



Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

para-Toluene sulfonic acid treated clay loaded sodium alginate membranes for enhanced pervaporative dehydration of isopropanol

D.P. Suhas^a, T.M. Aminabhavi^{a,b}, A.V. Raghu^{a,*}^a Materials Science Division, Poornaprajna Institute of Scientific Research, Bengaluru 562 110, India^b Department of Pharmaceutical Engineering and Chemistry, Soniya College of Pharmacy, Dharwad 580 002, India

ARTICLE INFO

Article history:

Received 4 April 2014

Received in revised form 16 August 2014

Accepted 20 August 2014

Available online xxxx

Keywords:

p-TSA

Acid modified clay

Pervaporation

Isopropanol dehydration

Clay composite

ABSTRACT

The *para*-toluene sulfonic acid (*p*-TSA) treated clay (5, 10 and 15 wt.% loadings) particles were inserted into sodium alginate (NaAlg) matrix to derive the composite membranes that showed enhanced pervaporation performance for isopropanol separation. The 10 wt.% modified clay-loaded NaAlg membranes showed the highest selectivity of 5781 with a permeance of 3423 GPU for 10 wt.% water containing isopropanol feed mixture at 30 °C, showing a 140% higher selectivity compared to pristine clay-loaded NaAlg composite membrane. This effect is ascribed to an enhanced surface area and hydrophilicity after *p*-TSA treatment of clay, as verified by BET and TGA studies. The membranes were characterized by a variety of physico-chemical techniques and their pervaporation performance was assessed in terms of selectivity, permeance, with extent of variations in filler loading, temperature and feed water composition.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, pervaporation (PV) technique has gained a much wider acceptance as an energy efficient method for obtaining pure alcohols (Hoof et al., 2004). For separating alcohol–water mixtures, distillation is effective only to a certain extent viz., 80–85 wt.%, after which separation is done by evaporating the entire alcohol (usually any process involving phase change from liquid to gas consumes large quantity of energy). Since the number of evaporating molecules is large, naturally energy consumption is also large. On the other hand, PV selectively removes the minor components from such mixtures and thus limiting the energy burden only to minor components. PV is also an environmentally benign technique, since it does not involve an entrainer like benzene, as applicable in azeotropic distillation (Jonquière et al., 2002; Lipnizki et al., 1999; Shao and Huang, 2007; Widagdo and Seider, 1996). In this research, isopropanol (IPA) dehydration is considered in view of its importance in cosmetics, gums, waxes, cleansing agent in industries and as a blend in gasoline (Papa, 2000). High purity grade IPA is required in all these areas. IPA forms an azeotrope at 12.3 wt.% of water, making it difficult to separate by conventional distillation (Ghazali et al., 1997). Hydrophilic polymers like poly(vinyl alcohol), sodium alginate (NaAlg), chitosan, polyacrylonitrile, and polyimide have been reported for IPA dehydration (Chapman et al., 2008; Suhas et al., 2013, 2014). NaAlg is a naturally occurring anionic bio-

compatible material with good film forming ability, moderate mechanical strength and good affinity to water (Bhat and Aminabhavi, 2007a, 2007b). However, nascent NaAlg suffers from uncontrolled swelling, thus exhibiting low PV performance. To circumvent these problems, composite membranes have been prepared by dispersing suitable fillers into NaAlg matrix. Such membranes have emerged to be the best for PV dehydration of aqueous–organic mixtures (Adoor et al., 2013; Chung et al., 2007; Zhao et al., 2013).

Typical fillers used in developing composite membranes are non-porous, porous or intercalated materials, whose presence creates tortuous pathways in the matrix favoring the selective permeation of water molecules. Examples of the widely used fillers include heteropolyacids (Teli et al., 2007), titanium dioxide (Liu et al., 2011), zeolites (Bhat and Aminabhavi, 2007a, 2007b), mesoporous silica (Patil et al., 2007), and clays (Anilkumar et al., 2008). Among these, montmorillonite clays, owing to their layered structure with a high aspect ratio and hydrophilic surface chemistry, have gained much wider acceptance as fillers in barrier membranes (Avagimova et al., 2013). Clays are the important class of layered silicates consisting of alumina octahedra sandwiched between two sheets of silica tetrahedra interconnected by sharing of O²⁻ atoms at the polyhedral corners and edges (Chen et al., 2008). Earlier studies on sodium montmorillonite clay incorporated PVA and NaAlg membranes have shown improved separation performance (Adoor et al., 2006; Bhat and Aminabhavi, 2006). Acid treatment is the most actively pursued method to improve the surface property of the clay. The technique involves leaching of the clay with suitable acids leading to deagglomeration of clay particles, elimination of mineral impurities as well as causing structural and chemical changes in the clay.

* Corresponding author at: Centre for Emerging Technologies, Jain Global Campus, Jain University, Kanakapura, Ramanagara 562 112, India.

E-mail addresses: grraghu2003@yahoo.co.in, raghu@poornaprajna.org (A.V. Raghu).

The acid treated clay has several attributes like high surface area and large number of hydrophilic sites compared to the nascent clay. It was found that the degree of clay structure decomposition depends on several factors like the type of acid used, concentration of acid, duration of treatment and experimental conditions (Madejova et al., 1998; Panda et al., 2010; Siddiqui, 1968). Earlier (Ramesh et al., 2012), it was shown that *p*-TSA treated smectic clay enhanced both the surface area and the catalytic activity compared to nascent clay. Moreover, to enhance the efficiency, we have incorporated a microwave irradiation technique, which is environmentally friendly.

In this work, organically modified clay particles prepared by treating with *p*-TSA were incorporated into the NaAlg matrix to derive composite membranes that were tested for PV dehydration of IPA–water mixture. Performance of the modified clay-loaded NaAlg composite membrane was compared with that of pristine clay-loaded NaAlg composite membrane for IPA dehydration. The composite membranes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), thermogravimetry (TGA) and contact angle measurements. Sorption and diffusion parameters along with their temperature dependencies have been used to estimate the Arrhenius activation parameters for permeation and diffusion processes. These along with selectivity and permeance data have been used to discuss the PV results for IPA dehydration. To the best of our knowledge, this is the first study on the use of *p*-TSA treated clay loaded NaAlg membranes used in PV dehydration of IPA.

2. Experimental

2.1. Materials

Sodium montmorillonite clay was purchased from Sigma Aldrich, USA, while sodium alginate (NaAlg), isopropanol (IPA), hydrochloric acid (35%) (HCl), *p*-toluene sulfonic acid (*p*-TSA) and glutaraldehyde (GA) were all purchased from s.d. fine chemicals, Mumbai, India. Absolute ethanol (EtOH) (99.9%) was purchased from Commercial Alcohols, Brampton, Canada. All other chemicals were of analytical reagent (AR) grade samples, used without further purification. Double distilled water was used throughout the experiments.

2.2. Preparation of *p*-TSA treated clay

In a typical procedure, 20 g of clay and 200 mL of 2 molar *p*-TSA were taken in a 500 mL round bottom flask connected to a double walled reflux condenser and digested under a microwave irradiation (Microwave Lab Station START-5 Italy, courtesy of Dr. Y.S. Bhat, BIT, Bangalore) for 10 min at 1000 W power and heated to 80 °C. The reaction mixture was centrifuged and the residual solid was washed thoroughly with water until the solution acquired neutral pH. The resulting solid was dried at 120 °C for 2 h in a vacuum oven and ground to fine powder. The increase in surface area as measured by BET isotherm was 113 m² g⁻¹ as against the original value of 29 m² g⁻¹ for pristine clay, confirms the modification of clay. Additionally, thermogravimetry showed an increase in water retention capacity of the modified clay, suggesting increased hydrophilicity (see the Thermogravimetry (TGA) section). The pristine clay used in this study was also prepared by the same approach, except that only double distilled water was used instead of *p*-TSA.

2.3. Membrane fabrication

The solution casting method was adopted to prepare composite membranes from a uniform suspension of *p*-TSA treated clay-loaded NaAlg. In a typical procedure, 4 g of NaAlg was dissolved in 100 mL of water with constant stirring followed by 24 h of degassing. In a separate flask, the required amount of clay was stirred by taking into 20 mL of

water for 30 min followed by 1 h of sonication. The suspension obtained was slowly added to the NaAlg solution and mixed over a magnetic stirrer for 24 h. The resulting uniform suspension was poured onto a perfectly aligned flat clean glass plate dried at ambient temperature. The dried membranes were peeled off from the glass plate and were further dried in a vacuum desiccator at ambient temperature before use.

The membranes formed were cross-linked by immersing in a cross-linking solution bath for 6 h that contained water–acetone (30:70) mixture with 2 mL of GA as a cross-linking agent and 2 mL of conc. HCl as a catalyst. The cross-linked membranes were alternatively rinsed with water and methanol for at least ten times followed by soaking in methanol for 24 h and then preserved in a desiccator before further testing. Using the above procedure, 5, 10 and 15 wt.% of *p*-TSA treated clay-loaded NaAlg composite membranes were prepared and are designated as: PCL-5, PCL-10 and PCL-15, respectively. As a control, the nascent NaAlg (cross-linked, but without adding fillers) and 10 wt.% pristine clay loaded NaAlg (designated as CL-10) membranes were fabricated.

2.4. Membrane characterization

Fourier transform infrared (FTIR) spectroscopy (Bruker Alpha-T spectrometer) was used to analyze the samples after mixing with KBr and pellets were made under applied hydraulic pressure (180 kg/cm²). Scanning was done in the range of 400–4000 cm⁻¹ for 32 times with a resolution of 4 cm⁻¹ and these data were accumulated in a transmission mode.

Wide-angle XRD analysis of the membranes was carried out in a powder form using Bruker D-2α Phaser X-ray diffractometer. The X-rays of wavelength 1.54 Å were generated by nickel filtered CuKα radiation source and samples were scanned in the 2θ range of 2–60° at the scanning rate of 2°/min.

Micro-structural morphology of the nascent NaAlg as well as composite NaAlg membranes were examined by a field emission scanning electron microscope (FE-SEM) using an FE-SEM ZEISS Ultra-55 instrument (available at CeNSE, Indian Institute of Science, Bangalore). To improve the image quality, a conductive layer of sputtered gold was coated prior to these measurements.

Thermal stability of nascent NaAlg and its composite membranes was examined by thermogravimetry (Universal V3.9A TA Instruments, Bangalore, India) over the temperature range of 40–650 °C at the heating rate of 10 °C/min. Analysis was carried out under an inert atmosphere at the nitrogen gas flow rate of 10 mL/min. For each analysis, about 6–9 mg of the sample was taken in aluminum pans. Similarly, TGA analysis of the pristine clay and *p*-TSA treated clay was performed from 40 to 800 °C in an ambient atmosphere.

Water contact angle on the surface of the membrane was measured as per the Sessile drop method using the Data Physics OCA 20 at 25 °C (courtesy of Prof. S.K. Biswas, Indian Institute of Science, Bangalore). Prior to these measurements, all the membranes were vacuum dried and kept in a desiccator. Then, a piece of membrane (1 cm × 7 cm) was adhered to clean and smooth glass slide for contact angle measurements. A 2 μL of deionized water droplet was placed on the sample surface and droplet image was captured by a microscope coupled to a charge coupled device (CCD) camera. All the measurements were done within 10 s to minimize the errors due to evaporation losses. A total of six measurements were taken at different locations for each membrane sample and the average value was taken with >3% standard deviation.

2.5. Equilibrium swelling

Equilibrium swelling experiments were performed gravimetrically at 30 °C for 10 wt.% water containing IPA feed mixture. Initial weights of all the circularly cut membranes were measured after vacuum drying in a hot air oven and the weight of dry membrane was noted as W_d . Dry membranes were placed inside the specially designed air tight test

Download English Version:

<https://daneshyari.com/en/article/8046940>

Download Persian Version:

<https://daneshyari.com/article/8046940>

[Daneshyari.com](https://daneshyari.com)