Chemosphere 141 (2015) 176–182

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Phenolic wastewater treatment through extractive recovery coupled with biodegradation in a two-phase partitioning membrane bioreactor

Prashant Praveen, Kai-Chee Loh *

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore

HIGHLIGHTS

- A two-phase partitioning membrane bioreactor (TPPMB) was designed and operated.
- TPPMB combined biodegradation with concomitant solvent extraction/stripping.
- 1000–3000 mg/L phenolic wastewater was treated within 2–4 h.
- 70–80% phenol was recovered and the remaining biodegraded.
- Biodegradation was carried out primarily by membrane/tubing attached cells.

ARTICLE INFO

Article history:
Received 9 March 2015
Received in revised form 22 June 2015
Accepted 10 July 2015

Keywords:
Biodegradation
Solvent extraction
Hollow fiber membranes
Phenol
Two-phase partitioning bioreactor

ABSTRACT

A two-phase partitioning membrane bioreactor (TPPMB) was designed and operated for treatment of high strength phenolic wastewater through extraction/stripping and concomitant biodegradation. Tributyl phosphate dissolved in kerosene was used as the organic phase, sodium hydroxide as the stripping phase and *Pseudomonas putida* for biodegradation. In a semi-dispersive approach, organic phase dispersed in the stripping solution was contacted with wastewater through semi-permeable membranes for removal of phenol from wastewater, while the microorganisms were inoculated directly into the wastewater for biodegradation. The TPPMB exhibited high phenol removal rates, and phenol concentrations of 1000–3000 mg/L were reduced to undetected amounts within 2–4 h. Up to 80% phenol was recovered through extraction, while the remaining was metabolized by the microorganisms. Phenol recovery in the TPPMB was enhanced by increasing the mass transfer rate of phenol through the membranes, and it was also estimated that phenol diffusion through the aqueous boundary layer on the tube side was the rate limiting step. The flexibility in adjusting inoculation time in the TPPMB prevented microorganisms from adverse effects of substrate inhibition, which facilitated complete removal of phenol from the wastewater. TPPMB retained the advantages of both solvent extraction and biodegradation, and it can be highly promising for the treatment of toxic industrial wastewater.

1. Introduction

Phenols constitute one of the most toxic, recalcitrant and bioaccumulating groups of pollutants found in industrial wastewater (Zilouei et al., 2008). These are often present in wastewater at high concentrations, detrimental for the aquatic ecosystems (González-Muñoz et al., 2003), and must be reduced to within safe limits, before the industrial effluents are discharged into the open environment.

Phenols can be removed from wastewater using non-destructive techniques such as adsorption or solvent extraction (Mohammadi et al., 2014), which can facilitate their recovery and reuse, and provide high removal rates. However, these are essentially equilibrium processes and they cannot effect complete removal of the pollutants (Busca et al., 2008). An efficient alternative to these techniques is biodegradation, which is based on the microbial metabolism of the pollutants into harmless products (Praveen and Loh, 2013b). However, microorganisms experience substrate inhibition at high concentrations of the toxic substrates, which may hamper cell growth and metabolism, leading to poor biodegradation rates (Daugulis et al., 2011).

One approach to mitigate substrate inhibition is the use of two-phase partitioning bioreactors (TPPB). TPPBs are based on equilibrium distribution of a toxic substrate between the aqueous cell growth medium, and a biocompatible non-aqueous phase

* Corresponding author.
E-mail address: chelohkc@nus.edu.sg (K.-C. Loh).

http://dx.doi.org/10.1016/j.chemosphere.2015.07.022
0045-6535/

(NAP) (Hernandez et al., 2012). Since most of the substrate is retained within the NAP, the microorganisms in the aqueous phase are exposed to only a low, sub-inhibitory substrate concentration, which allows them to achieve high growth and biodegradation rates. However, TPPBs have limitations, arising mainly from phase dispersion, diffusion limitation and solvent toxicity. Besides, biodegradation in the TPPBs is a two-step process which involves extraction in the first stage, back-extraction and biodegradation during the second stage (Rehmann et al., 2008; Juang et al., 2010;Praveen and Loh, 2013a). Furthermore, the regeneration of the NAP is solely through biodegradation with no attempt to recycle the substrate.

Recently, membrane-based TPPB configurations have been developed, wherein the aqueous and the organic phases could be physically separated using semi-permeable membranes (Juang et al., 2009; Praveen and Loh, 2013a, 2014). The resulting two-phase partitioning membrane bioreactors (TPPMB) had the advantage of dispersion-free mass transfer, easy NAP recycle, solvent-free cell growth environment and simultaneous extraction and biodegradation. This operational flexibility of the TPPMBs can be harnessed to improve the efficacy of two-phase biodegradation by removing the pollutant extracted in the NAP through concomitant biodegradation and chemical reaction. This novel strategy will not only retain all the advantages of TPPBs, it will prevent diffusion limitation and improve substrate removal rates. Moreover, recovery of commercially important pollutants, such as phenols, could potentially render TPPMB operation more economical.

In this research, the objective was to design and operate a TPPMB for the treatment of high-strength phenolic wastewater. Phenol extracted in the NAP was removed through biodegradation on one side, and through stripping using sodium hydroxide (NaOH) on the other side of the membrane. The factors affecting biodegradation and mass transfer of phenol were examined. Tributyl phosphate (TBP) was selected as the extractant due to its high chemical stability, low water solubility and high affinity for phenol (Hong et al., 2001).

2. Material and methods

2.1. Microorganisms, culture conditions, and chemicals

All the chemicals used in this research were of analytical grade. TBP was dissolved in kerosene to prepare the NAP.

Pseudomonas putida ATCC 11172 was 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 (Loh et al., 2000). 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 experiments.

2.2. Two-phase partitioning membrane bioreactor (TPPMB)

2.2.1. Contactor fabrication

The membrane contactor was fabricated by potting Accurel PP 50/280 hollow fiber membranes (Membrana GmbH, Germany) into a glass module using epoxy resins. The membrane specifications have been provided elsewhere (Praveen and Loh, 2013a). The effective membrane length was 30 cm and the packing density was 0.44 (v/v). These hydrophobic membranes exhibited low water permeability, and there was no movement of water from one phase to another under the experimental conditions, either from a difference in the osmotic pressure or due to the transmembrane pressure difference.

2.2.2. Bioreactor setup

Fig. 1 shows the schematic diagram of the experimental setup. Pure NAP was used to impregnate the membrane pores by filling the membrane contactor with the solvent for 2 h to enhance phenol transfer rate through the membranes. The NAP was also dispersed in the stripping solution, and uniformly mixed using a magnetic stirrer. Therefore, the extraction of phenol from wastewater to the NAP was dispersion free, whereas the back-extraction of phenol from the NAP to NaOH was dispersive. Contacting aqueous/organic with the NAP-wetted membranes on the shell side replenished any NAP loss from the membranes, and prevented problems arising from the instability of the supported liquid membrane (Ren et al., 2007). Two peristaltic pumps (L/S pump, Masterflex, USA) were used to pump the aqueous/organic dispersion from a 250 mL Erlenmeyer flask to the shell side, whereas the wastewater was pumped from a 500 mL Erlenmeyer flask to the tube side of the TPPMB. Water saturated air, sterilized by filtration through a 0.45 μm filter was sparged into the cell culture at 250 mL/min.

2.2.3. Bioreactor operation

Prior to bioreactor operation, the membranes were pre-wetted with the NAP for 2 h by pumping the NAP into the shell side of the membrane contactor. Thereafter, sterilized ultrapure water was pumped into the tube side to wash away any NAP leakage into the tube side. In all the experiments, 200 mL of mineral medium supplemented with 1000–3000 mg/L phenol was used as the synthetic wastewater. Ten milliliters of the NAP comprising of 5% TBP dissolved in kerosene was then added to 50 mL of stripping solution containing 0.2 M NaOH, and the mixture was stirred at 200 rpm to create a stable dispersion. Both liquids were contacted in cocurrent mode and a positive pressure was applied on the tube side to prevent solvent leak from the shell to the tube side. The shell side flow rate (Q_s) was varied between 4 and 14 mL/min, whereas the tube side flow rate (Q_t) was varied between 4 and 16 mL/min. The microorganisms were inoculated into the wastewater after 30–60 min of equilibration. Samples were periodically collected from the bioreactor to determine biomass and phenol concentrations. The pH of the wastewater was frequently measured and adjusted to the range of 6.5–7.0. At the end of each run, the tube side was washed with sterilized alkaline water (pH 10) to remove cells loosely attached to the membranes and the tubings.

2.3. Analytical methods

Cell density was determined by measuring the optical density (OD) of the aqueous medium at 600 nm using an ultraviolet–visible spectrophotometer (UV-1240, Shimazdu, Japan). The OD was converted to biomass concentration by the formula: dry cell weight (mg/L) = $385.1 * OD_{600}$. For determining phenol concentration, 1 mL of the aqueous sample was filtered through 0.45 μm syringe filter (Millex, Millipore, USA) and analyzed through HPLC (Waters 2487, USA) using a C18 column (Juang et al., 2012). The phenol detection limit for the HPLC was 0.2 mg/L, below which phenol concentrations could not be detected accurately. Therefore, complete removal of phenol from the feed wastewater in the TPPMB implied that phenol concentration had dropped below 0.2 mg/L. The distribution coefficient is defined as the ratio of phenol concentration in the organic and the aqueous phases.