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Use of membrane contactors as two-phase bioreactors for the removal of phenol in saline and acidic solutions

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Abstract

A microporous hollow-fiber membrane contactor was proposed as a two-phase bioreactor to treat phenol by solvent-tolerant *Pseudomonas putida* BCRC 14365 at 30 °C, in which phenol in saline/acidic solution was pre-extracted to kerosene in a batch stirred vessel or another membrane contactor. Phenol-bearing organic solution was passed through the lumen of the module and the biomass medium was flowed across the shell. The initial cell density was fixed at 0.025 g L^{-1}. The effects of NaCl concentration (100–200 g L^{-1}) and pH (1.0–9.0) in saline solutions, and the amount of added dispersing agent tetrasodium pyrophosphate (TSP) (0.5–1.5 g L^{-1}) in biomass medium on phenol biodegradation and cell growth were experimentally examined. It was shown that polyvinylidene fluoride (PVDF) hollow fiber was more suitable than polypropylene (PP) for this purpose because PVDF fiber had lower extent of phenol sorption and thus faster mass transfer to the biomass medium. Under the experimental conditions studied, the adjustment of saline solution pH to 3.0 and the addition of 1.0 g L^{-1} TSP in biomass medium revealed the best removal of 1500 mg L^{-1} phenol in saline solutions. Moreover, the overall removal process appeared to be favored when salt concentration in saline solution was higher than a threshold value (e.g. 200 g L^{-1}), in which salting-out effect on phenol partition occurred. The application potential of the hybrid liquid–liquid extraction and two-phase biodegradation in membrane contactor to the treatment of highly contaminated wastewaters was finally discussed.

Keywords: Liquid–liquid extraction; Biodegradation; Phenol; Saline solutions; Membrane contactors; Two-phase bioreactors

1. Introduction

Many of industrial effluents containing priority organic pollutants exhibit high salt concentrations and/or the extremes of pH, one or both of which prevents microbial growth or at least make it difficult to sustain [1]. For example, the main end markets for salt are the chemical industry (mainly the chloralkali sector), road deicing and agro-food industries. Other non-negligible uses of salt are found in petroleum, textile and leather industries as well as for softening hard water. All these sectors generate large amounts of saline wastewater, rich in both salt and organic matter [2]. When this effluent is discharged into the environment without prior treatment, it causes severe damage by contamination of soil, surface, and groundwater. Thus, Lefebvre and Moletta [2] have recently made a literature review on the treatment of organic pollution in industrial saline wastewater.

Practical saline effluents are often recalcitrant to biological treatment; thus, physicochemical treatment is generally required to remove the organic matter and salts from such effluents. The main technologies that have been studied are thermal methods such as solar and multiple-effect evaporation (to reduce the volume of effluents), coagulation–flocculation (to remove colloidal COD and turbidity), ion exchange (to remove salts), and membrane techniques such as ultrafiltration UF (to remove suspended solids and colloidal COD), reverse osmosis RO and electrodialysis (to remove salts). For salt removal, the use of RO is particularly efficient, yet the high amounts of suspended solids and organic matter in effluents reduce the lifetime and the efficiency of membranes involved [2]. Thus, the optimal treatment of highly saline wastewater usually involves a biological treatment prior to salt removal. On the other hand, biological treatment is inhibited by high salt concentrations. However, it has proved feasible to use salt-adapted microorganisms capable of withstanding high salinities and at the same time of degrading the pollutants that are contained in effluent [3]. Thus, the use of these microorganisms is also recommended in the

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treatment of saline effluents, prior to salt removal by physicochemical method. However, the effluent organic loading rate and salt concentration should be equalized as far as possible, as these microorganisms are sensitive to environmental shocks [2]. Moreover, high percentages of salt are known to compromise the correct operation of conventional aerobic wastewater treatment processes only above chloride concentrations of 5–8 g L^{-1} [4].

It is known that liquid–liquid extraction is a commonly used method to separate organic matter from salts in saline solutions [5]. Biodegradation occurs by partition of the organics to cell (biomass) medium when it is in contact with the loaded organic solvent as long as the solvent is biocompatible. In fact, Collins and Daugulis [6] have first studied the biodegradation of high-level phenol stream using so-called two-phase partitioning bioreactor (TPPB). This reactor uses a water-immiscible and biocompatible organic solvent that is allowed to float on the surface of a biomass-containing aqueous phase. Solvent is used to dissolve large concentration of xenobiotic substrates, which then partition to aqueous phase at low levels. The biomass experiences only low concentrations although high amounts of toxic organic substrates are added to the TPPB. When the biomass consumes some of the substrate, disequilibrium is created, which causes more of xenobiotic substrate to be partitioned to aqueous phase when the system tries to maintain thermodynamic equilibrium [7,8]. Because microorganisms are essentially colloidal substances, direct mixing of the two immiscible solutions may lead to the formation of emulsions particularly at high levels of organic matter. This makes phase separation and subsequent treatment more difficult.

In the past 10 years, extractive membrane bioreactor (EMBR) has been proposed to solve the problems outlined above [1,9,10]. EMBR uses a dense membrane that is virtually permeable to chlorinated aromatic and aliphatic compounds but nonpermeable to water or ionic species. The membrane separates wastewater from biomass medium where biodegradation takes place under controlled conditions, making it useful for the treatment of some saline effluents typically resulting from fine chemicals and pharmaceuticals synthesis [1,10]. The permeated organics are either swept off by cell medium or organic solvent, constituting the so-called one-phase [1,9,10] or two-phase EMBR [11]. Splendiani et al. [11] has used two-phase EMBR to remove monochlorobenzene from synthetic solution and biodegrade by *Burkholderia* sp. strain in single polydimethylsiloxane membrane tube using perfluoromethyldecalin as the organic solvent. However, EMBR process is extremely time-consuming due to slow mass transfer within the dense membrane. For instance, Livingston [9] has used one-phase EMBR to treat phenol in the solution containing 52 g L^{-1} NaCl and 1.4 M HCl using a silicone rubber membrane, and found that 1000 h is required to degrade 98.5% of phenol at an inlet level of 1000 mg L^{-1}.

An attempt was hence made here to overcome the problems encountered in TPPB, after liquid–liquid extraction of saline solutions, and to enhance such biodegradation occurring in EMBR using hollow-fiber membrane contactor as a novel type of two-phase microporous membrane bioreactor (MMBR). Basically, membrane contactors allow restricted and/or regulated passage of one or more species through the pores although they act as the barriers to prevent bulk mass movement. They have thus been widely used in gas absorption, air stripping, and liquid–liquid extraction to avoid direct contact between the gas/liquid and organic/aqueous phases [12]. This means that the present liquid–liquid extraction operation can also be achieved in other membrane contactor, which is known as the non-dispersion solvent extraction. In fact, biomass immobilized on membrane contactors has been used for biotechnology applications such as culture [13] and biodegradation [14–18], mainly because hollow fibers offer higher surface area per unit module volume than other bead supports.

Phenol was selected as model substrate here because it is one of the most common representatives of toxic organics even at extremely low levels [19]. *Pseudomonas putida* (*P. putida*) was used due to their high removal efficiency [20,21]. The feasibility of using two-phase MMBR for biodegradation of phenol in such saline and acidic solutions in was focused, and the effects of operating parameters on the performance were studied. Experiments were conducted in microporous polypropylene (PP) or polyvinyldiene fluoride (PVDF) hollow fibers. The synthetic wastewater contained 1000–1500 mg L^{-1} phenol and 100–200 g L^{-1} NaCl in the pH range of 1.0–9.0. The initial concentration of *P. putida* BCRC (Bioresource Collection Research Center) 14365 in mineral salt (MS) medium was fixed at 0.025 g L^{-1}, which consisted of 0.5–1.5 g L^{-1} of tetrasodium pyrophosphate (TSP). An optimal temperature of 30 °C for *P. putida* growth was chosen [20]. This study could be a pioneered one in using membrane contactors for this purpose, because the effluents were nearly free of inorganic salts and neutral in previous biodegradation studies using membrane contactors [14–18].

2. Materials and methods

2.1. Microorganism, nutrient medium, and solutions

P. putida BCRC 14365 used was obtained from the Food Industry Research and Development Institute, Hsinchu, Taiwan. The stock cultures were stored at 4 °C. The nutrient medium contained 3 g L^{-1} beef extract, 5 g L^{-1} peptone, and the mineral salt (MS) medium at pH 7.0. The compositions of MS medium (in g L^{-1}) were KH_2PO_4 (0.42), K_2HPO_4 (0.375), $(NH_4)_2SO_4$ (0.244), NaCl (0.015), $CaCl_2{\cdot}2H_2O$ (0.015), $MgSO_4{\cdot}7H_2O$ (0.05), and $FeCl_3{\cdot}6H_2O$ (0.054). The phosphate buffer (pH 7.0) was prepared by mixing equal volumes of 0.375 g L^{-1} K_2HPO_4 and 0.465 g L^{-1} KH_2PO_4 solutions in deionized water (Millipore, Milli-Q). All these inorganic chemicals were supplied by Merck Co. as analytical reagent grade. Prior to use, the MS medium and phosphate buffer were sterilized in an autoclave at 121 °C for 15 min. The organic solvent kerosene (Union Chemical Co., Taiwan) was washed twice with 20 vol.% H_2SO_4 to remove aromatics and then with deionized water (Millipore Milli-Q) three times before use. Kerosene was chosen in this work because it is cheap, stable, and biocompatible. The partition coefficients of phenol between kerosene and various aqueous solutions were measured and listed in Table 1.

The wastewater was synthesized by dissolving 1000–1500 mg L^{-1} phenol (Merck Co.) and 100–200 g L^{-1} NaCl