Journal of Membrane Science 451 (2014) 243–251

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Transport of organic acids through polybenzimidazole based membranes by 'Chemodialysis'

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ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form
6 October 2013
Accepted 8 October 2013
Available online 15 October 2013

Keywords:
Chemodialysis
Acid transport
Sorption
Organic acid
Polybenzimidazole

ABSTRACT

A method of 'Chemodialysis' (CD) involving polybenzimidazole (PBI) as a chemically active membrane material is demonstrated for carrying out selective separation of organic acids. PBI membranes possessing basic functionality selectively sorb acid, which is transported to the permeate side by concentration gradient. Transported acid is removed from the permeate side by using stripping agent. The sorption of non-acidic organic (glucose) and inorganic (NaCl) solutes being absent in PBI membranes, they were not transported on the permeate side. This offered high selectivity towards transporting acid. Three structurally different PBIs were evaluated as membrane materials for acid sorption and transport. Effects of variation in operational temperature, concentration and type of stripping solvent were evaluated. A single step process with appreciable acid transport rate coupled with very high selectivity convey promises of 'Chemodialysis' towards its applicability for the separation of organic acids from various industrial process streams (e.g. during production of organic acids by biological routes, which usually involve number of steps and extensive usage of chemicals for their recovery from fermentation broth). Moreover, this process holds additional benefit of low energy requirement, since it works with concentration gradient as the driving force and requires energy only for the circulation of solutions.

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1. Introduction

A large potential exists for the fermentation based production of organic acids; *viz*., lactic, citric, butyric, itaconic, glutamic, succinic, levulinic, *etc*. They are used in various industries such as food, pharmaceutical, cosmetics, textile, *etc*. Their use as the feedstocks for producing wide variety of chemicals is well reviewed [1–5]. Biotechnological synthesis of organic acids is advantageous over their chemical route, since cheap renewable biomaterials (lignocellulosic biomass, agro-industrial wastes, waste wood chips, waste paper, *etc*.) can be utilized [1–3,6–8]. The traditional recovery of acids from fermentation broth is quite lengthy and complicated. The primary technological barrier for the cost-effective acid production is attributed to their separation from the fermentation broth [5,9]. A conventional downstream processing for the acid recovery from fermentation broth includes acid precipitation in the form of salt (using calcium hydroxide), separation by filtration and re-acidification of calcium salt by using H_2SO_4 to obtain the acid [3,9–12]. This sequence leads to the formation of large quantity of sludge (gypsum), disposal of which is a major environmental concern today [9,10,12]. Separation and purification of acids by this route is energy intensive and requires large amount of chemicals, leading to high cost of acid production. As an example, separation and final purification stages for the production of lactic acid by fermentation account up to 50% of the total production cost [9].

Various alternatives are being evaluated for the acid separation from fermentation broth including reactive distillation [2,10,13], reactive extraction [9,10,14], adsorption [3,9,10,15], ion-exchange [3,12,15] and membrane based processes (diffusion dialysis [9,14,16], electrodialysis [4,5,9,10,14], nanofiltration combined with reverse osmosis [11,17] and liquid membranes [4,9,14]). In reactive distillation, acid with high purity can be obtained by the esterification of crude acid, distillation of formed ester, followed by its hydrolysis to yield pure acid [2,10,13]. This process requires a large quantity of alcohol than the stoichiometric amount, has limited yield and leaves behind a thick residue of impurities and partially reacted materials [13]. Though reactive extraction offers high selectivity, toxicity of the extractant to microbes is a major issue [9,10,14]. Adsorption and ion-exchange are associated with the need of pre-clarification of feed solution, regeneration of adsorption media and disposal of the generated waste [3,9,10,12,15]. Use of nanofiltration and reverse osmosis demands an additional step of pretreatment by ultrafiltration [11,17]. With diffusion dialysis, co-transport of non-acidic solutes and membrane fouling is reported [9,14,18]. Electrodialysis (ED) is not only energy intensive, but is also associated with additional drawbacks such as passage of glucose, salts and proteinaceous impurities through

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0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.10.014

the membrane [9,10,14]. This co-transport of non-acidic solutes affects purity of the separated acid. Though use of supported liquid membrane (SLM) offers advantages (lower energy consumption, higher separation factor and ability to concentrate the acid during its separation); it often suffers from membrane instability issue [9,14].

It could be inferred that most of the existing processes of acid separation have limitations, leading to low purity of acid, high production/separation costs or have detrimental effects on the environment. A more efficient and environmentally benign method is thus required, which would address techno-economical and environmental concerns associated with the current processes. We have observed that inorganic acids can be selectively transported through polybenzimidazole (PBI) based membrane by a process, termed as 'Chemodialysis' (the process aided by chemical interaction of basic PBI and inorganic acid as the solute) [19]. This method combines unique features of liquid membranes (higher separation factors due to selective acid uptake) and diffusion dialysis (polymeric membranes with low operational cost) using chemically active PBI as the membrane material. PBI, a family of thermo-mechanically stable polymers possessing high sorption capacity of inorganic acids (esp. H_3PO_4 and H_2SO_4) is widely used as a proton exchange membrane material for fuel cell (PEMFC) [19–22]. It is reported that H_3PO_4 molecules sorbed in PBI can exist either as a bound or free acid and the 'free acid' can be easily released by immersing the membrane in methanol or water [20,23]. A combination of sorption of inorganic acids in PBI and fast release of unbound acid was effectively utilized in our earlier work on transport of inorganic acids by 'Chemodialysis' [19]. The stripping of carboxylic acids from PBI resin using aqueous NaOH is reported [24]. It is also known that amine based extractants possess selective sorption of carboxylic acids but not their salts [25]. In view of this, objective of the present work was to investigate applicability of Chemodialysis (CD) for the transport of organic acids using structurally different polybenzimidazoles as membrane materials. Effects of acid concentration in the feed, type of stripping solution, nature of transporting acid, amount of acid sorption and temperature of operation on the acid transport characteristics were evaluated.

2. Experimental

2.1. Materials

3,3′-Diaminobenzidine, isophthalic acid (IPA), 5-*tert*-butylisophthalic acid (BuI) and 2,6-pyridinedicarboxylic acid (Py) were procured from Aldrich Chemicals. Polyphosphoric acid (PPA, ca. 84% as P_2O_5) was procured from Lancaster. D-Glucose was procured from Qualigens Fine Chemicals. Hexane, *N*,*N*-dimethyl acetamide (DMAc), lactic acid (90% aq. solution), acetic acid, citric acid, H_2SO_4, NaOH, Na_2CO_3, triethyl amine (Et_3N), $NaHCO_3$, NaCl, 3,5-dinitrosalicylic acid (DNSA) and calcium chloride ($CaCl_2$) (GR/extrapure grade) were obtained from Merck. All these chemicals were used without any further purification.

2.2. Synthesis of polybenzimidazoles (PBIs) and dense membrane preparation

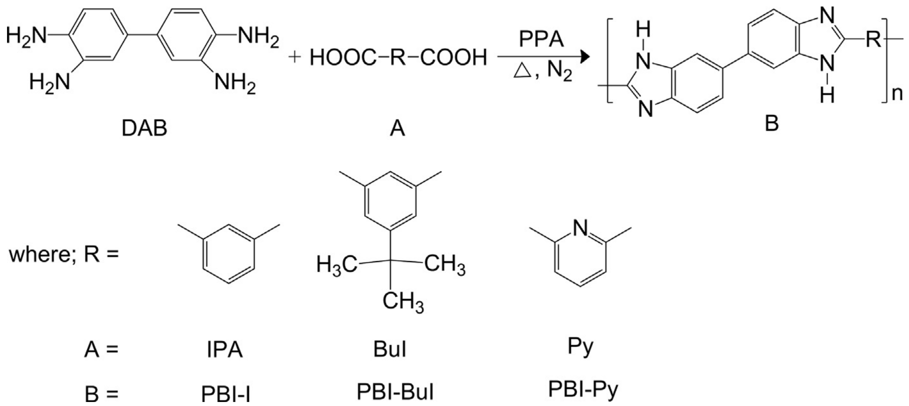
Three polybenzimidazoles (PBIs) based on 3,3′-diaminobenzidine and a dicarboxylic acid (IPA, BuI or Py) were synthesized as described earlier [21].

Typically, a three-neck round bottom flask equipped with a mechanical stirrer, N_2 inlet and an outlet fitted with $CaCl_2$ guard tube was charged with 2400 g of PPA, heated to 140 °C under constant flow of N_2 and added 80 g (0.3738 mol) of 3,3′-diaminobenzidine with stirring. An equimolar quantity of a dicarboxylic acid was added, the temperature was raised to 170 °C and maintained for 5 h. It was further raised to 200 °C and maintained for 12 h. Obtained reaction mixture was poured into stirred water in order to precipitate the polymer. It was sequentially washed with water, $NaHCO_3$ solution and again with water, till the filtrate was neutral to pH. The polymer was dried at 100 °C under vacuum for a week. It was further purified by dissolving in DMAc at 120 °C, centrifugation at 2800 rpm (2 h), followed by precipitation in stirred water. The precipitated polymer was dried at 100 °C under vacuum for a week. Structure and abbreviation of monomers and PBIs are given in Scheme 1.

The dense membranes were prepared by the solution casting method using 2% (w/v) PBI solution in DMAc on a flat glass surface. The solvent was evaporated at 80 °C under dry conditions. Formed membranes were peeled off from the glass plate, kept in water bath at 60 °C for 3 days in order to remove traces of solvent and finally vacuum dried at 100 °C for a week. The variation in obtained membrane thickness was within ± 3 μm.

2.3. Physical properties

Inherent viscosity of PBIs was determined using its 0.2 g/dL solution in conc. H_2SO_4 at 35 °C. They were characterized by FT-IR (recorded on Perkin Elmer-16-PC FT-IR spectrophotometer) and thermogravimetric analysis (TGA-5000, TA instruments, under N_2 atmosphere with a heating rate of 10 °C/min). Surface of the PBI based membranes was analyzed by scanning electron microscope (SEM) recorded on FEI QUANTA 200 3D.



Scheme 1. Structure and abbreviation of monomers and PBIs.

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