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Sodium alginate–magnesium aluminum silicate mixed matrix membranes for pervaporation separation of water–isopropanol mixtures☆

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Abstract

Sodium alginate (NaAlg) is a well-known carbohydrate polymer occurring in natural sources. In this study, mixed matrix membranes of NaAlg filled with sub-micron size magnesium aluminum silicate (MAS) particles have been prepared by incorporating different amounts (5, 10 and 15 wt.%) of MAS into NaAlg by solution casting and crosslinked with glutaraldehyde. The membranes prepared have been tested for pervaporation (PV) separation of water–isopropanol mixtures at 30 °C. Membranes were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to confirm the chemical interactions and homogeneity of the mixed matrix membranes. PV separation characteristics of the crosslinked NaAlg–MAS membranes have been studied by varying the feed water compositions and temperature. It was found that NaAlg membrane filled with 15 wt.% MAS gave the highest selectivity of 17,991 when tested for 10 wt.% of water containing feed mixture. Comparatively, a lower selectivity of 653 was observed for plain crosslinked NaAlg membrane for 10 wt.% water containing feed mixture; selectivity was further decreased with increasing water concentration of the feed mixture up to 50 wt.%. Water flux for the plain NaAlg membrane increased from 0.062 to 0.177 kg/m^2 h for the feed compositions ranging from 10 to 50 wt.% water; however at these compositions, flux values of NaAlg filled with 15 wt.% of MAS increased from 0.056 to 0.174 kg/m^2 h, suggesting no significant improvement. The observed water flux is lower for the mixed matrix membranes, but higher for the plain NaAlg membrane; nevertheless, selectivity is higher for NaAlg–MAS mixed matrix membranes than observed for the plain NaAlg membrane. Similar trends have been observed at 40 and 50 °C for the feed water compositions of 10–30 wt.%. The PV performance has been studied in terms of flux (J), selectivity (α), pervaporation separation index (PSI) and enrichment factor (β). Permeation flux followed the Arrhenius trend over the investigated temperature range.

Keywords: Pervaporation; Isopropanol; Sodium alginate; Magnesium aluminum silicate; Mixed matrix membranes

1. Introduction

Sodium alginate (NaAlg) is a linear chain structure consisting of (1-4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues arranged in block-wise fashion in three different ways: homopolymeric MM blocks, homopolymeric GG blocks and heteropolymeric sequentially alternating MG blocks [1,2]. Alginate is a sodium salt of alginic acid, a naturally occurring non-toxic polysaccharide, which belongs to carbohydrate group of polymers, found in brown algae. The presence of α-L-guluronic acid in various ratios alters the physico-chemical properties of the polymer [3]. In the earlier literature, NaAlg and its modified membranes have been successfully used to separate aqueous–organic mixtures [4–8]. Zeolites are the versatile materials used in a variety of applications including catalytic reactions and adsorbents in hydrocarbon processing. However, in recent years, zeolites have been used as filler particles to form dense mixed matrix membranes that can be conveniently used in pervaporation (PV) dehydration of organics [9,10]. The hydrophilicity of plain NaAlg membrane is not only the essential factor in dehydration of organics, but also it needs high mechanical strength properties in the presence of water or aqueous–organic media. A good water solubility and poor mechanical strength property of NaAlg membrane has been a major drawback in its usage as a PV membrane. Despite these disadvantages, many studies have been devoted to utilize the modified NaAlg membranes to improve its flux and selectivity to water. Generally, NaAlg has been crosslinked with glutaraldehyde using HCl as a catalyst in acetone solution to

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develop PV membranes [11]. Over the years, the importance of potential use of NaAlg based membranes is greatly increased. Literature findings suggest that the modified NaAlg membranes can extract almost pure water from water + isoproponol mixture [9].

Recently, mesoporous/microporous molecular sieves/clay particles are continued to be interesting filler materials into polymers in developing cost-effective high performance membranes in pervaporation (PV) separation and purification technologies. Particularly, extensive research has been devoted to develop polymer-layered nanocomposites, wherein filler inorganic particles in a polymer matrix could exhibit improved physical and mechanical properties of the virgin polymers. The easily tailored pore size and compositional variability available with montmorillonite clay particles when embedded into polymer network will provide the versatile range of applications that span from material development to membrane separations [12,13]. There are many studies in the literature [14,15] to incorporate various types of particles of inorganic origin including zeolites to develop the filled matrix membranes that can be used in PV separation studies of aqueous–organic mixtures. In a previous study from our laboratory, we have incorporated the cobalt(III)(3-acetylpyridine-*o*-aminobenzoyl hydrazone) complex particles as fillers into NaAlg to develop the mixed matrix PV membranes for dehydration of acetic acid [16].

In continuation of this study and as a part of our ongoing program of research, we now use magnesium aluminum silicate (MAS), a mixture of natural smectite clays like montmorillonite and saponites as fillers to develop the mixed matrix membranes of NaAlg. Smectite clays have the layered structures and each layer is constructed from the tetrahedrally coordinated silica atoms fused into an edge-shared octahedral plane of either aluminum hydroxide or magnesium hydroxide [17,18]. The layered structures of clay can be separated when these are hydrated in water. Once MAS is hydrated, the weakly positive edges are attracted towards the negatively charged faces. However, attraction of face to edge of these colloidal layers creates a three-dimensional colloidal structure throughout the dispersion, which exhibits thixotropic property [19]. These charges on the layers of MAS will lead to increased interaction with anionic natural carbohydrate polymer such as NaAlg leading to the ionic complexation [20].

Isopropanol is chosen in the present study, since it is a very important and commonly used solvent in biopharmaceutical and chemical industries. It is miscible with water in all proportions and forms an azeotrope at 12.5 wt.% of water. This mixture is hard to be separated by the normal distillation process, but can only be done through azeotropic distillation. However, azeotropic distillation is more energy consuming than conventional distillation. For azeotropic distillation, benzene, a highly carcinogenic and toxic substance is used as an azeotropic dehydrating agent in many plants, making the process health hazardous. In this regard, PV eliminates the use of benzene and the process is more economic than distillation. Table 1 shows energy consumptions required by different separation methods in isopropanol dehydration [21]. In terms of energy requirement, PV is therefore, an alternative choice for water–isopropanol separation. Liu et al. reported potential use of P84 co-polyimide hollow fibers for PV dehydration of isopropanol [22]. In other studies, Qiao et al. used BTDA-TDI/MDI (P84) co-polyimide and cross-linked P84 co-polyimide membranes for PV dehydration of isopropanol [23,24].

Table 1
Energy requirements by different separation processes for isopropanol dehydration

Purification (wt.%)	Energy required (kJ/kg) isopropanol	Process
8–99.5	10,376	Distillation
95–99.5	3,305	Azeotropic distillation
95–99.5	423	PV

The present study addresses the utilization of mixed matrix membranes of NaAlg for the PV separation of water from isoproponol. Incorporation of MAS into NaAlg (MG block type was used in the present study) helps to form a complex matrix due to the interaction between silanol groups of MAS and carbonyl groups of NaAlg [25]. However, stable membranes have been prepared by covalently crosslinking the mixed matrix membranes with glutaraldehyde, which would help to reduce the swelling characteristics and induce better mechanical strengths along with thermal stability. In fact, polyion complex membranes made from anionic k-carrageenan and cationic poly(1,3-bis [4-alkyl pyridinium] propane bromide) were reported to exhibit high selectivity (45,000) and permeability (0.150 kg/m^2 h) with a good mechanical stability in separating alcohol/water feed mixtures [26]. The principle objective of this study is to prepare mixed matrix membranes of NaAlg by incorporating different amounts of MAS into NaAlg by high-speed sonication followed by solution casting/solvent evaporation technique and crosslinking the membrane to offer better membrane performances. Physicochemical interactions and equilibrium swelling studies of the membranes have been performed to support the PV performance of the mixed matrix membranes as compared to plain unfilled NaAlg membrane. The temperature dependence of PV has been investigated to estimate the Arrhenius energy values for permeation. The results are discussed in terms of the polymer–particle and polymer–solvent interactions.

2. Experimental

2.1. Materials

Sodium alginate, isoproponol, acetone, glutaraldehyde (GA) and HCl were purchased from S.D. Fine Chemicals, Mumbai, India. Magnesium aluminum silicate (MAS) was purchased from Hi Media Chemicals, Mumbai, India. Viscosity of 1% (w/v) solution of NaAlg sample as measured by Brookfield Rheometer (Model DV-III; Middleboro, MA, USA) at 30 °C at the shear rate of 69.8 s^{-1} was found to be 170 mPa s (high viscosity grade sample). The viscosity average molecular weight of NaAlg is 1,22,596 Da. The deionized water having a conductivity of 20 μS/cm used was produced in the laboratory itself using