Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.946725

55 (2015) 2700–2704
August

Taylor & Francis
Taylor & Francis Group

Molecularly imprinted membrane system for endocrine removal

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Received 30 October 2013; Accepted 16 June 2014

Molecular imprinting polymer (MIP) technique is well known for creating polymer materials with molecule selectivity in adsorption and separation. MIPs have mostly been prepared by bulk polymerization and grinding the resulting brittle polymer to prepare particles of the desired dimensions. However, this technique also suffered some backdrops such as limitation in its application due to powder shape and limitation in binding ability. To circumvent these problems, we had extended such a technique in the formation of membrane adsorbents using phase inversion imprinting technique. Namely, copolymerization of template-containing monomers with commercial scaffold monomer was achieved in such membranes in order to selectively separate the target molecules. One main feature of this system is the imprinted polymer forming film, which is possible to be used as filtration materials for selective separation. In the present study, we prepared the Bisphenol A (BPA)-imprinted membranes by copolymerization of various covalently linked functional monomer and polymer matrix, followed by phase inversion in water non-solvent for membrane formation. Herein, the evidence included advantage in phase inversion covalently imprinting technique in their binding natures to targeted endocrine compound as well as system selectivity in competitive study. Scatchard analysis indicated that the BPA-imprinted membranes exhibited high affinity and good selective binding of targeted endocrine compound relative to its analogs.

Keywords: Molecular imprinting membrane; Endocrine; Adsorption; Selectivity

1. Introduction

Synthetic receptor materials having selective guest recognition abilities have been well documented and might be a promising tool for separation and analytical methods due to its high efficiency and easy operation. Recently, an imprinting technique has been expanded to be used in the analytical fields of chemicals and drugs since molecular imprinting technique is an effective method for preparation of advantageous functional polymers which selectively recognize and separate a target molecule from mixture solution [1–3]. We have reported that the membrane technique of hybrid molecular imprinting is very useful, because the hybridization is successfully performed by only mixing imprinted polymer powders with scaffold polymer, which is available for membrane preparation. Such advantage results in effective applications to wastewater treatment containing endocrine disruptor, bisphenol derivatives [4], and medical field

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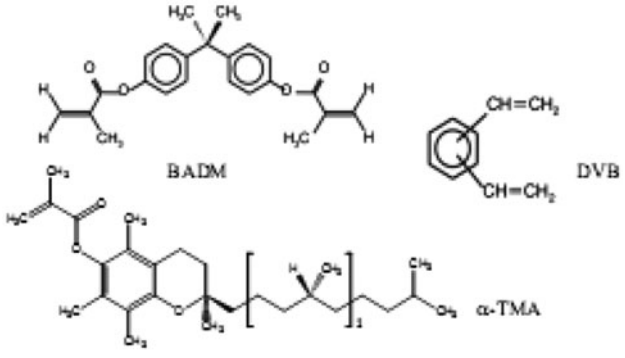
Presented at the Conference on Desalination for the Environment: Clean Water and Energy 11–15 May 2014, Limassol, Cyprus

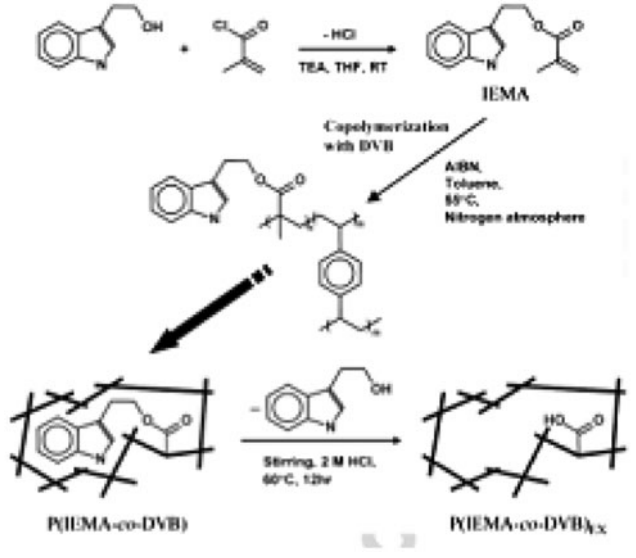
targeted to indole derivatives [5]. For instance, Bisphenol A (BPA), which is known as endocrine disruptor, affects the reproduction and development of animal organism in extra-diluted concentration [6]. Therefore, the materials having high recognition and selective capture to BPA are surely required in the viewpoint of environmental conservation in near future. For development of BPA adsorbents, molecular imprinting was applied as an alternative method [7]. We have studied that preparation and characterization of molecularly imprinted polymer (MIP), which selectively and effectively adsorbs BPA [8]. We also have extended such technique on uses of cross-linking polymer imprinted for indole [5] and tocopherol derivatives [9]. Herein, methacrylate containing indole ethanol (IE) and Tocopherol was selected as target molecule. For their targeted molecules, the evidence included for advantage in HMIP membrane technique in their binding on basis of selectivity of the HMIP membrane. Through these works, it will be focused and considered on viewpoint of hybridized imprinting technique, which contained fabrication characteristics of the MIP for membrane applications due to its powder shape. Accordingly, in order to fabricate selectively permeable membrane, we would propose hybrid MIP powder in porous membrane scaffolding as a new separation material. Results of our recent topics for imprinted behavior of BPA, indole, and tocopherol using cross-linked copolymer with divinylbenzene and each functional monomer are presented.

2. Methods

In the presence of 0.5 wt.% of 2,2-azobis(isobutyronitrile) under nitrogen atmosphere, the BPA-imprinted powder was prepared with Bisphenol A dimethacrylate (BADM) and divinylbenzene (DVB) (1:10 mol ratio) according to our previous report [4]. The resulting rigid copolymer was ground by pestle and mortar. Then, the BPA-MIP granule was sieved through 80-mesh sieve (177 μm aperture) and used for preparation of hybrid membranes.



Indole-3-ethyl methacrylate (IEMA) was used as functional monomer for imprinting indole-3-ethanol (IE) and synthesized by H3C esterification of IE and methacrylic acid chloride [5]. In the presence of AIBN, the resultant IEMA monomer was copolymerized with divinylbenzene (DVB) (1:10 mol ratio). In order to synthesize IE-imprinted polymer, IE segments from the P(IEMA-*co*-DVB) (Scheme 1) were extracted as follows: the P(IEMA-*co*-DVB) was hydrolyzed in 2 M HCl aqueous solution with stirring for 12 h at 60˚C. In order to prepare HMIP membrane, the resultant IE-imprinted polymer was hybridized with polysulfone (PSf) membrane by phase inversion process [4,5]; the imprinted polymer (1.5 g) powder was mixed in PSf (1.5 g) N-methyl-2-pyrrolidone solution. The mixture solution was spread on glass plate at 50˚C and then coagulated in water. As a reference, PSf membrane without MIP powder was also prepared. Functional monomer, α-tocopherol methacrylate (α-TMA), was copolymerized in covalent networks of divinyl benzene (DVB). For α-tocopherol (α-Toc) imprinting, esterification of α-Toc with metacryloyl chloride was carried out. The resulting TMA monomer was copolymerized with DVB (1:20 mol ratios) in the presence of AIBN. The copolymer was hydrolyzed in 2 M H_2SO_4 for 24 h to remove the template from the copolymer. The resulting MIP was hybridized in range of 50 wt.% toward scaffold membranes PSf. The scaffold membrane solution contained the MIP powder was similarly prepared by phase inversion process. As the reference, each scaffold membrane without MIP



Scheme. 1. Synthesis of functional monomer (IEMA) and illustration of preparation of IE imprint.

powder also was prepared in the same manner. Uptake experiments of substrate for resultant HMIP were carried out in ethanol or hexane solvent (20 mL) containing each 100 μM of α-Toc, δ-Toc, pentamethyl-6-chromanol (PMC), and 4-chromanol by shaken at 30°C for 24 h. The binding amounts of each substrate to HMIP membranes were calculated by concentration changes before and after the uptake experiments.

3. Results and discussion

3.1. Membrane characterization of HMIP

Each imprinted membrane was prepared under phase inversion process, in which water was selected as coagulation medium for each system [4,5,9]. This was because water showed high solubility for each solvent such as N-methyl-2 pyrrolidone.

Therefore, the polymer phase inversion process formed the solidified membrane, which involved the BPA-MIP powder inside. The resultant membranes were opaque in appearance and satisfactorily strong for experiments.

Fig. 1 shows SEM images of cross-section of (a) PSf and (b) HMIP membranes. These pictures were for hybridization successfully performed in PSf scaffold polymer. This was because that void space between the imprinted polymer powder and the scaffold was absent in the cross-section of the resultant HMIP membrane. The BPA-MIP powders were embedded in the scaffold polymer layer. In order to confirm interaction between BPA-MIP powder and scaffold polymer membrane in the HMIP membrane, IR spectra of the BPA-MIP powder and the PSf membranes were measured. In spectrum for BPA-MIP powder and PSf membrane, IR bands of 1,749 and 1,236 cm^{-1} were assigned to C=O stretching and S(=O)2 stretching, respectively. In PSf-HMIP membrane, it was found that the C=O and S(=O)2 stretching bands were shifted toward side of longer wavenumber of 1,751 from 1,749 cm^{-1} and also 1,244 from 1,236 cm^{-1}, respectively. It was also clear that the S(=O)2 band near 1,919 cm^{-1} for PSf membrane was disappeared in the PSf-HMIP membrane. These IR data suggested that there were interactions between the BPA-MIP powder and the membrane scaffold in the PSf-HMIP membrane.

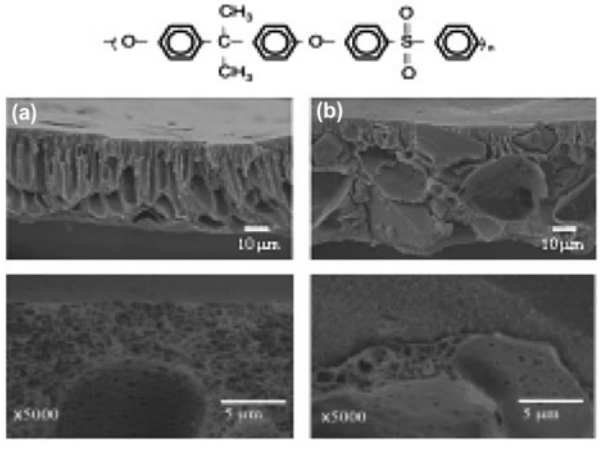


Fig. 1. SEM pictures of cross-section of (a) PSf and (b) HMIP membrane embedded for BPA-imprinted polymer powders.

3.2. Binding experiments by Scatchard analysis

In order to investigate the binding ability for BPA in the resultant HMIP membranes, we carried out the Scatchard analysis for BPA-MIP powder and the membranes. In the resultant plots, two straight-line regions were obtained except for those of non-hybridized PSf membrane. This means that there were sites of specific and non-specific binding for the BPA molecule in BPA-MIP powder and HMIP membranes. From the straight area, in the range of 1–150 μmol/g of binding amounts, binding equilibrium constants (Ka) were estimated (Table 1). In the slope data of 1–150 μM region, the obtained value of Ka for the PSf-HMIP membrane was almost similar to that of the BPA-MIP powder, while the binding capacity for PSf-HMIP membrane was about 14 times higher than that of the BPA-MIP powder. Therefore, it was clear that the PSf-HMIP membrane exhibited effective binding ability to BPA relative to the BPA-MIP powder.

Table 1
BPA binding abilities in BPA-MIP powder, scaffold PSf membranes, and HMIP membranes containing 50 wt.% of BPA-MIP powder for BPA binding by Scatchard analysis

	Binding constants (Ka) (M^{-1})	Binding capacity (n) (mol g^{-1})	Binding constants (KaH)[b] (M^{-1})
BPA-MPA powder	19,700[a]	20[a]	2,290
PSf membrane	480	310	480
PSf-HMIP membrane	20,700	279	8,970

[a]The value in specific binding region was shown.
[b]As non-specific parameter, the value of equilibrium constant (KaH) was estimated from high concentration region.

3.3. Permselective separation of mixture by HMIP membranes

Fig. 2 compares HPLC chromatogram charts of the mixed substrate solution containing BPA, BPE, BPF, and HPA in (a) the PSf membrane and (b) the PSf-HMIP membrane. Each peak area of substrates was observed before and after permeation through the membrane. For the PSf membrane, insignificant changes of each peak intensity were determined in four substrates as obtained before and after the permeation. On the other hand, in the PSf-HMIP membrane, the peak intensity of HPA (peak 1) was almost kept constant before and after the permeation. It was noted that the peak intensities of bisphenol derivatives remarkably decreased by the permeation. Especially, the decrease of the BPA peak was larger than those of other BPE and BPF. Accordingly, the HMIP membranes effectively separated the mixture of bisphenols and HPA by permeation experiments. Table 2 lists the obtained values of binding amounts and imprint efficient, α_i, each sorbent retained by the each HMIP membrane. Almost similar to that of the α-TMA-MIP powder was observed in HMIP, while the binding capacity for HMIP membrane was about 2–4 folds higher than that of the α-TMA-MIP. Therefore, it was clear that the HMIP membrane exhibited effective binding ability to α-Toc relative to that of the α-TMA-MIP. This indicated that the covalent imprinting of α-Toc was able to recognize both chemical structures of tocopherol derivatives with or without methyl group in their chemical structures. Furthermore, the reason of high recognition ability for α-Toc in the HMIP membrane was considered that surrounding environment of the scaffold polymer changed the binding ability of the MIP powder.

Table 2
Binding amounts, μmol/g, of substances and imprint efficient (αi) of substrates

Sorbents	α-Toc	δ-Toc	PMC	4-chromanol
α-TMA-MIP	11.8 (1)	5.8 (0.49)	3.7 (0.31)	0.5 (0.04)
PSf	20.5 (1)	16.6 (0.81)	18.3 (0.89)	10.3 (0.50)
PSf-HMIP	42.7 (1)	25.8 (0.60)	21.6 (0.51)	21.1 (0.49)

Fig. 3 shows HPLC chromatogram charts of the mixture solution containing pyrrole, HQ, IE, and indole before and after the solution was permeated through the membranes. For the PSf membrane, insignificant changes in each peak intensity were found for four substrate peaks obtained before and after the permeation. On the other hand, for the HMIP membrane, the peak intensities of pyrrole and HQ were almost kept constant before and after the permeation and the peak intensities of IE, and indole remarkably decreased by the permeation.

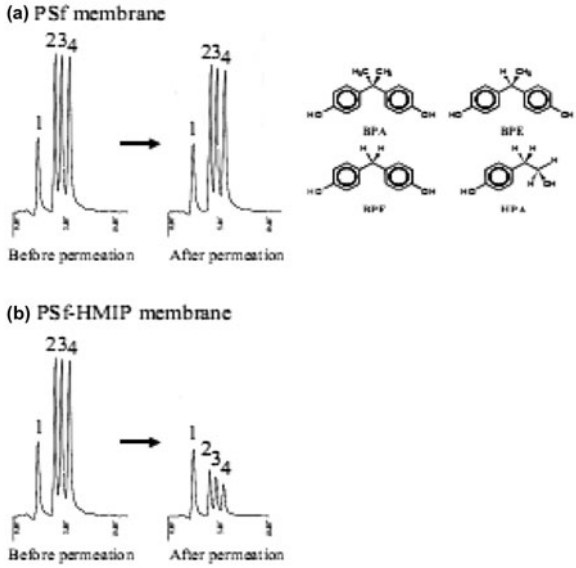


Fig. 2. HPLC charts of aqueous solution containing HPA (1), BPF (2), BPE (3), and BPA (4) before and after permeation by the PSf and PSf-HMIP nmembrane.

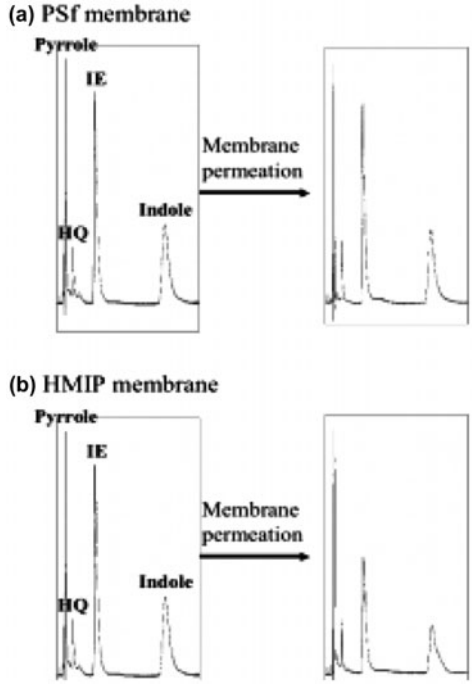


Fig. 3. HPLC charts of each 25 μm of Pyrrole, HQ, IE, and indole in mixture aqueous solution before and after permeation by (a) PSf and (b) HMIP membrane.

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