Journal of Membrane Science 518 (2016) 216–228

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Separation and concentration of ionic liquid aqueous solution by vacuum membrane distillation

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ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form
3 June 2016
Accepted 9 July 2016
Available online 16 July 2016

Keywords:
Ionic liquid
Membrane distillation
Concentration
Fouling
Wetting

ABSTRACT

Due to the high cost of ionic liquids (ILs), how to economically recycle them from aqueous solutions is one of the critical issues for their large-scale applications. In this work, vacuum membrane distillation (VMD) technique was proposed to separate and concentrate the 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) aqueous solutions at high concentration (e.g. ≥ 20 wt%), where a polyacrylonitrile-based (PAN-based) hydrophobic membrane was prepared and used. The chemical resistance and VMD separation performance of the PAN-based membrane were estimated. The results showed that the homemade membrane possessed good chemical resistance to several kinds of media and favorable VMD flux and rejection. Four different groups of VMD concentration processes with intermittent operation mode were then carried out to separately concentrate a 20 wt% [Bmim]Cl solution. The concentration process, membrane fouling and wetting, as well as cleaning strategy were compared and discussed. It was found that for the hydrophobic PAN-based membrane, surface hydrophilization resulted from surface chemistry rearrangement happened especially at high feed temperature, which might aggravate the adsorption of [Bmim]Cl on membrane surface. Membrane top layer wetting would occur due to the synergistic effect of surface hydrophilization and deposition of [Bmim]Cl, which not only induced the reductions of the membrane flux and rejection, but also further caused internal pore wetting. Therefore, the fouling mechanism during the VMD concentration might be divided into three stages, surface deposition, top layer wetting and internal pore wetting. Timely cleaning (i.e. before surface wetting) could effectively prevent the fouling deterioration (i.e. from surface deposition to surface wetting) and improve the VMD concentration process, resulting in a high flux recovery over 95%. Under the optimal conditions, a final [Bmim]Cl concentration as high as 65.5 wt% with a total [Bmim]Cl recovery over 99.5% was achieved, indicating that VMD was a promising candidate for concentrating ILs aqueous solutions.

1. Introduction

Lignocellulosic biomass, mainly consisting of cellulose, hemicellulose and lignin is a kind of promising renewable resource to be converted into biofuels through sugar fermentation [1–3]. However, pretreatment of the biomass is necessary to increase the hydrolysis rates [4,5]. Recently, pretreatment with ionic liquids (ILs) has attracted more and more academic and industrial interests due to the distinct features of ILs including hypotoxicity, nonvolatility, high-polarity and designability, etc. [3,6–10]. However, there are limited numbers of industrial processes employing ILs. One of the main reasons is that they are very expensive [5,11]. After pretreatment of the biomass by ILs, a large amount of water should be added to precipitate regenerated cellulose, resulting in a diluted ILs solution (about 5 wt%) [2,3]. Therefore, how to recycle ILs from aqueous solutions is a critical issue for their large-scale and cost-effective applications, which has been rarely researched [12].

The technique for recycling ILs was mainly affected by the properties of ILs, such as the size of ILs, hydrophobicity and hydrogen bonding ability of both cations and anions [13,14]. Hydrophobic ILs can be easily separated from water by decantation. But hydrophilic ILs are completely miscible with water in arbitrary proportions at ambient conditions, so it is more difficult to recycle hydrophilic ILs from water than hydrophobic ones. Due to the nonvolatility of ILs, distillation and vacuum evaporation were always attractive choices to dehydrate ILs aqueous solutions especially with high ILs concentration [12,15]. Besides, other techniques have also been utilized, such as adsorption, extraction, supercritical carbon dioxide and membrane separation, etc. [12,14]. Among

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http://dx.doi.org/10.1016/j.memsci.2016.07.017
0376-7388/

them, membrane separation technology is a commercially available choice and has realized industrial applications in the separation and purification of a large variety of compounds [16].

The pressure-driven membrane processes such as nanofiltration (NF) and reverse osmosis (RO) were mostly used to separate, concentrate or purify ILs [17–19]. Wu et al. [17] used NF membrane to separate ILs like 1-butyl-3-methylimidazolium bromide ([Bmim]Br) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) from their aqueous solutions, and the obtained maximum rejection rates were 67% and 60%, respectively. Haerens et al. [18] used three NF membranes and two RO membranes to separate and concentrate a 5% ethaline200 aqueous solution, respectively. They found that the rejection of ethaline200 by FilmTec NF90 membrane was very low (20%) while Desal DK, FilmTec BW30-XLE and FilmTec102326 membranes retained 88.0%, 90.5% and 91.1% of ethaline200, respectively, and after concentration, the maximum concentration of ethaline200 was up to 25%. Desal DK, Desal DL and Starmem 240 membranes were also used to remove water from the 1, 3-dimethylimidazolium dimethylphosphate ([C_1mim][DMP]) solutions with various feed concentrations [19]. The permeate fluxes of the three membranes all decreased significantly with increasing the feed concentration from 0 to 40 wt%. And, there was no rejection of [C_1mim][DMP] at high feed concentration (40–80 wt%) for the three membranes [19]. The osmotic pressure was found to be the limiting factor when using NF or RO to concentrate ILs solutions. That is, for concentrating ILs solutions, the pressure-driven membrane techniques cannot realize satisfactory concentration factor due to the intrinsically high osmotic pressure of ILs and the low rejection of ILs at high feed concentration. Pervaporation process is unaffected by osmotic pressure in principle and has also been attempted to separate ILs-water mixtures [18]. However, both membrane flux and recovery rate were very low resulting in an unfavorable requirement of lager pervaporation membrane area. Electrodialysis (ED), a kind of electrically-driven membrane separation technique, has also been investigated for the separation of ILs from their aqueous solutions [20,21]. ED was considered to be an effective method to concentrate ILs aqueous solution and a highest 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) recovery of 85.2% was achieved [20].

Membrane distillation (MD) is a kind of thermally driven membrane technique for removing water vapor from a heated aqueous solution across a hydrophobic and porous membrane [22–24]. MD process can be run at low hydrostatic pressure and low operating temperature, and can be coupled with solar energy or low-grade heat sources. Particularly, MD process is also unaffected by osmotic pressure. Very recently, using MD technique to concentrate ILs aqueous solution was reported in a short communication for the first time [25]. The authors used commercially available hydrophobic membranes to separate and concentrate two ILs solutions by a direct contact membrane distillation process, respectively. A tenfold concentration from 5 wt% to 50 wt% was obtained. Compared to the above-mentioned membrane techniques, MD seems to be a very promising candidate for separating or concentrating ILs aqueous solutions due to both high flux and high rejection.

It should be pointed out that MD may not be the best alternative to concentrate dilute ILs aqueous solution (e.g. about 5 wt%) from the economic aspect. Regarding the target concentration for directly reusing ILs to pretreat lignocellulosic biomass, it should be better to reduce the water content to that lower than 1 wt%. But on the other hand, there was also reports that an IL-water mixture (e.g. water content <40 wt%) could be well used to dissolve lignocellulosic biomass and the addition of proper amount of water (e.g. <20 wt%) accelerated the dissolution of lignin compared to the use of pure ILs [26]. Moreover, IL-water mixture was found to be more favorable than pure IL for cellulose dissolution and lignin depolymerization due to the hydrogen bond existing in the mixture [27]. Thus, combining conventional pressure-driven membrane techniques (NF or RO) with MD may provide a better and feasible strategy to recycle ILs for pretreating lignocellulosic biomass. That is, using NF or RO to separate, purify and pre-concentrate a dilute ILs solution (from about 5 wt% to 20–25 wt%), and then, using MD to further concentrate to 60–80 wt%. Accordingly, it is very necessary to study the MD concentration process of the ILs solution with high concentration. In addition, because of the high viscosity and high polarity of hydrophilic ILs, membrane fouling is expected to occur during MD process, which is also an important issue for investigation. To the best of our knowledge, no research has been done on the abovementioned two aspects.

In this work, a vacuum membrane distillation (VMD) process was carried out to separate and concentrate an IL solution with high concentration, where [Bmim]Cl was used as a model IL because [Bmim]Cl is a highly efficient solvent to dissolve and regenerate cellulose [20]. Because fabrication of porous hydrophilic membranes is quite mature and hydrophilic materials generally have higher thermal resistance than hydrophobic ones [28,29], surface hydrophobic modifications of hydrophilic membranes have been proposed for MD process [30]. Polyacrylonitrile (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. Firstly, a hydrophobic VMD membrane was developed by CF_4 plasma treatment of the PAN membrane. The chemical resistance of the modified PAN membrane was evaluated before VMD process. Then, the effect of operating parameters on VMD performance was investigated in detail. Finally, four different groups of VMD concentration processes with intermittent operation mode were performed to concentrate a 20 wt% [Bmim]Cl solution. Meanwhile, membrane fouling and wetting were also examined and discussed.

2. Experimental

2.1. Materials and chemicals

Hydrophilic PAN flat-sheet membrane with the molecular weight cut-off of 20000 Dalton was purchased from Sepro Membranes, Inc., USA. The commercial PAN membrane had a nonwoven fabric as support layer.

Sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol (C_2H_5OH) and methanol (CH_3OH) were of analytical grade, supplied by Xilong Chemical Co., Ltd., China. Argon (Ar) gas was purchased from Beijing Qianxi Gas Limited Company, China. Carbon tetrafluoride (CF_4) gas was purchased from Linggas Tianjin Limited Company, China. [Bmim]Cl was provided by Henan Lihua Chemical Reagent Company, China. Deionized (DI) water was produced by Millipore DI system. All chemicals were used as received without further purification.

2.2. Membrane surface modification

Plasma modification was performed in a YZD08-2C Plasma Reactor made by Scie-lab (Beijing) Tech. Co., Ltd., China. The diameter of plasma chamber is 10 cm and its length is 25 cm. 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 80 W for 1 min. The purpose of the