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Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates

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ABSTRACT

A novel polyethersulfone (PES) mixed matrix nanofiltration membrane containing graphene oxide (GO) nanoplates was prepared via the phase inversion method. The effect of the embedded nanosheet on the morphology and performance of the fabricated new membranes was investigated in terms of pure water flux, dye removal and fouling parameters. Scanning electron microscopy (SEM), atomic force microscopy (AFM), water contact angle and porosity measurements were employed to characterize the prepared membranes. FT-IR spectra of the graphene oxide nanoplates revealed that the hydroxyl and carboxylic acid groups are formed on the surface of the graphene oxide. The water flux from the nanocomposite membranes improved significantly after addition of graphene oxide to the casting solution, due to the higher hydrophilicity of the prepared membranes. The water contact angle measurement confirmed the increased hydrophilicity of the modified membranes. The morphology studies by SEM showed the wider finger-like pores of the GO incorporated membranes in comparison with those of the unfilled PES membrane. Evaluation of the nanofiltration performance was performed by investigating the retention of Direct Red 16. It was observed that the GO membranes have higher dye removal capacity than the unfilled PES. Fouling resistance of the membranes assessed by powder milk solution filtration revealed that 0.5 wt% GO membrane had the best antibiofouling property. In addition, the results showed that the 0.5 wt% GO membrane had the highest mean pore radius, porosity, and water flux. The prepared GO nanocomposite membrane showed noteworthy reusability during filtration.

1. Introduction

After successful isolation of graphene into the free standing form in 2004, i.e. a single 2D carbon sheet with one-atom-layer-thick and the same structure as the individual layers in graphite [1], research in this field has become more attracting for scientific community. This is due to its unique two-dimensional structure, large specific surface area, good mechanical properties, high transparency, etc [2,3].

Application of graphene and its derivatives such as graphene oxide in the preparation of membranes can be designed from two aspects. The first one is direct use of graphene as a separating layer [4–7] and second one is incorporating graphene in polymer matrix for improving the membrane performance [8–10]. The selective properties of nanoporous graphene membranes have been considered in literature. The investigations show that the nanoporous graphene films can be employed for selective separation of various gases [4] and ions [5] through design of various nanopores with different shapes, sizes, and chemical functionalities. Han et al. [6] presented a procedure for fabrication of ultrathin (≈22–53 nm thick) graphene nanofiltration membranes (uGNMs) on microporous substrates (polymeric microfiltration membranes). They used chemically converted graphene (CCG) for efficient water purification. In another study, Sun et al. [7] fabricated free standing graphene oxide (GO) membranes by a simple drop-casting method. The GO colloidal suspension was drop-cast onto a piece of smooth paper, allowed to dry in air at room temperature and consequently peeled from the underlying paper. The resulted NF membranes showed that sodium salts could be effectively separated from copper salts and organic contaminants.

When graphene is appropriately incorporated into a polymer [11,12] or ceramic [13] matrices, the special properties of obtained nanocomposites improves remarkably. Polymeric nanocomposites of graphene derivatives have been used in the preparation of different membranes for fuel cell exchange membrane [8,9], ultrafiltration [10,14,15], nanofiltration [16,17], pervaporation [16] and gas separation [18] applications.

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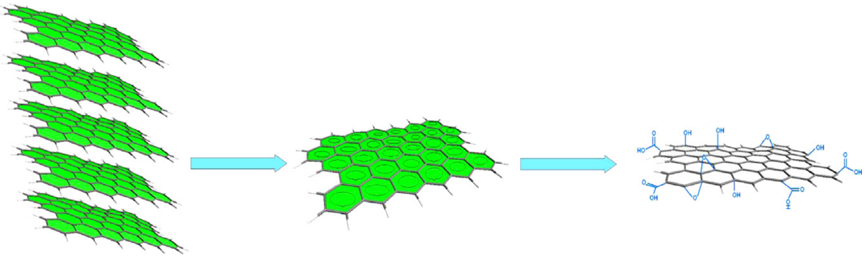

Fig. 1. The schematic of graphene oxide preparation.

Zhang et al. [14] prepared polyvinylidene fluoride (PVDF)–graphene oxide composite ultrafiltration membranes using the phase inversion method. The prepared composite membranes exhibited a bigger mean pore size and higher roughness parameters compared with pristine membranes. Moreover, they demonstrated an impressive prospect for the anti-irreversible fouling performance in multi-cycle operations from bovine serum albumin (BSA) treatment. Wang et al. [15] described fabrication of PVDF/GO organic–inorganic-blended ultrafiltration membranes. Due to the hydrophilic nature of GO, the resulted membranes appeared to be more hydrophilic and have higher pure water fluxes recovery ratio. GO incorporation caused a decrease in the contact angle and improve in antifouling ability. Ganesh et al. [17] reported preparation of GO dispersed polysulfone (PSf) mixed matrix membranes and their performance was tested in terms of pure water flux and salt rejection. The prepared membranes enhanced the salt rejection, pure water flux and hydrophilic properties after GO doping. However, influence of graphene oxide nanoplates on fouling reduction of PSf membrane was not investigated.

Polyethersulfone (PES) is one of the most used polymers in the preparation of commercial and laboratory ultrafiltration and nanofiltration membranes [19–21]. However, fouling is the major problem in this type of polymers as well as in other polymeric membranes. Membrane fouling negatively affects membrane performance by decreasing water permeability. In order to mitigate PES membrane fouling, several approaches such as blending with hydrophilic polymers [22,23], grafting with hydrophilic monomers [24,25], grafting with short-chain molecules [26], embedding hydrophilic nanoparticles [20,27], etc. have been suggested. The blending of inorganic nanoparticles into the membrane matrix has also been utilized to reduce fouling in membranes, attributed to an increase in hydrophilicity or change in membrane morphology [28].

Therefore, hydrophilic properties of the membranes can be induced by GO incorporation due to its functional hydrophilic groups. It can also change the roughness and mechanical strength of the host polymer and has an influence in membranes fouling.

In the present work, the influences of blending GO on performance and antifouling properties of the polyethersulfone nanofiltration membrane have been investigated. GO was incorporated in PES matrix using the phase inversion method. The membrane structure and properties were characterized using AFM, SEM, FTIR and water contact angle measurements. Nanofiltration performance was tested by rejection of Direct Red 16 dye. Fouling resistance of the prepared mixed matrix membranes was also studied.

2. Experimental

2.1. Materials

All chemicals used in the experiments were of reagent grade. Polyethersulfone (Ultrason E 6020P, M_w=58,000 g/mol and glass transition temperature T_g=225 °C) and dimethylacetamide (DMAc) as solvent were supplied from BASF Co., Germany. Polyvinylpyrrolidone (PVP) with a molecular weight of 25,000 g/mol, potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) (98 wt%) were supplied from Merck. The azo dye, Direct red 16, $C_{26}H_{17}N_5Na_2O_8S_2$ (M_W=637.26) with purity of 99% was purchased from Alvan Sabet Co., Iran. Extra pure fine graphite with a particle size less than 50 μm was obtained from Merck Co. Deionized water was used throughout this study.

Table 1
The compositions of casting solutions.

Membrane type	PES (wt%)	PVP (wt%)	GO nanoplate (wt%)
Unfilled PES	20.0	1.0	–
M_1	20.0	1.0	0.1
M_2	20.0	1.0	0.5
M_3	20.0	1.0	1.0

2.2. Preparation of graphene oxide (GO) nanoplate

The graphene oxide (GO) was prepared from natural graphite by the Hummers method as reported in the literature [29,30]. In the first stage, 5 g of graphite powder was added to the concentrated H_2SO_4 in an ice-bath. Consequently, 7 g potassium permanganate was slowly added while preserving the temperature below 20 °C. The mixture was stirred at 35 °C for 30 min and slowly added into the deionized water (250 ml), followed by stirring the mixture at 98 °C for 15 min in order to increase the oxidation degree of the GO product. The treatment of graphene was terminated by adding 750 ml of 2 wt% H_2O_2 with stirring at 10 °C. The GO slurry was washed with de-ionized water and centrifuged several times to clean out the remained salt until a neutral pH was reached. The final GO slurry was sonicated for 1 h followed by filtering and drying in a vacuum oven at 40 °C for 24 h. A schematic view from the GO preparation process is presented in Fig. 1.

2.3. Fabrication of asymmetric GO nanoplate/PES nanofiltration membranes

The asymmetric flat sheet PES dense membranes containing graphene oxide nanoplates were fabricated by phase inversion induced by the immersion precipitation technique. The component of casting solutions was PES (20 wt%), PVP (1 wt%) and measured amounts of GO nanoplates in DMAc as solvent. The compositions of casting solutions for all membranes are listed in Table 1. Precise amounts of GO nanoplates were dispersed into DMAc and sonicated for 30 min to prepare homogenous solutions using DT 102H Bandelin ultrasonic (Germany). After sonication, PES and PVP were dissolved in the dope solution by continuous stirring for 24 h. A sonication-assisted method was again used for 10 min to remove air bubbles. Afterwards, the solution was cast