.

2.3. Membrane synthesis

Asymmetric fGO-polysulfone membranes were synthesized using wet phase inversion method. Membrane solutions were prepared using polysulfone (15 wt.%) in NMP, PEG-600 and GO/GO-EDA/GO-DETA/GO-TETA as additives. Composition of various membranes cast is shown in Table 2. GO/fGO was initially dispersed in NMP under sonication at 30 °C to prepare the casting solution. Polysulfone was then dissolved in GO-NMP solution at 60 °C under continuous stirring until homogeneous solution was obtained. Entrapped air bubbles were removed by sonication of polymer solution prior to the membranes synthesis. The membranes were cast on a glass plate with a film applicator. The film was kept undisturbed for 10 s, after which the glass plate along with the film was immersed in DI water coagulation bath at room temperature for phase inversion. Due to the rapid mixing of anti-solvent (water) and solvent (NMP), polymer precipitated to give finely porous asymmetric polysulfone membrane. After 30 min, membranes were transferred to another water bath containing DI water and left undisturbed for 24 h to ensure complete phase inversion. The membranes were stored in DI water at room temperature until use.

2.4. Characterization of GO and amine-functionalized GO

X-ray diffractometer (XRD) (D8 ADVANCE, Bruker) was used to identify the stacking in GO and fGO. The presence of amide linkages on fGO was determined using Fourier Transform Infrared Spectroscopy (FT-IR, Spectrum BX, Perkin Elmer). The extent of amination of GO was estimated from nitrogen content obtained by elemental analysis (FLASH EA 1112, Thermo-Finnigan). The surface charge of dispersion of GO and fGO water (10 ppm) was estimated using zeta potential measurements and the average particle size of GO and fGO was measured by dynamic light scattering (DLS, Nano ZS90, Malvern Instruments). Zeta potential and average particle size measurements were repeated three times for each synthesized GO/fGO and average of three different synthesized GO/fGO samples is reported.

2.5. Characterization of membranes

Rheological characteristics of the membrane dope solutions were analysed using rheometer (Physica MCR 101, Anton Paar). The relationship of viscosity and shear rate for each casting solution was obtained at

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