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Selective separation of Bisphenol A from aqueous solution using supported ionic liquid membrane

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ABSTRACT

The objective of the present study was to remove of Bisphenol A (BPA) from aqueous solution using supported ionic liquid membranes (SILMs). For SILM experiments polyvinyldene fluoride (PVDF) membrane was used as a support medium. In this work the preparation of SILM, transportation experiments, pH mechanism and percentage permeation were reported. Ionic liquids based on different cations such as phosphonium, imidazolium, ammonium and pyridinium were used. SILM experiments were carried out at 100 mg L^{-1} of initial concentration of BPA with and without pH control. Obtained results proved that % permeation of BPA from feed phase to receiving phase was 44% for $[TBP][PF_6]$ followed by 39.88% for $[OMIM][PF_6]$. A Maximum of 62% permeation was obtained for $[TBP][PF_6]$ with pH control. The permeation rate followed the order: $[TBP][PF_6] > [C_8MIM][PF_6] > [C_2DMIM][PF_6] > [THTDP][Br] > [BTNH][BTA] > [TBTDP][BTMPP] > [THTDP][Cl] > [MTONH][Cl] > [BMPYR][BTA]$. After 24 h of the experimentation weight loss of the membrane was noted to be 2% as a maximum, which confirms the good mechanical stability of the SILM. Effect of pH on membrane separation and its detailed mechanism was studied. Morphological and elemental analysis of membrane before and after the immobilization was also carried out.

1. Introduction

The environment has been continuously polluted due to the introduction of a large number of chemical substances by humans through their various domestic, industrial and agricultural activities. Many of these are designated as geomorphological materials and others have been considered to perform a variety of functions such as healing the illness or killing pests and waste weeds. It is believed that some chemicals function as hormones in the living human and animal bodies and may prove hazardous to human health and ecosystem. These designated chemicals are known as endocrine disrupting chemicals (EDCs), and in recent times become a social issue [1]. Among those chemicals Bisphenol A (BPA) is such a kind and is a known endocrine disruptor. BPA has been known to be estrogenic compound since the mid 1930s [2]. Evidently some of these chemicals are functional but at the same time many are toxic and they harm the environment, human as well as animal health.

Bisphenol A was first synthesized in 18th century and is usually found in detergents, resins, plasticizers and monomers in plastic packaging materials [3]. The major sources of human exposure to BPA occur through direct contact in the workplace or at home, or through intake of contaminated water, food, or air [4]. Since 1957, BPA was used mainly to make plastics. Almost all food and beverage cans made of epoxy resins are coated with BPA. In paper industry it is used to develop carbonless copy paper and thermal paper. In September 2010, Canada became the first country to declare BPA as a toxic substance [5]. In the European Union and the Canada, BPA use is banned in baby feeding bottles. Because of its adverse health effects and its carcinogenicity there is a need to remove BPA from aqueous phase. Several methods were proposed and published in literature, details of several process was described by Gong et al. [6]. Table 1 describes the molecular structure and properties of BPA.

In recent years, room temperature ionic liquids (RTILs) are gaining attention and interest towards research in lab scale and industrial scale due to their various advantages over traditional organic solvents. Ionic liquid is an organic and inorganic anionic media combined with organic cation which is having unique physicochemical properties such as being air and moisture stable, tunable viscosity, negligible volatility, miscibility with organic solvents (some miscible with water) and having good thermal stability. These RTILs are alternatives to other conventional organic solvents in many fields of catalytic, synthetic, and electrochemical applications [7]. Furthermore, these RTILs better known as green solvents have been used in separation sciences immobilized with membranes which are so called the supported ionic liquid membrane

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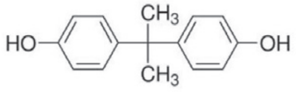
Table 1
Molecular structure and properties of BPA.

Molecular structure (IUPAC name)	Molecular formula (mol. wt.)	pKa	Density (g/cc)	Water solubility (mg/L)	MP/BP (°C)
 4,4'-(propane-2,2-diyl)diphenol	$C_{15}H_{16}O_2$/228.29 g mol^{-1}	9.7	1.2	120–300	158/220

for the extraction of different pollutants from effluent streams [8–10] and industrial gases [11,12]. The cellulose acetate filters impregnated with an aqueous hemoglobin solution was the first reported supported liquid membrane (SLM) [13].

A SILM is one of the three phase liquid membrane system in which the membrane phase (ionic liquid) is held by capillary forces in the pores of microporous polymeric or inorganic film. This method has the great advantage of energy preserving, low capital and operating cost and possibility to use expensive extractants such as RTILs, due to the small amounts of the membrane phase required. More details of the principles and applications of SILM technique has been reviewed and reported several times in literature [7,14–16]. It is well known fact that every process has some advantages and disadvantages. The stability of the SLMs is one of the major limitations of this separation technique. In this study, high viscous ionic liquids were used to make the SLMs more stable. Table 2 describes the different cations used in this study with their corresponding acronyms and chemical formulae.

The objective of the present study was to study the separation of BPA from aqueous solution using SILM. Ionic liquids were chosen based on their commercial availability as well as viscosity. The parameters such as membrane weight loss, permeation rate, effect of pH with respect to time were studied. The mechanism of BPA permeation through the SILM was also proposed. Further, scanning electron microscopy was used to study the morphology of the SILM before and after transport experiments.

2. Materials and methods

2.1. Reagents used

All chemicals used were purchased from Sigma Aldrich until unless stated and were used without further purification. The ionic liquids used in this study were: Tryhexyltetradecylphosponiumchloride [THTDP][Cl] (CYPHOS® IL 101), Tryhexyl-tetradecylphosponiumbromide [THTDP][Br] (CYPHOS® IL 102), Trybutyltetradecylphosponium-bis(2,4,4-trimethylpentyl)phosphinate [TBTDP][BTMPP] (CYPHOS® IL 104), Methyltrioctylammoniumchloride [MTONH][Cl] (Aliquat®336), Tetrabutylphosphonium-hexaflourophosphate [TBP][PF_6], 1-Octyl-3-methylimidazolium-hexaflourophosphate-[C_8MIM][PF_6], Butyltrimethylammoniumbis(trifluoromethylsulfonyl)amide [BTNH][BTA], 1-Butyl-1-methylpyrrolidiniumbis(trifluoromethylsulfonyl)amide [BMPYR][BTA] and 1-Ethyl-2,3-dimethylimidazoliumhexaflourophosphate [C_2DMIM][PF_6]. The pH alterations of the aqueous solutions were done with adding either H_2SO_4 or NaOH. HCl, H_2SO_4 and NaOH were purchased from Merck, India. PVDF membranes used in this study were procured from Millipore, India. All the experiments were carried out at 300 RPM and all the reported results were average of three experiments. Table 3 describes the physical characteristics of ionic liquids used in this study.

2.2. Preparation of standard stock solution

A 100 mg L^{-1} of standard aqueous solution of BPA was prepared in 1 L of tap water by dissolving the required amount of BPA. The detailed characterization study of BPA was given elsewhere [1]. Table 4 describes the tap water characteristics of River Brahmaputra water before and after the treatment (during winter season) used in this study [17]. Due to the sparing solubility of BPA, the solution was stirred at 80 °C on a hot plate about 2 h to obtain the clear solution. The small test solutions of various required ranges were prepared by proper dilution of stock solution with tap water. Calibration curve was prepared by taking known concentrations of BPA (10–50 mg L^{-1}) analyzed through UV–vis spectrophotometer (Thermo Scientific Spectra scan UV 2300) at a wave length of 277 nm.

2.3. Preparation of the SILM

A porous hydrophilic Polyvinyldene Fluoride (PVDF) membrane (Durapore® Membrane filters, Millipore, India) was used as the support to maintain the ionic liquid as a carrier in the membrane. Supplier specifications indicated pore size of 0.45 μm, diameter of 90 mm, thickness of 125 μm and porosity of 70%. The PVDF membrane was soaked in a particular ionic liquid in a petri dish. These membranes were covered and left in soaked state for 24 h. The membrane was then wiped using Pro-wipe tissue paper and left in the vacuum desiccator for 24 h to dry off the excess ionic liquid remaining on the membrane surface. After that the membrane was weighed on a balance and its weight was recorded. These membranes were used as the supported ionic liquid membrane for the transport experiment. Similarly, this process was repeated for all the ionic liquids used in this study. Before and after the preparation of supported ionic liquid membrane, the respective morphology and elemental analysis study of the PVDF membranes was done by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) respectively.

2.4. Transport experiment

The transport studies were carried out at 25 ± 3 °C using a glass diffusion cell with two independent compartments, 100 mL volume each and placed on a magnetic stirrer as shown in the schematic diagram (Fig. 1). The prepared SILM was sandwiched between the two cells by applying vacuum grease to the glass cells to prevent slipping of glass cells and leakage of feed and permeate solutions. The entire assembly was tightened by a stainless steel screw connector. The effective membrane contact area (A) between the glass cells is 12.0 cm^2.

The transport experiments were carried out with and without pH control on the feed phase. For all the experiments 0.01 N HCl ($pH = 2.1 \pm 0.1$) was used as stripping/permeate side solution. The model solution consisted of 100 mg L^{-1} BPA (aq.). Sodium hydroxide was used to maintain the initial pH approximately equal to 11.1 ± 0.1 on feed side whenever required. 100 mL of BPA solution was taken as the feed phase (F) and receiving phase (permeate (P)) was 0.01 M aqueous solution of HCl ($\sim pH = 2.1 \pm 0.1$). The transport experiments for the SILM begins by adding 100 mL of each solution into their respective glass cell compartments (feed and permeate).