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Importance of uniform distribution of impregnated trioctylphosphine oxide in hollow fiber membranes for simultaneous extraction/stripping of phenol

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HIGHLIGHTS

- Trioctylphosphine oxide impregnation in polypropylene membranes was optimized.
- Air drying conditions were found to be crucial to achieve uniform distribution.
- Morphological analysis indicated uniform distribution under optimal conditions.
- Impregnated membranes were used for simultaneous extraction and stripping.
- High removal rates, efficiency and stability were achieved during phenol extraction.

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ABSTRACT

Trioctylphosphine oxide (TOPO) was impregnated in polypropylene hollow fiber membranes. The impregnation process was optimized and a uniform distribution of TOPO was achieved within the membrane walls, when the membranes were treated with a carrier solution containing 600 mg/L TOPO, and air-dried for 30 min at a low air flow rate (Re_{air} = 9.2). The resulting extractant impregnated hollow fiber membranes (EIHFM) were characterized by scanning electron microscopy, water entry pressure, gas permeability and mercury porosimetry analysis, all of which showed significant structural and morphological changes in the EIHFMs; pore size, porosity and tortuosity were estimated to be 0.5 μm, 0.09 and 33, respectively. The EIHFMs exhibited high mass transfer rates and removal efficiency during simultaneous extraction and stripping of phenol. At an initial phenol concentration of 200 mg/L, 99% phenol was extracted from the wastewater within 7 h, whereas more than 91% phenol was recovered in the stripping solution, yielding a concentration factor of 1.79. The performance of the EIHFMs did not change significantly during consequent operations under identical conditions, indicating the stability of impregnation. These results suggest that uniformly impregnated TOPO-based EIHFMs can be promising in the recovery of phenols from wastewater.

1. Introduction

Phenol and its derivatives are aromatic compounds of high commercial interest as they are used as raw materials in manufacturing various chemicals, plastics, pulp/paper, dyes, pigments, adhesives and pharmaceutical products [1]. Unfortunately, they are also common pollutants in industrial wastewater. The presence of phenols in industrial effluents is a matter of concern as they exert adverse effects on aquatic ecosystem due to their high toxicity, molecular recalcitrance and high reactivity, which may result in formation of even more hazardous compounds [2–4]. Hence, it is important that phenol and its derivatives be removed from industrial effluents before their discharge into natural water streams.

Liquid-Liquid extraction using immiscible organic solvents is widely used in the removal of phenol from wastewater [5–8]. However, this technique exhibits certain limitations associated with phase dispersion and emulsion formation, which leads to difficulty in phase separation at later stages [9]. Membrane-based liquid/liquid extraction, especially the use of supported liquid membranes (SLM), can prevent phase dispersion and offers the advantages of compact design, low solvent and energy requirement, low operating cost and high mass transfer rates. However,

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SLMs are inherently unstable as the organic solvent is gradually lost from the membranes due to erosion [10,11]. Non-dispersive solvent extraction can also be performed using solvent encapsulated polymeric microcapsules [12,13]. However, these microcapsules cannot perform simultaneous extraction and stripping.

Recently, Praveen and Loh [14–17] developed extractant impregnated hollow fiber membranes (EIHFMs) for the extraction of phenol from wastewater by impregnating polypropylene hollow fiber membranes with a solid organophosphorus extractant, trioctylphosphine oxide (TOPO) [18]. The EIHFMs exhibited high stability, high mass transfer rate and high partitioning capacity for phenol. Moreover, a very small amount of organic solvent was required in EIHFM preparation, whereas no organic solvents were needed during EIHFM-based extraction, which made this technique 'solventless'. However, the EIHFMs failed to perform simultaneous extraction and stripping of phenol due to the non-uniform distribution of TOPO within the supporting membranes, which resulted in a high mass transfer resistance for phenol diffusion through the membranes.

So far, the approach used in EIHFM preparation has been based on soaking hydrophobic membranes in dichloromethane (DCM) enriched with a high concentration of TOPO; DCM was subsequently evaporated from the membranes to facilitate TOPO impregnation in the membrane pores and surfaces [14–17]. The major drawback of this approach was that DCM evaporation was not performed under controlled conditions. The carrier solvent exited the membranes mainly through the outer surface resulting in a much higher deposit of TOPO on the outer membrane surfaces, as compared to that in the membrane walls or the inner membrane surfaces. We anticipated that this limitation in EIHFM preparation could be addressed by controlling the solvent evaporation from the membranes through careful adjustment of the drying time and the air flow rate during drying. DCM could also be forced to exit the membranes through the inner membrane surface by pumping air through the tube sides of the membranes, or by slowing DCM removal through the outer membrane surface by submerging the solvent soaked membranes in water. Using this approach, EIHFMs with uniform extractant distribution could be prepared which could be used for simultaneous extraction and stripping of phenol. The resulting EIHFMs would then be used as both, a membrane contactor, as well as a partitioning phase. Apart from the changes in the impregnation strategy, a systematic and detailed characterization of the EIHFMs is also needed for better understanding of the changes in the morphology and mass transfer properties of the membranes.

The objective of this research was to design and optimize the membrane drying process in EIHFM preparation to achieve a uniform distribution of TOPO within the polypropylene membranes. A detailed characterization of the EIHFMs was undertaken to determine the optimal conditions which could maximize TOPO impregnation. The enhanced performance of the EIHFMs with uniformly distributed extractant was investigated through simultaneous extraction and striping of phenol from synthetic wastewater using a contactor module packed with the EIHFMs. The novelty of this research lies in developing a methodology for uniform TOPO impregnation within polymeric membranes that would result in better performance to simultaneously extract and strip phenol in the phenol recovery process.

2. Materials and methods

2.1. Reagents and analytical methods

All the chemicals used in this research were of analytical grade and were purchased from Merck or Sigma-Aldrich. The chemicals were used as received from the suppliers.

Phenol concentration in the aqueous phase was determined by measuring absorbance at 270 nm using a UV spectrophotometer (UV-1240, Shimadzu, Japan). Phenol concentration in the solid phase was calculated using mass balance from the difference between initial phenol concentration in the wastewater and total phenol concentration in the two aqueous phases (wastewater and stripping solution) at any time. The concentration factor was calculated as the ratio of the concentration of phenol recovered in the stripping solution to the initial feed phenol concentration.

2.2. EIHFM preparation and characterization

2.2.1. Membrane module

The membrane modules were prepared by potting Accurel PP 50/280 polypropylene membranes (Membrana GmbH, Germany) using epoxy resin into contactors that resembled shell-and-tube heat exchangers as described in Loh et al. [19]. The specifications of the modules are given in Table 1.

2.2.2. TOPO impregnation

The carrier solvent (DCM) containing TOPO was circulated through the shell side at 5 ml/min for 2 h to impregnate TOPO into the membranes. This was followed by the drying process wherein water was circulated in the shell side to prevent DCM evaporation through the outer surface of the membranes, while air was pumped through the lumen side at a controlled flow rate. The EIHFM preparation process was varied by changing TOPO concentration in DCM (200, 400 and 600 g/L), air flow rate (Re_{air} = 4.6, 9.2 and 18.4) and drying time (15, 30, 60 and 90 min) to determine the optimum impregnation conditions. Re_{air} was calculated using air velocity in the lumen of the membrane module, the inner diameter of the membranes, and the density and viscosity of air at room temperature. After DCM had been evaporated, the lumen of the hollow fiber membranes was flushed with water to remove loosely attached TOPO from the membrane surface followed by a leakage test. All the experiments were conducted in triplets for reproducibility.

2.2.3. EIHFM characterization

The EIHFMs were characterized by measuring the amount of TOPO impregnated, by visualizing the cross sections and the surfaces of the EIHFMs under SEM, and by performing liquid entry pressure of water (LEPw) test, gas permeability test and mercury porosimetry to observe any structural or morphological changes and to determine the pore size, porosity and tortuosity of the EIHFMs.

The amount of TOPO impregnated into the fibers was determined by measuring the weight of the module before and after the impregnation of TOPO. The distribution of TOPO in the membrane cross-sections and on the surfaces was analyzed using Scanning Electron Microscopy (SEM) (JEOL JSM 5600-LV) after sputtering the membrane samples with platinum.

Table 1
Specifications of the membrane contactor.

Characteristics	Values
Casing material	Glass
Casing inner diameter	0.7 cm
Membrane inner diameter	280 μm
Membrane thickness	50 μm
Pore size	0.2 μm
Porosity	0.5
Effective Fiber Length	20 cm
Number of Fibers	50
Effective shell volume	6.5 ml
Effective lumen volume	0.62 ml