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Block copolymer based novel magnetic mixed matrix membranes-magnetic modulation of water permeation by irreversible structural changes

Lakshmeesha Upadhyaya[a,d,e], Mona Semsarilar[a], Damien Quémener[a], Rodrigo Fernández-Pacheco[b], Gema Martinez[c,d], Reyes Mallada[d], Isabel M. Coelhoso[e], Carla A.M. Portugal[e,*], João G. Crespo[e]

[a] Institut Européen des Membranes, IEM, UMR 5635, Université de Montpellier, ENSCM, CNRS, Place Eugène Bataillon, 34095 Montpellier Cedex 05, France
[b] Laboratorio de Microscopías Avanzadas (LMA), Instituto de Nanociencia de Aragón (INA), Edificio I+D, Campus Rio Ebro, Universidad de Zaragoza, 50018 Zaragoza, Spain
[c] Networking Research Centre on Bioengineering, Biomaterials and Nanomedicine, CIBER-BBN, 28029 Madrid, Spain
[d] Department of Chemical and Environmental Engineering and Aragon Nanoscience Institute, Campus Río Ebro, C/ Mariano Esquillor s/n, 50018 Zaragoza, Spain
[e] LAQV- REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

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ABSTRACT

This contribution focuses on understanding the effect of magnetic field intensity on the performance of novel hydrophilic and hydrophobic mixed matrix membranes (MMMs). The hydrophilic MMMs were made up of polymeric nanoparticles (PNPs) that were synthesized through polymerization-induced self-assembly (PISA) and iron oxide nanoparticles prepared in presence of poly (methacrylic acid)-*b*-poly quaternized (2-dimethylamino) ethyl methacrylate. The hydrophobic MMMs were prepared by the addition of iron oxide nanoparticles with different surface properties to a linear poly (methacrylic acid)-*b*-poly (methylmethacrylate) diblock copolymer dissolved in tetrahydrofuran (THF). Three different types of hydrophilic membranes were prepared with polymeric nanoparticles of different morphologies (spherical, vermicular and vesicular). In case of the hydrophobic membranes, six different membranes containing different iron oxide core coated with different stabilizers such as poly (methacrylic acid), quaternized poly(2-dimethylamino)ethyl methacrylate and meso-2,3-dimercaptosuccinic acid were prepared. An external magnetic field with intensity values up to 1.15 T was used for the permeation studies and the results were compared with those obtained in the absence of magnetic field. The collected data indicate an increase in the water flux of up to 16% and 29% under the magnetic field for hydrophobic and hydrophilic membranes, respectively. The STEM analyses suggest that the magnetic nanoparticles move within the membrane structure during the application of the magnetic field. This displacement/rearrangement causes constant changes in the membrane structure (structure of the active layer) and consequently on the membrane permeability. These results suggest that the application of the magnetic field could be used as a pretreatment step to obtain high flux membranes.

1. Introduction

The fabrication of novel functional materials with complementary properties from organic and inorganic building blocks has attracted a major attention in the field of separation science [1–3]. Hybrid materials in the form of membranes have better chemical and pressure stability due to the presence of inorganic nanoparticles (INPs) and excellent flexibility due to the high structural versatility of polymer matrix or their building blocks [4]. The successful application of these nanocomposite membranes depends on the organic and inorganic components, as well as the chemical interaction between them. Previously various types of INPs such as MgO, TiO_2, Fe_2O_3, and Fe_3O_4 have been incorporated in the development of nanocomposite membranes [5–23].

Iron oxide nanoparticles are versatile nano-platforms which are mainly used in sensors, smart devices, catalysis, bioseparation, magnetically controlled drug delivery, magnetic resonance imaging (MRI), as well as in water treatment [24–30]. There are several references in the literature describing the preparation of mixed matrix membranes using INPs to enhance their hydrophilicity, reduce the surface roughness and, thereby, improve the performance of membranes for liquid and gas separations [15,31–33].

* Corresponding author.
E-mail address: cmp@fct.unl.pt (C.A.M. Portugal).

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However, only a few references in the literature explore the magnetic properties of the incorporated INPs for separation applications. Himstedt et al. [34] developed a magnetoresponsive nanofiltration membrane by grafting a magnetically responsive nanolayer consisting of hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) chains, grown from the surface of a thin film nanofiltration membrane by surface-initiated atom transfer radical polymerization (SI-ATRP). Superparamagnetic materials were attached to chain ends, and an oscillating magnetic field was applied, producing the oscillation of the chains. Incorporation of NPs enhanced fouling resistance and reduced cake formation during filtration by disrupting the concentration polarization boundary layer. Later, Yang et al. [35] used the modified Gabriel synthesis procedure to attach superparamagnetic nanoparticles to the chain ends of PHEMA, and the membrane performance was studied using $CaCl_2$ and $MgSO_4$ filtration. It was found that salt rejection of the membrane, under an alternate magnetic field, increased compared to membrane filtration in the absence of an external magnetic field. This increase was greater for higher densities of attached INPs.

Santos et al. [36] used supported magnetic ionic liquid membranes for CO_2 separation using PVDF as porous support. There was an increase in gas permeability for CO_2, N_2, and air. This was related to the decrease of the viscosity of the ionic liquid, in the presence of an external magnetic field. Recently, Gebreyohannes et al. [23] used superparamagnetic ferric oxide NPs coated with polyethylene glycol dispersed in PVDF matrix. The INPs were used as an enzyme carrier, as well as, nanofillers in the membranes which were reversibly magnetizable due to the presence of the superparamagnetic iron oxide nanoparticles. These nanocomposite membranes were used in bioreactor showing a 75% reduction in membrane filtration resistance, due to reduced pore clogging resultant from the use of magnetic nanoparticles with immobilized enzyme.

In our previous work [37], we have demonstrated the possibility of making novel block copolymer based hydrophilic mixed matrix membranes made from polymeric nanoparticles of different morphologies (spheres, worms, and vesicles) using the polymerization induced self-assembly (PISA) technique and iron oxide nanoparticles with positive surface charge (iron oxide core coated with quaternized poly(2-dimethylamino)ethyl methacrylate)). The primary purpose to add the INPs was to enhance the mechanical stability of the active layer made up of block copolymer via opposite electrostatic charges (PNPs with negative surface charge and INPs with positive surface charge). Later, we demonstrated [38] the fabrication of hydrophobic mixed matrix membranes from simple linear diblock copolymer (PMAA-*b*-PMMA) and iron oxide nanoparticles coated with different types of stabilizers ($PMMA_{47}$, $PMAA_{47}$-*b*-$PQDMAEMA_{50}$ and DMSA). The polymeric particles of linear block copolymer in casting solution were produced using iron oxide NPs dispersed in water followed by the preparation of the membranes via both tape casting and spin coating technique by non-solvent induced phase separation. The goal of the current work is to explore the performance of these hydrophilic and hydrophobic mixed matrix membranes under different magnetic field intensities. Analysis of the magnetic field effect on membrane performance was accomplished, based on the hydraulic permeability at pH 7.1, and interpreted based on the influence of the magnetic field on permeate flux and on the relaxation behavior of the membrane after exposure to the magnetic field.

2. Experimental

2.1. Materials

Methacrylic acid (contain 250 ppm of MEHQ as inhibitor, 99%), methyl methacrylate (contain ≤ 30 ppm MEHQ as inhibitor, 99%), 4-cyano-4 (phenylcarbonothioylthio) pentanoic acid (> 97%), 4,4′-azobis(4-cyanovaleric acid) (ACVA; 98%), 2-dimethylaminoethyl methacrylate (contains 700–1000 ppm of monomethyl ether hydroquinone as inhibitor, 98%), methyl iodide, tetrahydrofuran (THF), iron (III) chloride hexahydrate (97%, Reagent grade), iron(II) chloride tetrahydrate (≥ 99%), ammonium hydroxide(28%), Triethylene glycol (99%) and meso-2,3-dimercaptosuccinic acid (98%) were purchased from Sigma-Aldrich and were used as received. NMR solvents, CD_3OD, $CDCl_3$, and D_2O were purchased from Eurisotop, Saint Aubin, France.

2.2. Membrane fabrication and characterization

The hydrophilic mixed matrix membranes were prepared following the method described by Upadhyaya et al. [37]. The nanocomposite membranes were prepared from poly(methacrylic acid)-*b*-poly(methyl methacrylate) (PMAA-*b*-PMMA) of different morphologies such as spheres ($PMAA_{47}$-*b*-$PMMA_{185}$; Polydispersity Index, Đ = 1.06, Number Average Molecular weight, M_n = 19.5 kg/mol), worms ($PMAA_{47}$-*b*-$PMMA_{267}$; Đ = 1.08, M_n = 27.4 kg/mol) and vesicles ($PMAA_{47}$-*b*-$PMMA_{356}$; Đ = 1.24, M_n = 28.4 kg/mol) synthesized via polymerization induced self-assembly (PISA) and iron oxide nanoparticles coated with quaternized poly(2-dimethylamino)ethyl methacrylate. The casting solutions were then spin coated on microporous nylon support.

The hydrophobic mixed matrix membranes were prepared following the method described by Upadhyaya et al. [38]. The membranes made by using a mixture of a linear diblock copolymer (poly(methacrylic acid)-*b*-poly(methylmethacrylate); $PMAA_{47}$-*b*-$PMMA_{69}$; Đ = 1.02 M_n = 10.1 kg/mol) and magnetic iron oxide nanoparticles. The well-defined linear diblock copolymer of poly(methacrylic acid)-*b*-poly(methyl methacrylate) was synthesized using RAFT polymerization. The iron oxide cores employed here were prepared using 3 different types of stabilizers ($PMAA_{47}$, $PMAA_{47}$-*b*-$PQDMAEMA_{50}$ and meso-2,3-dimercaptosuccinic acid). The membranes were prepared from casting solutions containing the diblock copolymer dissolved in THF, forming the PNPs by the addition of 0.35 mL of water containing dispersed iron oxide nanoparticles. Membranes were casted using either traditional tape casting or spin coating methods on microporous nylon support. Fig. 1 shows the schematic preparation of both hydrophilic and hydrophobic membranes using PNPs and INPs.

Membrane top surface and cross section before and after filtration were observed by scanning electron microscopy (SEM). The SEM images were obtained using a Hitachi S4800 operating under 0.1–30 kV working voltage. To prepare the SEM samples, the membranes on nylon film were frozen in liquid nitrogen for 10 min followed by sectioning.

To analyze the effect of magnetic field on membranes, atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM) analysis were carried out. AFM images were obtained with a Pico SPM II provided by Molecular Imaging. The image was controlled by the PicoView 1.10 software. The experiments were all carried out in tapping mode. The types of tips used were PPS-FMR purchased from Nanosensors with a frequency resonance between 45 and 115 kHz and a force constant between 0.5 and 9.5 N/m. Gwyddion 2.25 software was used to treat the images.

High Angle Annular Dark Field (HAADF) images were obtained with a Technai F30 (FEI) microscope, equipped with a Fischione HAADF detector at 300 keV working voltage, in STEM mode. Also, in order to elucidate about the chemical composition of the materials, X-ray Energy Dispersive spectra (EDS) were obtained with an EDAX detector. In order to follow structural changes induced by the magnetic field at the same membrane spot, STEM analysis were not conducted with the membranes used in filtration experiments. Instead, the membranes were formed at a specific copper grid for STEM analysis. A diluted solution (10 times) of the original casting solution, containing 1 mL of spherical particles in water with a concentration of 6.7 mg/mL and 2.1 mL of INPs in water, was cast on the top of a grid surface and then let to dry. Afterwards, 3–4 square sections on grids were marked and images were obtained without the presence of magnetic field and immediately upon exposure (to avoid analysis in the presence of magnetic

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