Journal of Membrane Science 490 (2015) 282–293

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Cellulose multilayer membranes manufacture with ionic liquid

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ARTICLE INFO

Article history:
Received 17 February 2015
Received in revised form
29 April 2015
Accepted 4 May 2015
Available online 9 May 2015

Keywords:
Cellulose
Membranes
1-ethyl-3-methylimidazolum acetate
Interfacial polymerization
Ultrafiltration

ABSTRACT

Membrane processes are considered energy-efficient for water desalination and treatment. However most membranes are based on polymers prepared from fossil petrochemical sources. The development of multilayer membranes for nanofiltration and ultrafiltration, with thin selective layers of naturally available cellulose has been hampered by the availability of non-aggressive solvents. We propose the manufacture of cellulose membranes based on two approaches: (i) silylation, coating from solutions in tetrahydrofuran, followed by solvent evaporation and cellulose regeneration by acid treatment; (ii) casting from solution in 1-ethyl-3-methylimidazolum acetate ([C2mim]OAc), an ionic liquid, followed by phase inversion in water. By these methods porous supports could be easily coated with semi-crystalline cellulose. The membranes were hydrophilic with contact angles as low as 22.0°, molecular weight cut-off as low as 3000 g mol^{-1} with corresponding water permeance of 13.8 L m^{-2} h^{-1} bar^{-1}. Self-standing cellulose membranes were also manufactured without porous substrate, using only ionic liquid as green solvent. This membrane was insoluble in water, tetrahydrofuran, hexane, N,N-dimethylformamide, 1-methyl-2-pyrrolidinone and N,N-dimethylacetamide.

1. Introduction

Water scarcity and access to clean water are major problems worldwide, directly affecting around 1.2 billion people, one-fifth of the world's population [1]. Even countries like Brazil known in the past for water abundance recently experienced alarming periods of drought. While seawater desalination has been an indispensible strategy in the Middle East as a source of drinking water, water treatment is essential everywhere in the world to assure sustainable life quality with high environmental standards. This includes treating municipal and agriculture wastes and recycling industrial effluents. Increasing need for safe drinking water, purification of effluents with small pollutant molecules and recovery of valuable products has placed membrane separation processes such as nanofiltration (NF) among the fastest growing technologies. The global membrane-based technology market for the treatment of industrial water and wastewater has been estimated to reach $5.5 billion in 2015, driven by different applications and motivations in different continents [2]. With economic growth, many countries are facing an enormous challenge of water pollution. For example, 55% of the groundwater in China has been reported to have poor water quality, while 78% of urban rivers are polluted to an extent that they might not serve as drinking water source anymore [3,4]. In European countries, which have been intensively fighting to reach high level of water quality, wastewater treatment has satisfactorily reduced the content of regular pollutants, but there is an increasing concern with emerging new pollutants such as endocrine disrupters. NF is under consideration for their elimination from waste. Besides environmental aspects, water reuse might become mandatory to bring water autonomy to desert areas in the Middle East far from the coast and therefore with restrict access to seawater. Water availability has also been a question of security and a reason for potential conflict in many countries.

For seawater desalination reverse osmosis is a well-established technology. Compared to reverse osmosis, NF membranes have higher flux with lower operational pressure, and subsequently, lower energy and lower costs are attained. NF becomes attractive when high salt rejection is not essential, for instance in applications, which do not require drinking water quality. In water scarcity areas, there is a potential for using NF to produce partially desalinated water for growing salt-tolerant crops. Besides NF, ultrafiltration (UF) is a well-established pretreatment process in water treatment and food industries. Nowadays many dairy products and beverages processing includes an ultrafiltration step

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http://dx.doi.org/10.1016/j.memsci.2015.05.009
0376-7388/

[5]. The potential of membrane technology to substitute more traditional separation processes in other industrial sectors is far from being completely explored. For instance recovery of metals from mining effluents or valuable chemical products like catalysts in chemical processes using membranes could be a profitable investment if better membranes would be tailored for these applications.

Membrane technology is recognized as energy efficient, easy to scale-up and environmentally friendly, with large perspective of expanding its application with the growing need of implementing more sustainable industrial processes. Membranes have been optimized with selectivity/permeation characteristics useful for quite diverse separation tasks. However the membrane manufacture itself could be much more sustainable and greener than it is now, as pointed out in excellent reviews recently published by Figoli et al. [6] and Szekely et al. [7].

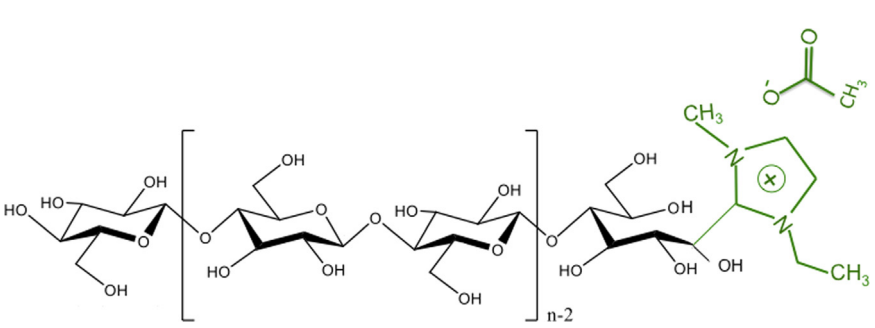
For more sustainable membrane manufacture two aspects have to be taken into consideration: (i) the membrane material and (ii) the manufacture process. Most membrane materials are produced from petrochemical sources. The most applied membrane manufacture process involves non-solvent induced phase separation (NIPS), solution casting followed by immersion in water. Large amount of solvents like N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) or 1-methyl-2-pyrrolidone (NMP) are frequently used for phase inversion. Furthermore membranes are frequently prepared as multilayers, with the asymmetric porous support being only the substrate, which is coated by additional solutions, constituted also by solvents, which are environmentally harmful. There is an increasing discussion on the possibility of banning their application in large scale and the need for finding alternatives at least for part of the manufacture processes. One of the main motivations of this work is to substitute at least part of the solvents used in the multilayer membrane manufacture by greener alternatives. We propose new the production of membranes based on natural cellulosic materials, in which ionic liquid is employed for coatings.

Another motivation for this paper is the following. For the manufacture of multilayer membranes, by dip coating, a solvent is needed, which dissolves the coating polymer without damaging the substrate. The coating layer is usually responsible for the selectivity and the porous substrate, which is frequently made of polysulfone, poly(vinylidene fluoride) or polyacrylonitrile, improves the mechanical stability without compromising flux. Multilayer membranes have been successfully applied for gas separation, pervaporation, nanofiltration and reverse osmosis. However the application of cellulose coating for multilayer membranes has been hindered by the lack of solvent for cellulose, which would not damage the morphology of the porous polymeric support. Cellulose (Scheme 1) [8,9] is one of the most abundant natural materials and has been used as starting material for membrane manufacture for long time. However cellulose can be hardly dissolved in common solvents due to strong hydrogen bonds and crystallinity. Chemically modified cellulose in the form of cellulose acetate has been successfully used in large scale for instance as reverse osmosis hollow fibers for seawater desalination or more recently as commercialized flat-sheet membrane for forward osmosis. However the use of cellulose itself has been restricted by the availability of industrial process for dissolution, which is currently done in aggressive medium, by chemical modification and regeneration. Cellulose fibers (e. g. viscose and rayon) and films (cellophane) are being produced for more than a century by the viscose technology, which uses a metastable solution of cellulose xanthogenate, with hazardous byproducts like heavy metals and H_2S [10]. The other well-known method for production of regenerated cellulose is the cuprammonium process also with negative environmental impacts [11]. In the 60s cyclic amine oxides have been proposed to dissolve cellulose [12]. N-methylmorpholine-N-oxide (NMMO) has then been used for production of films and membranes [13]. The membrane manufactured with cellulose/NMMO is considered a more environmentally friendly technology [7,14,15].

Ionic liquids have a growing interest being considered as green solvents [16] and can dissolve lignocellulosic biomass partially or in total, depending on the subsequent addition of water and solvent. It is important to mention that the production of ionic liquids is still costly. Due to the very low vapor pressure they are expected to bring less health risks to process operators, when compared to volatile solvents, but the toxicity of some ionic liquids in water might be a cause of concern [17]. Therefore for environmental and cost reasons the recovery of ionic liquids is important. Most of the recovery is done through the evaporation and precipitation processes, but a significant recovery of ionic liquid with a purity of 80%, using nanofiltration has been reported by Abels et al. [18].

Independent of the level of toxicity, ionic liquids are among the few solvents for cellulose. The dissolution of the cellulosic materials is driven by the anion of the ionic liquid, as reviewed by different groups [9,19–23]. Anions such as halides, carboxylates and phosphates have the ability to break the hydrogen bonds within the cellulose structure. We chose 1-ethyl-3-methyl imidazolium acetate [C2mim]OAc (Scheme 1), which is liquid at room temperature and highly miscible with water [19]; it has high dissolving power even in the presence of up to 10 wt% of water and relatively low viscosity compared to other ionic liquids, and shows no corrosion against stainless steel [19]. In addition, [C2mim]OAc has low toxicity, melting point lower than -20° C, viscosity 10 mPa s at 80 °C and high hydrogen bond acceptor abilities [20,21].

Hydrogen bond acceptor sites in the anion structure and lack of hydrogen bond donors in the ionic liquid cation favor the dissolution of cellulose. The acetate anion in the [C2mim]OAc can form hydrogen bonds with hydroxyl protons of cellulose. Heinze et al. [23] and Pinkert et al. [9] proposed that [C2mim]OAc forms even covalent bond between the glucose unit of cellulose and the imidazolium ring (Scheme 1). This is specific for acetates and not



Scheme 1. Schematic representation of cellulose and 1-ethyl-3-methylimidazolium acetate [C2mim]OAc covalent binding.