Separation and Purification Technology 197 (2018) 178–188

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Modification of polyacrylonitrile membranes via plasma treatment followed by polydimethylsiloxane coating for recovery of ethyl acetate from aqueous solution through vacuum membrane distillation

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ARTICLE INFO

Keywords:
Plasma modification
PDMS coating
Ethyl acetate
Membrane distillation

ABSTRACT

For the recovery of ethyl acetate (EtAc) from aqueous solution via vacuum membrane distillation (VMD), hydrophobic porous membranes with high and stable separation performance were prepared by carbon tetrafluoride (CF_4) plasma treatment on polyacrylonitrile (PAN) membrane followed by polydimethylsiloxane (PDMS) coating. The effects of plasma treatment conditions and PDMS contents on the morphology, surface porosity and separation performance of modified membranes were investigated. It was found that both the two modification operations increased the hydrophobicity of the PAN membrane. CF_4 plasma treatment increased the hydrophobicity (the contact angle increased from 42° to 124° measured by 2.5 wt% EtAc solution), surface mean pore size (from 24.6 nm to 150.5 nm) and porosity (from 7% to 32.3%) of hydrophilic PAN membrane, suggesting that the CF_4-modified membranes (PAN-C membranes) with high hydrophobicity could be used in VMD. Optimized PDMS coating on the PAN-C membranes (PAN-C-P membranes) further narrowed the pore size distribution but retained porous and hydrophobic surface. The PAN-C membranes were much less efficient and stable in separating EtAc from water comparing with the PAN-C-P ones. For instance, for the separation of 1 wt% EtAc/water mixture, the best VMD performance in this work was achieved by the PAN-C3-P3 membrane with a separation factor of 70 and a total flux of 7.85 kg/m^2 h (PSI = 542). Moreover, the PAN-C3-P3 membrane showed a very stable separation performance than that of the PAN-C3 membrane during a 90 h intermittent VMD operation, indicating a very promising application prospect for EtAc recycling.

1. Introduction

Ethyl acetate (EtAc) is an important chemical solvent, widely used in producing antibiotic and some intermediates in pharmaceuticals industry [1]. It is also used in large volumes as industrial solvents, adhesives, extraction agents and perfume material etc. [2]. However, huge amounts of wastewaters containing EtAc have been produced, which can cause serious environmental problems and harm to human health without appropriate treatment [3]. Due to the fact that EtAc and water form azeotrope easily, it is difficult to recycle EtAc from wastewater [4]. To eliminate or recycle EtAc from wastewater, treatment methods mainly include distillation, adsorption, air striping, advanced oxidation, biological treatment and membrane technology [3,5–15]. Among them, membrane technologies, especially pervaporation (PV) and membrane distillation (MD), are attractive methods for this application with obvious advantages of high efficiency, energy saving and being environment-friendly [3,5–11,14,15].

PV process uses dense membranes and its separation mechanism is adsorption-dissolution-diffusion, generally resulting in a high separation factor but low membrane flux. Both inorganic and polymeric PV membranes were prepared and used for the removal of EtAc from water [3,6–8,10,14,15]. For example, inorganic PV membrane was prepared by using hydrophobic silica for removal of 5 wt% EtAc, and the permeation flux and separation factor were 1.94 kg/m^2·h and 216, respectively [6]. Kujawa et al. [3] prepared perfluoroalkylsilanes-modified hydrophobic titania ceramic membranes for concentrating EtAc/water mixture from 1 wt% in feed to 23 wt% in permeate; their permeation flux and separation factor were 4.83 kg/m^2·h and 30, respectively. Polymeric membranes have also been fabricated and used to remove EtAc from water, such as poly(vinylidene fluoride-co-hexafluoropropene), polydimethylsiloxane (PDMS), polyurethaneurea, poly (methyl hydrogen siloxane) and polyether-block-polyamides etc. [7,8,14,15]. Zhou et al. [7] prepared a kind of PDMS membrane modified by alkyl grafting and obtained a total flux of 0.188 kg/m^2·h

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https://doi.org/10.1016/j.seppur.2018.01.011
Received 22 March 2017; Received in revised form 17 October 2017; Accepted 5 January 2018
Available online 06 January 2018
1383-5866/

and a separation factor of 592 for 1 wt% EtAc in feed. Bai et al. [14] synthesized hydroxy-terminated polybutadiene-based polyurethaneurea membranes and found that the permeation flux of 0.256 kg/m^2·h and separation factor of 655 could be obtained when the EtAc concentration in feed was 2.5 wt%. Although these reported PV membranes showed high permeate flux or high separation factor in the separation of EtAc-water mixtures, a trade-off between membrane flux and separation factor still existed, in general, resulting in the reported low process separation index (PSI) values of no more than 418 at present [3,6–8,10,14,15].

MD process, however, uses a hydrophobic porous membrane to separate volatile components from solution according to the principle of liquid-vapor equilibrium. Actually, MD technique has become a noteworthy alternative for the selective separation of EtAc from aqueous solutions in recent years [5,9,11]. Li et al. [11] used polyvinylidene fluoride (PVDF) membrane to separate 1 wt% EtAc solution by vacuum membrane distillation (VMD), and the highest permeate flux was 37.90 kg/m^2·h in spite of a low separation factor of 9. Hydrophobized ceramic membranes [5,9] were also used in VMD for separating a 2 wt % EtAc solution, and showed a separation factor of 60 with a total flux of 10.80 kg/m^2·h (PSI = 637), and the separation factor depended strongly on membrane's pore size. Comparing with PV process, VMD process showed a much higher permeation flux despite a lower separation factor. In general, it seemed that VMD possessed higher PSI values and removed EtAc more quickly, indicating that VMD had a comparable and promising application potential.

However, membrane wetting is a big concern in VMD especially when tackling the solution containing organic solvents with low surface tension (e.g. EtAc) due to the fact that such solvents are more likely to wet porous membranes with big pore size [16–18]. Actually, long-term VMD operation for EtAc removal has not been studied until now. Membrane wetting not only decreases the stability of VMD process, it almost means the failure of the separation process. In order to improve membrane's resistance to wetting, in recent years, more attentions have been focused on the development of highly hydrophobic layer with suitable pore size distribution [5,9,19]. Up to now, a wide variety of hydrophobic surfaces have been constructed by plasma modification [20], surface-coating [21], layer-by-layer methods [22], and chemical vapor deposition or electrochemical deposition [23].

Plasma modification has shown advantages in changing the surface wettability of the materials without affecting the bulk properties. In particular, carbon tetrafluoride (CF_4) plasma modification has been widely used in the membrane hydrophobization for MD [20,24,25]. Wei et al. [20] introduced a CF_4 plasma modification to turn a hydrophilic polyethersulfone membrane into hydrophobic ones for MD. Tian et al. [24] fabricated hydrophobic polysulfone-based membranes with comparable performance stability in MD via CF_4 plasma surface modification and the modified membranes showed higher flux than a commercial PVDF membrane. Yang et al. [25] recently prepared a superhydrophobic PVDF-based membrane with higher MD flux compared with virgin PVDF membrane and inferred that the flux enhancement was due to the increased effective evaporation area of the modified membrane. It seemed that CF_4 plasma treatment had a strong fluorination effect of introducing a hydrophobic layer onto substrate surface efficiently, and rendered membranes high desalination performance. But up to now, it has not been reported that whether such CF_4-modified membranes can be suitable for the removal of volatile organic compounds via MD process.

On the other hand, due to the good flexibility, oxidative stability and high hydrophobicity, silicone rubber like PDMS has also been applied to modify porous membranes to improve their hydrophobicity or stability in MD [21,26,27]. However, it was often a thin but dense PDMS layer formed on base membrane, which increased the stability but at the expense of the flux of membranes in MD.

In this work, the hydrophobic modification strategy of CF_4 plasma treatment on polyacrylonitrile (PAN) membrane followed by PDMS coating was proposed for EtAc recycling via VMD process. PAN is a kind of typically hydrophilic polymer used to prepare membranes for ultrafiltration and microfiltration etc., due to its good thermal stability, solvent resistance and ageing resistance. Hence, a hydrophilic PAN membrane was chosen to act as a base membrane here [28]. The plasma power and PDMS content were the main parameters studied to manipulate the membrane surface chemistry and pore structure. The stability of the modified membranes was also evaluated by a prolonged experiment up to 90 h.

2. Experimental

2.1. Materials and chemicals

Hydrophilic PAN flat-sheet membrane with the molecular weight cut-off of 20,000 Dalton was purchased from Sepro Membranes, Inc., USA. The commercial PAN membrane had a non-woven fabric support layer.

PDMS was purchased from GE Toshiba Silicones Co., Ltd., Japan. EtAc and n-heptane (analytical grade) were supplied by Beijing Chemical Reagent Co., Ltd. Argon (Ar, 99.99%) gas was purchased from Beijing Qianxi Gas Co., Ltd., China. CF_4 gas (99.99%) was purchased from Linggas Tianjin Limited Company, China. Deionized (DI) water produced by Millipore DI system. All chemicals were used as received without further purification.

2.2. CF_4 plasma surface modification of PAN membrane

Plasma modification was performed in a YZD08-2C Plasma Reactor made by Scie-lab (Beijing) Tech. Co., Ltd., China. The diameter and length of plasma chamber is 10 cm and 25 cm, respectively. A piece of pristine PAN membrane with 8 cm × 15 cm dimension was fastened on a steel plate in the plasma chamber and fixed in a distance of 4.0 cm from the electrode. Subsequently, Ar gas was injected into the chamber at 0.5 L/min for 1 min after the chamber was evacuated to a base pressure of less than 100 Pa, and then, glow discharge was initiated at the radio-frequency (RF) power of 80 W for 1 min. The purpose of the Ar plasma pretreatment was to make the membrane free of dust particles and ready for further treatment. Afterwards, CF_4 was introduced into the chamber at 0.7 L/min, and the RF power was varied from 80 to 160 W, while the exposure time was maintained at 12 min. The modified membrane was named as PAN-C membrane. After plasma treatment, the PAN-C membrane was taken out from the chamber for further characterization and use.

2.3. Preparation of PDMS-coated membranes

PDMS were dissolved in n-heptane with different mass fraction (2–5 wt%) at 80 °C for about 2 h. Prior to coating, substrate (the pristine PAN or PAN-C membrane) was immersed in DI water at room temperature for 5 h. Residual water at the substrate surface was then quickly wiped off with a filter paper when the substrate was removed from water. Then, the PDMS solution was poured and spread over the membrane surface using a coating knife. Subsequently, the as-cast membrane was left for 30 min at room temperature to evaporate the solvent. Finally, the PDMS-coated membrane was placed in a vacuum oven at 80 °C for more than 8 h to ensure complete curing. The final PDMS-coated membrane was named as PAN-C-P membrane or PAN-P membrane, when the PAN-C membrane or PAN membrane was used as base membrane, respectively. The membrane modification conditions and some characterization results are presented in Table 1.

2.4. Characterizations

Contact angle (CA) of membrane was measured by the sessile drop method using an optical contact angle goniometer (OCA20, Data