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Membrane separation processes: Optical resolution of lysine and asparagine amino acids

Pravin G. Ingole [a], Hari C. Bajaj [a,*], Kripal Singh [b]

[a] Discipline of Inorganic Materials & Catalysis, Central Salt & Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR-CSMCRI), Bhavnagar 364 002, Gujarat, India
[b] Reverse Osmosis Discipline, Central Salt & Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR-CSMCRI), Bhavnagar 364 002, Gujarat, India

HIGHLIGHTS

- The chiral composite membranes were prepared by interfacial polymerization.
- Membranes are mechanically stable and suitable for pressure driven separation.
- These membranes are useful for enantiomeric separation of racemic mixture of lysine and asparagine.
- Membranes exhibited high permeability and selectivity for D-enantiomers.

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ABSTRACT

Enantioselective thin film composite polymer membranes were prepared by interfacial co-polymerization of L-arginine with trimesoyl chloride in-situ on polysulfone ultrafiltration membrane. The chemical compositions of composite membranes were determined by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. Membranes are characterized by using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The optical resolution of α-amino acids was performed in pressure driven separation mode. The performances of membranes were compared in terms of flux, permselectivity, enantioselectivity and separation factor. The composite membranes exhibited 64–78% separation of amino acids. The membrane permeated D-enantiomers preferentially such that enantiomeric excesses of ~92% for D-enantiomer of lysine in permeates were achieved. The corresponding separation factors (α) were in the range of 4–21. As an immediate application, this study would help us design more efficient, nature-inspired selective chiral membranes that are able to separate enantiomers of chiral species.

1. Introduction

Optical resolution of enantiomeric drugs has fascinated great attention because of the increasing demands for enantiomerically pure drugs from government agencies. The biological response such as therapeutic activity, toxicity, smell or immune response is strongly dependent on the configuration of a given molecule, including its chirality [1]. Chirality plays an important role in the human life. The best example of chiral influence is given by nature itself. Most recognition systems in nature (e.g. enzymes, receptors) [2–9] distinguish paired of enantiomers. Majority of biologically active molecules including naturally occurring amino acids and sugars are chiral [10,11]. The instant challenge faced by membrane separation technology is to achieve the high selectivity while retaining the productivity. A superior membrane must be able to maintain its separation properties in the complex and rigorous environment. Optical resolution is a very important separation process, in the field of medicine and agricultural chemicals because of their effectiveness and safety. Optically active compounds are closely related to biological and pharmacological activity and their development as an effective method for producing optically active compound is very important. The separation of enantiomers from racemic mixtures is an easy and convenient route to get optically pure compounds. The enantioseparation can be performed by several methods including chromatography, diastereomer formation and preferential crystallization [12,13]. Chromatographic methods particularly gas–liquid (GLC) [14] and solid–liquid (HPLC) [15–17] chromatography are employed for the optical resolution at analytical scale. The liquid chromatography is an efficient method at preparative scale [18,19], however all chromatographic methods are batch processes [20]. Enantioseparation through membrane process is promising as membrane based processes are continuous, eco-friendly, economical and are easy to scale up.

Research towards solid membranes is focused on two alternatives: the use of chiral or achiral polymers. Optical resolution through solid

* Corresponding author. Tel.: +91 278 2471793; fax: +91 278 2567562.
E-mail addresses: ingolepravin@gmail.com (P.G. Ingole), hcbajaj@csmcri.org (H.C. Bajaj), kripal@csmcri.org (K. Singh).

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membrane is expected to be effective for a large amount of racemic compounds. Enantioselective permeation through a polymer membrane was first demonstrated using poly-L-glutamates with amphiphilic n-nonylphenoxy-oligo-ethyleneglycol side chains [21]. In diffusion experiments with tryptophan and tyrosin, selectivities of >8 for the D vs. L-isomers had been observed [22–25], and Teraguchi et. al. reported some chiral membranes for optical resolution [26–28]. C. Palet et. al. have synthesized a lot of membrane material for the enantiomeric separation of chiral compounds including aromatic amino acids and some chiral alcohols [29–31]. In our previous reports we investigate several types of enatioselective membranes for the optical resolution of chiral compounds [32–42].

Herein we report the preparation of chiral composite membrane using L-arginine, as a diamine monomer with a chiral carbon atom through interfacial polymerization with trimesoyl chloride. The composite membrane was prepared from the solutions of different concentrations to study the effect of monomer concentrations on the performance of the membrane as the performance of composite membrane largely depends on the composition of monomer solutions involved in interfacial polymerization [43]. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) have been used to study the superficial and internal morphology of the prepared polymeric membranes.

2. Materials and methods

2.1. Materials

Polysulfone polymers (Udel P-3500, Solvay Advanced Polymers, USA), L-arginine, DL-lysine and its enantiomers, DL-asparagine and its enantiomers, trimesoyl chloride from Sigma-Aldrich, USA were used. Other chemicals and solvents were of analytical grade from SD fine Ltd. India. Aqueous solutions of all reagents were prepared using high purity RO water obtained from ultra purifier water plant developed at CSIR-CSMCRI, Bhavnagar Gujarat, India.

2.2. Methods

2.2.1. Preparation of polysulfone membrane

The microporous polysulfone membrane was prepared by phase inversion technique as discussed elsewhere [44,45]. Polysulfone polymer (15 wt.%) dissolved in N, N-dimethylformamide at 60–70 °C under continuous stirring was evacuated to remove air bubbles and cast on a non-woven polyester fabric 'Nordyl' (Filtration Sciences Corporation, USA; thickness 90–110 μm) using doctor's blade under controlled conditions of temperature (25–26 °C) and relative humidity (30–35%). The membrane was air exposed for 30 s before precipitation in de-ionized water containing DMF (2%) and sodium lauryl sulfates surfactant (0.1%). It was removed from the precipitation solution after 30 min and washed thoroughly with de-ionized water to remove surfactant and solvent. The polysulfone membrane was characterized for porosity and molecular weight cut off (MWCO) value. The porosity of membrane was determined by capillary flow porometer (Porous Materials Inc., USA, Model CFP AEX 1500) using dry air. The molecular weight cut off value was determined by gel permeation chromatography (Water Inc., USA) using dextran solutes. The characteristics of polysulfone membrane are listed in Table 1.

2.2.2. Preparation of enantioselective composite membrane

The enantioselective composite membrane was prepared by coating chiral selective layer in-situ on the surface of polysulfone membrane by interfacial polymerization of L-arginine with trimesoyl chloride (TMC) as reported earlier [39–41]. Thoroughly washed polysulfone membrane was immersed in an aqueous solution of L-arginine (pH 13) for 5 min followed by draining off for 3–5 min to remove excess solution. It was then immersed into hexane solution of TMC of desired concentration for 1 min followed by draining off excess solution. The composite membrane obtained was cured in hot air circulation at 70–80 °C for 10 min whereby polymer layer attains chemical stability. The compositions of aqueous and non-aqueous solutions used for the membrane preparation have been given in Table 2.

Table 1
Characteristics of polysulfone membrane.

Entry	Characteristics	Value
1	Polymer concentration in casting solution	15% by weight
2	Thickness (micrometer)	60
3	MWCO	100 KDa
4	Bubble point pressure (psi)	47.345
5	Bubble point diameter (micrometer)	0.0563
6	Pure water permeability (PWP) at trans-membrane pressure of 344.77 kPa	371 L/m^{-2} h

2.2.3. Characterization of chiral selective layer

The selective layer of all thin film composite membranes was characterized by variable angle attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to elucidate chemical structure of the chiral selective layer. This technique allows identification of main functional groups present on the surface of polyamide membrane thereby it is possible to establish the chemistry of the selective layer. ATR-FTIR spectra were recorded on a Perkin-Elmer spectrometer (Perkin-Elmer, GX-1). The morphology of all membranes was studied by scanning electron microscope (LEO, FESEM model 1430) using dried, fractured in dry ice and gold sputtered samples at a potential of 5–20 kV. The topography of membranes surface was studied by Atomic Force Microscope/Surface Probe Microscope (Ntegra Aura Model NT-MDT-MOSCOW) in semi contact mode.

2.2.4. Resolution of racemic lysine and asparagine

The optical resolution of aqueous solutions (concentration 1.0 gL^{-1}) of racemic lysine and asparagine was performed in crossflow closed loop mode on reverse osmosis testing module. The experimental setup used in this study has been described in our previous work [42]. The experimental setup has four test cells connected in series. Each cell has a circular shape membrane of effective membrane area of 0.001954 m^2. The permeation experiments were conducted at fixed trans-membrane pressure of 100 psi up to 10 h to study the effect of time on the performance of the membrane.

2.2.5. Analysis of permeates

The concentrations of lysine and asparagine enantiomers in permeates were determined by high pressure liquid chromatography (LC-Net II/ADC System, Jasco Co., UK) equipped with PDA detector using Chiral Chrompak CR (+) column (Daicel Chemical Industries, Ltd., Japan) and perchloric acid (pH = 1.5) as mobile phase at a flow rate of 0.6 mL/min.

Table 2
Compositions of aqueous and non-aqueous solutions used for the preparation of selective layer.

Entry	Membrane code	Composition	
		Aqueous solution (w/w)	Non-aqueous solution (w/v)
1	M1	1% L-arginine	0.1% trimesoyl chloride in hexane
2	M2	2% L-arginine	0.1% trimesoyl chloride in hexane
3	M3	1% L-arginine	0.2% trimesoyl chloride in hexane
4	M4	2%L-arginine	0.2% trimesoyl chloride in hexane