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Trioctylphosphine oxide-impregnated hollow fiber membranes for removal of phenol from wastewater

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ABSTRACT

Trioctylphosphine oxide (TOPO) was immobilized in polypropylene hollow fiber membranes for removal of phenol from wastewater. Scanning electron microscopy showed white deposits of TOPO dispersed non-uniformly within the resulting extractant-impregnated hollow fiber membranes (EIHFM). The EIHFMs manifested high adsorption capacity and mass transfer rates, with adsorption equilibrium attained within 10–30 min of operation. Experimental equilibrium adsorption capacities with a feed of 1000 mg/L phenol were 32, 42, 52 and 57 mg/g at 50, 100, 200 and 400 g/L TOPO, respectively. During repeated operation with 1000 mg/L phenol, the adsorption capacities of the EIHFMs remained stable at 32.2 ± 1.3 and 52.3 ± 0.9 mg/g for 10 subsequent runs at TOPO concentrations of 50 and 100 g/L, respectively. The EIHFMs, when used as adsorbents in a two phase partitioning bioreactor, alleviated substrate inhibition on *Pseudomonas putida* by rapidly adsorbing phenol to sub-inhibitory levels. Biodegradation of 1000 and 2000 mg/L phenol was completed within 26 and 36 h, respectively. These results suggest that the EIHFM is a promising technology for solventless extraction of aromatic compounds in wastewater treatment.

1. Introduction

Phenol and its derivatives are used as raw materials for manufacturing a wide variety of useful chemicals including dyes, polymers, pharmaceuticals and pesticides. As a result, these aromatic compounds are prevalent in industrial effluents and are major sources of water pollution. The discharges from oil refineries and coal conversion processes, too, are rich in these contaminants with concentrations above 6 g/L [1]. Phenols are highly toxic and recalcitrant compounds and are major threats to the ecosystem. They may cause severe health hazards for humans upon entering the body, while their presence in water can be detrimental for the aquatic life [2]. The removal of phenols from industrial wastewater is, therefore, crucial to prevent contamination of natural water streams and subsequent environmental damage.

Liquid–liquid extraction using an immiscible, organic solvent has been widely used for the removal of phenol from wastewater [2–5]. The main drawback of solvent extraction here is phase dispersion which requires high energy input and results in emulsification and consequent separation problems [6,7]. Membrane based technologies such as hollow fiber supported liquid membrane (HFSLM) can alleviate these problems by facilitating dispersion-free contact between the phases. However, HFSLMs are inherently unstable due to the gradual erosion of the liquid membrane from the polymeric support by the shear forces generated by the aqueous phase flowing over the liquid membrane [8].

The formation of liquid membranes often requires the use of extractants dissolved in a non-volatile carrier solvent to achieve high distribution coefficients for the solute [9,10]. Some of these extractants such as trioctylphosphine oxide (TOPO) exists as white crystalline powder at room temperature. In this research, we propose a novel technique to immobilize solid extractants within the pores of hydrophobic hollow fiber membranes for the separation of phenol from wastewater. The strategy is to create HFSLM on the polypropylene membranes using TOPO dissolved in a volatile carrier solvent and then evaporate the solvent to entrap the TOPO on the membrane pore walls. Using membranes of small pore size, TOPO can be effectively confined and the performance of the resulting extractant impregnated hollow fiber membrane (EIHFM) should be stable.

When the hollow fiber supported liquid membrane metamorphoses into extractant-impregnated hollow fiber membranes, liquid–liquid extraction is transformed into a solventless adsorption process. While this technique is more economical and eco-friendly, its simplicity obviates complex polymerization reactions as used in the preparation of liquid-core microcapsules [11,12] or impregnation of conventional adsorbents [13]. Moreover, the hollow fibers based design also inherits the advantages of large specific surface area, compact design and flexible equipment configuration. In the

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first ever application of EIHFMs to the best of our knowledge, EIHFMs with varying TOPO content were prepared and characterized; the EIHFMs were used for adsorption/desorption of phenol and the feasibility of applying the EIHFMs as the partitioning phase in a solid/liquid two phase partitioning bioreactor (TPPB) was demonstrated in two-phase biodegradation of phenol.

2. Materials and methods

2.1. Microorganisms, culture conditions, and chemicals

Pseudomonas putida ATCC 11172 was used in this study. Stock cultures were maintained on nutrient agar slants by periodic subtransfer and were stored at 4 °C. The microorganisms were grown in a chemically defined mineral medium supplemented with phenol in a 500 mL Erlenmeyer flask on a shaking water bath (GFL 1092, Burgwedel, Germany) at 30 °C and 150 rpm. The composition of the mineral medium has been described elsewhere [14]. All media (except phenol), pipette tips, and Erlenmeyer flasks fitted with cotton plugs were autoclaved at 121 °C for 20 min before use. Prior to inoculation, cells were induced by transferring stock culture from the nutrient agar slant to the mineral medium containing 200 mg/L phenol as the sole carbon source. Activated cells in the late exponential growth phase were used as inoculum for all the experiments.

All the chemicals used in this research were of analytical grade. Phenol was dissolved in 0.02 M sodium hydroxide to prepare stock solution of 10 g/L. The stock solution of 400 g/L TOPO was prepared in dichloromethane (DCM).

2.2. Analytical methods

Cell density was determined by measuring the optical density (OD) of the aqueous medium at 600 nm using an ultraviolet–visible (UV) spectrophotometer (UV-1240, Shimazdu, Japan). The OD was used to compute the biomass concentration using the formula: Dry Cell Weight (mg/L)$=385.1*OD_{600}$. Phenol concentrations during the abiotic experiments were determined by measuring the OD at 270 nm. For determining phenol concentration in the TPPB, 3 mL of cell culture was filtered through 0.45 μm syringe filter (Millex, Millipore, USA) and extracted into an equal volume of DCM containing 100 mg/L *o*-cresol as internal standard. Phenol in the extract was analyzed by gas chromatography (GC) equipped with a flame ionization detector (Clarus 600, Perkin Elmer, USA). TOPO concentration in DCM was also determined by GC. Biomass yield refers to the ratio of maximum cell concentration observed during biodegradation to the initial phenol concentration. The concentration of TOPO in the hollow fibers refers to the concentration of TOPO solution used to prepare the EIHFMs.

2.3. TOPO immobilization in hollow fiber membrane

Commercial symmetrical polypropylene hollow fiber membranes (Accurel PP 50/280, Membrana GmbH, Germany) were used for the immobilization. Membrane specifications have been provided in Table 1. The fibers were cut into small pieces of 6 cm each and bundles of 20 pieces were prepared using epoxy resins (Araldite, England). For immobilization, TOPO/DCM stock solution was diluted with DCM to the desired concentration and the bundles were added to it. The solution was then stirred on the shaking water bath for an hour at 150 rpm to allow the solvent to penetrate the fibers. The solvent wetted fibers were then removed and rinsed twice with ultrapure water to remove DCM present on the outer surface of the fibers. Finally, the fibers were dried under dry air stream for 24 h to evaporate the DCM, leaving TOPO inside the fibers. The resulting EIHFMs were washed thoroughly to remove loosely held extractant on the outer surface of the fibers.

Table 1
Characteristics of the hollow fiber membranes.

Characteristics	Values
Material	Polypropylene
Inner diameter	280 μm
Thickness	50 μm
Porosity	0.5
Pore size	0.2 μm

Four sets of EIHFMs were prepared with TOPO concentrations of 50, 100, 200 and 400 g/L. The fibers were characterized using a scanning electron microscope (SEM) (JEOL JSM-5600LV) after sputtering with platinum.

2.4. Adsorption/desorption of phenol

The adsorption/desorption experiments were carried out in batch mode in a 50 mL Falcon tube with 40 mL of solution on a thermomixer (MKR11, HLC Biotech, Germany) operating at 30 °C and 200 rpm. A total of 15 bundles of EIHFMs prepared with 0.5 g of the original polypropylene fibers with four different concentrations of TOPO were used to investigate the adsorption of 500, 1000, 1500 and 2000 mg/L phenol. Samples were collected from the tubes periodically to measure aqueous phenol concentration and the amount of phenol adsorbed on the EIHFMs fibers was calculated by material balance. Phenol desorption was carried out in 0.2 M sodium hydroxide solution. Each experiment was repeated three times for reproducibility.

2.5. TPPB operation

Biodegradation of 1000 and 2000 mg/L phenol in the solid/liquid TPPB was carried out in batch mode in a 500 mL flask with total volume of 150 mg/L. Sixty bundles of EIHFMs prepared using 400 g/L TOPO were added to the phenol solution and the two phases were allowed to equilibrate on a shaking water bath at 30 °C and 150 rpm. After half an hour, the TPPB was inoculated with *P. putida* from the preculture and the bioreactor was aerated with sterile humidified air at a rate of 2 gas volume per reactor volume per minute (VVM). Samples were collected periodically to measure biomass and phenol concentrations.

3. Results and discussion

3.1. Characterization of EIHFM

To estimate the total amount of TOPO immobilized into the hollow fiber membranes, the fibers were weighed before and after the immobilization. It was observed that the composition of TOPO (weight %) in the EIHFMs was 13%, 26%, 42% and 59%, respectively, when the fibers were treated with TOPO/DCM solution of concentration 50, 100, 200 and 400 g/L, respectively.

Fig. 1 shows the cross sections and external surface of polypropylene membrane as captured by SEM before and after immobilization with the extractant. The untreated fibers (Fig. 1a–c) exhibited smooth surfaces and cross sections and could be easily distinguished from the EIHFMs which were characterized by white deposits of TOPO on every surface. The distribution of TOPO within the membrane was non-uniform and a higher concentration was observed toward the outer surface of the fibers. This distribution trend could have resulted from the movement of DCM during evaporation. Since the carrier solvent could only leave through the