Pervaporative performances of mixed matrix membranes filled with silica/silicalite-1 particles for purification of toluene from dilute aqueous solution

Elnaz Alizadeh Nourani[a], Hamid Reza Mortaheb[b,*], Mohammad Reza Ehsani[a]

[a]Chemical Engineering Department, Isfahan University of Technology, Isfahan 84155, Iran
[b]Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

A B S T R A C T

In this study, the performance of mixed matrix membranes for the removal of toluene from water by pervaporation was tested. Silicalite-1 or silica nanoparticles were incorporated into the PDMS matrix on a PES support layer. Silicalite-1 was synthesized and characterized by XRD, particle size analyzer, and ATR-FTIR. The fabricated membranes were characterized by SEM, XRD, and AFM. The results showed that the fillers up to a certain value (2.5 wt% of silicalite-1 or 5 wt% of silica) can be distributed uniformly in the membrane matrix. The sorption of membrane is improved by incorporating these fillers. To obtain the optimum amount of fillers, the prepared membranes by different filler contents were tested on a pervaporation setup. The results showed that incorporating each of the fillers greatly enhances the enrichment factor of the composite membrane (in the range of 82–236%) while it generally decreases the permeation flux (in the range of 2–90%). The best enhancement in performance was achieved by adding 10 wt% silicalite-1 where it increased the enrichment factor by 289% and the normalized total flux by 15% compared to the unfilled membrane.

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Introduction

Volatile organic compounds (VOCs) are widely emitted from petrochemical and chemical units. Among VOCs, BTEX (benzene, toluene, ethyl benzene, and xylene) are highly toxic even in trace amounts [1–3]. As these materials are present in low concentrations in water, applying conventional separation processes such as distillation, liquid–liquid extraction, air stripping, and adsorption to remove them incurs extra treatment costs.

Alternatively, pervaporation is a separation process, in which components permeate selectively through a non-porous membrane, driven by a gradient in partial vapor pressure. One of the main advantages of this process compared to the conventional treatment methods is that the costly secondary treatments for the permeate phase is unnecessary. Among the main applications of pervaporation including organic/water and organic/organic separations, removal of VOC components from dilute aqueous solutions namely organophilic pervaporation is of great importance [1–6].

The membrane in pervaporation is often used in the form of composite membrane, where the selective top layer is supported by a sublayer, which can reinforce the composite membrane against high vacuum [2]. The VOC components can selectively dissolve in the dense top layer of the membrane and then diffuse through the membrane and transport to the gas phase in the permeate side of the process setup. The main key for the success of a pervaporation process is to select proper top layer for the specified target. The rubbery poly-dimethyl siloxane (PDMS) exhibits preferable diffusion properties in comparison to the glassy polymers due to its flexible chains and high free volumes [2,7–9]. This polymer is highly hydrophobe with a high affinity to dissolve organic compounds as well as good thermal and chemical stabilities [6,10,11].

Incorporating inorganic fillers into a polymeric membrane matrix can enhance its separation performance by improving the selective sorption of the organic solvents and/or decreasing the unfavorable diffusion [2,8,10]. The filler improves the stability of the membrane, increases the stiffness, and controls the swelling of the membrane by acting as a physical crosslinker [12]. The filler content, particle size, and homogeneous dispersion are important parameters in adding fillers into the polymer matrix [1,13,14]. Effects of various inorganic fillers such as carbon black, activated carbon, and zeolites on pervaporative performance have been investigated [1,2,15–18].

Zeolites are widely used in the pervaporative separation of organic compounds from water because of either their hydrophobic/hydrophilic natures or different adsorption potentials. Chovau et al. [2] examined unfilled and filled PDMS top layers with a commercial ZSM-5 zeolite (CBV 3002) on PI supports in pervaporative removal of toluene from water. Based on their results, incorporating fillers enhances the membrane selectivity. The higher selectivity of the membrane was attributed to the hydrophobic nature of those zeolites and

consequently their higher affinities to toluene. Vane et al. [19] tested filled PDMS membranes with ZSM-5 zeolites on a polyvinylidene fluoride support for removal of ethanol from water where a significant increase in the selectivity was observed. Silicalite-1 with an MFI structure (a structural name proposed by Structure Commission of the International Zeolite Association (IZA) for zeolite ZSM-5 and its zeosil analogue silicalite-1 [20]) is a hydrophobic zeolite whose hydrophobic nature is improved as the ratio of Si/Al is increased [21]. Chung et al. expressed that zeolites usually have hydroxyl groups on their surface. Therefore, if a polymer has a group in its chain that can react with those hydroxyl groups, this can effectively prevent from the interface void formation during the polymer chain shrinkage [22].

Silica nanoparticles are also inorganic particles with high affinities to organic compounds that increase the tortuous pattern of the matrix against undesirable compounds [18,23–25]. Gevers et al. state that silanol groups at the surface of silica can produce hydrogen bonds with the oxygen atoms of the PDMS chains, and therefore can adsorb the polymer chains [26]. Kim et al. [23] added 12–400-nm silica nanoparticles to a PDMS matrix on a polysulfone support for removal of propylene from off-gas stream. As a result, separation factor and propylene permeability were increased. They examined two types of silica; the sol–gel silica and the fumed silica. The sol–gel silica can disrupt the chain packing and increase the polymer free volume and propylene permeance in comparison to the smaller fumed silica particles. Wang et al. [12] fabricated PDMS membranes filled with hydrophobic nanosilica for separation of methanol from dimethyl carbonate/methanol azeotropic mixture via pervaporation. It was shown that the separation factor is increased by increasing silica content up to 15% while the permeation flux follows a reverse trend because of enhancing physical crosslinking and improving plasticization resistance.

In the present study, zeolite particles of silicalite-1 and two different sizes of silica particles are used as fillers to fabricate mixed matrix membranes containing a PDMS top layer coated on a polyethersulfune (PES) for removal of toluene from water by pervaporation. The effects of filler type, filler content, and particle size on these membranes are investigated by a pervaporation setup.

Materials and methods

The hydroxyl-terminated polydimethyl siloxane (PDMS), polyvinylpyrrolidone (PVP) (K90, Mw = 360,000), dibutyltindilaurate (DBTL), and 1M-solution of tetrapropyl ammonium hydroxide (TPAOH) were purchased from Sigma–Aldrich. Tetraethyl orthosilicate (TEOS), n,n-dimethylacetamide (DMAc), triethylamine (TEA), n-heptane, ethanol, and toluene were provided from Merck. Polyethersulfone (Ultrason® E 6020 P, Mw = 58,000) was purchased from BASF. All the materials were used as they received without further purification.

Silica nanoparticles (10 and 80 nm) were provided by a local supplier (Nano Pars Lima Co., Table 1). The zeolite of silicalite-1 was synthesized in our laboratory.

Preparation of supporting membrane

The merits of hydrophilic additives including PVP on the structure of supporting membrane were discussed in a previous paper [27], in which the optimum additive content and preparation conditions were determined. Those results are adopted in this research for preparation of the supporting membrane; a mixture of 15 wt% PES, 82 wt% DMAc, and 3 wt% PVP is stirred for 24 h at room temperature to obtain a homogeneous solution. The solution is set aside for 1 h until all bubbles exit. The solution is then cast by a casting knife with a preset thickness on a flat glass plate with a final thickness of about 75 μm, which is determined from the SEM images. The prepared film is immediately immersed in a coagulation bath filled with distilled water (electrical conductivity = 9.5 μS/cm) at 40 °C. The coagulation bath temperature is one of the affecting factors on morphology of PES supporting membranes as examined in our previous work [27]. By increasing the temperature of coagulation bath from room temperature to 40 °C, the replacement rate between the solvent and the non-solvent is improved. Thus, wide channel-like macrovoids with less sponge areas are created.

The precipitation occurs right after immersing the film in the coagulation bath while the added PVP increases the exchange rate between the solvent and the non-solvent and thus it increases the porosity of the support membrane. Water in the pores of prepared membrane is then replaced by glycerin in a glycerin bath to prevent penetration in the support membrane during casting of the top layer.

Preparation of unfilled composite membrane

PDMS, the crosslinker (TEOS), and the catalyst (DBTL) are dissolved in n-heptane with a weight ratio of 1:0.1:0.02:1, respectively [28]. The casting solution is then stirred for 2 h and is cast on a two-part glass mold where the PES support membrane is placed in the mold beforehand. The cast solution is left for 24 h in room temperature. The crosslinking is completed after drying membrane in an oven at 70 °C for 4 h. In order to leaching out of glycerin, the prepared composite membrane is immersed in water for 24 h. Due to high solubility of glycerin in water, the large volume of water, and high retention time, glycerin is removed completely from the PES pores. The membrane is then dried in an oven at 70 °C for 1 h.

Preparation of silicalite-1

The crystals of silicalite-1 are synthesized by a hydrothermal method. 5 g TPAOH, 5 g TEOS, 7.5 g distilled water, 1.25 g ethanol, and 1.25 g TEA are mixed in a sealed polypropylene bottle. TEOS and ethanol are used as the sources of silica and hydroxyl ions, respectively. Tetrapropyl ammonium cation is used as a directing template. The mixture is sonicated for 10 min in an ultrasonic bath (Bandelin, 560 W, 35 kHz). The mixture is then placed in a closed stainless steel autoclave and heated at 100 °C for 48 h. After cooling in room temperature, 50 ml of distilled water and 5 ml of ethanol are added to the solution. The solids in the mixture are centrifuged three times at 12,000 rpm for 2 h to be separated from the liquid phase. In order to remove the organic cation template, the solid particles are dried at 100 °C and calcinated for 12 h in a furnace at 550 °C with a heating rate of 1 °C/min. The produced solids are ground to tiny particles by a laboratory mortar.

Preparation of filled composite membranes

The filler is dispersed in the mixture of polymer (PDMS)/solvent (n-heptane) by a magnet stirrer for 1 h. The mixture is then sonicated for 30 min before the crosslinker and catalyst are added. The solution is mixed for 1 h and is cast into the mold on the top of fixed supported membrane. As the filler is added before the cross-linker, a homogeneous mixture is obtained and the filler is uniformly dispersed in the prepared membrane [14]. Four values of 2.5, 5, 7.5, and 10 wt% of filler content are used in the experiments.

Characterization methods

The structure of the synthesized silicalite-1 and membranes are characterized by an X-ray diffractometer (XRD, D8-advance, Bruker Co., Germany) using Cu Kα radiation (1.5418 Å) where the intensity is recorded at $2\theta = 4-70°$.

In order to determine the size of silicalite-1 particles, the particles are sonicated in the distilled water for 1 h. The particle size in this