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Treatment of phenol in synthetic saline wastewater by solvent extraction and two-phase membrane biodegradation

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ABSTRACT

Phenol in synthetic saline (100 g L^{-1} NaCl) and acidic (pH 3) wastewater was treated by a hybrid solvent extraction and two-phase membrane biodegradation process at 30 °C. Kerosene was adopted to be the organic solvent because it was biocompatible and had a suitable partition coefficient for phenol. Phenol in water was first extracted by kerosene in a batch stirred vessel and the loaded solvent was passed through the lumen of a polyvinylidene fluoride (PVDF) hollow-fiber membrane contactor; in the meantime, *Pseudomonas putida* BCRC 14365 in mineral salt medium was flowed across the shell, to which tetrasodium phyophosphate (1 g L^{-1}) was added as a dispersing agent. The effect of the initial phenol level in wastewater (110–2400 mg L^{-1}) on phenol removal and cell growth was experimentally studied. At a cell concentration of 0.023 g L^{-1}, it was shown that the removal of phenol from saline wastewater was more efficient at a level of 2000 mg L^{-1} when 0.02-m^2 membrane module was used. The effects of bigger membrane module size (0.19 m^2 area) and higher initial cell concentration (0.092–0.23 g L^{-1}) on the performance of such a hybrid process for the treatment of higher-level phenol in saline wastewater was also evaluated and discussed.

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 make it very difficult to sustain [1,2]. Lefebvre and Moletta [3] have made a literature survey on the treatment of organic pollutants in industrial saline wastewater. They reported that the main end markets for salt are the chemical process 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 generate large amounts of saline wastewaters, rich in both salt and organic matter. When such industrial effluents are discharged into the environment without prior treatment, they cause severe damage by contamination of soils, surface water, and groundwater.

Physicochemical treatment of practical saline wastewaters is often suggested because such effluents are recalcitrant to biological treatment; however, the removal of organic matter from saline effluents is generally required prior to physicochemical processes. The main methods that have been studied are thermal processes such as solar and multiple-effect evaporation (to reduce volume of the effluents), coagulation–flocculation (to remove colloidal COD and turbidity), ion exchange (to remove salts), and some membrane processes such as UF (to remove suspended solids and colloidal COD), RO and electrodialysis (to remove salts). For removal of salts, the use of RO is particularly efficient, yet the large amounts of organic matter and suspended solids in effluents reduce the life time and the efficiency of membranes involved [3]. Hence, the optimal treatment of highly saline wastewater usually involves a biological treatment prior to salt removal.

On the other hand, although biological treatment is inhibited by high salt levels, it has proved feasible to use salt-adapted microorganisms capable of withstanding high salinities and of degrading the pollutants that are contained in effluent [4]. That is, the use of suitable microorganisms is also suggested in the treatment of saline effluents, prior to salt removal by physicochemical methods. However, the organic loading rate and salt level in the effluent should be equalized as far as possible, as these microorganisms are sensitive to environmental shocks [3]. Moreover, high amounts 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} [5].

The possibility of using hollow-fiber microporous membrane contactors as two-phase bioreactors for the degradation of phenol in saline and acidic solutions by *Pseudomonas putida* (*P. putida*) BCRC (Bioresource Collection Research Center) 14365 has been

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Nomenclature

S	phenol level at any time (mg L^{-1})
S_0	initial phenol level (mg L^{-1})
S_{cm}	phenol level in the cell medium (mg L^{-1})
$S_{cm,max}$	maximum phenol level in the cell medium (mg L^{-1})
t_{95}	time required for degrading 95% of the total phenol (h)
X	cell concentration (g L^{-1} or OD)
X_0	initial cell concentration (g L^{-1} or OD)

Greek letter

μ	specific cell growth rate defined in Eq. (3) (h^{-1})

evaluated at 30 °C [6]. After extraction of phenol from saline solutions into kerosene, kerosene was passed through the lumen of membrane module and the aqueous cell medium was flowed across the shell. Phenol was back-partitioned from kerosene to cell medium when cell medium is in contact with the loaded solvent through the mouth of the pores, and biodegradation occurs in the cell medium as long as the solvent is biocompatible. The proposed solvent extraction and two-phase membrane biodegradation process can treat 1000 mg L^{-1} phenol in wastewater containing NaCl up to 200 g L^{-1}, and the efficiency increases with increasing NaCl level due to salting-out effect for enhanced partition of phenol from wastewater to kerosene [6]. Except highly saline solutions, this hybrid process is suitable for the treatment of organic matter in acidic (pH < 3) and basic solutions because solvent extraction is an efficient way to separate organic matter from salts and ionic species (e.g., H^+, OH^-) in aqueous streams [7]. However, further studies are needed to extend the applicability of such a hybrid process including the treatment of increased level of organic matter in wastewater, and to establish the relationship among partition coefficient of organic matter and key operating parameters.

Some two-phase alternatives can be referred for treatment of high-level organic matter in saline solution. Collins and Daugulis [8] have studied the biodegradation of phenol up to 10 g L^{-1} in the so-called two-phase partitioning bioreactors, which uses a water-immiscible and biocompatible organic solvent (2-undecanone) that is allowed to float on the surface of a biomass-containing aqueous phase. Solvent is used to dissolve large amounts of organic matter, which then partition to aqueous phase at low levels. When cells consume some of the substrate, disequilibrium is created, which causes more of the organic matter to be partitioned to aqueous phase as the system tries to maintain thermodynamic equilibrium [9]. Because cells are basically colloidal substances, direct mixing of the two immiscible phases may lead to the formation of emulsions or the third phase due to the existence of metabolic products, particularly at high cell densities. This may make phase separation and subsequent treatment (e.g., solvent recovery) more difficult. On the other hand, an extractive membrane bioreactor (EMBR) has been proposed to solve the problems outlined above [1,10,11], which uses a dense membrane that is virtually permeable to organic compounds but non-permeable to water or ionic species. The membrane separates wastewater from cell medium where biodegradation occurs under controlled conditions, making it useful for the treatment of saline effluents. The permeated organic matter is swept off by either cell medium or organic solvent, constituting the so-called one- or two-phase EMBR. Splendiani et al. [11] have used two-phase EMBR to remove monochlorobenzene from water using single polydimethylsiloxane fiber and to degrade it by *Burkholderia* sp. strain using perfluoromethyldecalin as the organic solvent. However, both types of EMBR processes are extremely time-consuming due to slow mass transfer within the dense membrane.

In this work, the effect of initial phenol level on the removal of phenol from saline and acidic solutions by solvent extraction coupled with biodegradation in membrane contactors was studied. Phenol was selected as model organic matter because it is one of the most common pollutants even at an extremely low level [12], and *P. putida* was used due to its high biodegradation efficiency [13,14]. Experiments were carried out using polyvinylidene fluoride (PVDF) hollow fibers. The wastewater contained 110–2400 mg L^{-1} phenol and 100 g L^{-1} NaCl at pH 3, whereas the cell medium consisted of *P. putida* BCRC 14365 and 1 g L^{-1} dispersing agent, tetrasodium phyophosphate (TSP). An operating temperature of 30 °C was selected since it is optimal for *P. putida* growth [14]. The possibility for improved treatment of higher-level phenol in saline wastewater by changing membrane module size (0.02–0.19 m^2 area), initial cell concentration (0.023–0.23 g L^{-1}), and cell medium volume were finally evaluated.

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. 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) 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 possible aromatics impurities and then with deionized water (Millipore Milli-Q) three times before use. Kerosene was chosen because it is cheap, stable, and biocompatible. The partition coefficients of 1000 mg L^{-1} phenol, defined below, between kerosene and wastewater as well as kerosene and cell medium were measured to be 0.50 and 0.35, respectively, at 30 °C.

$$\text{partition coefficient} = \frac{\text{equilibrium phenol level in the organic phase}}{\text{equilibrium phenol level in the aqueous phase}} \quad (1)$$

The wastewater was prepared by dissolving 110–2400 mg L^{-1} phenol (Merck Co.) and 100 g L^{-1} NaCl in deionized water, in which the pH was adjusted to be 3 by adding 0.1 M HCl. The cell medium contained MS medium at pH 7, to which 1 g L^{-1} TSP (RDH Co.) was added as a dispersing agent. The solution pH was measured using a pH meter (Horiba F-23, Japan). The initial cell concentration was fixed at 0.023 g L^{-1} in cell medium, otherwise stated elsewhere.

2.2. Free suspension cultivation

P. putida cells were activated at 30 °C in nutrient medium, into which 100 mg L^{-1} phenol was added for adaptation for 24 h. The cells collected after centrifugation at 6000 rpm for 10 min was re-suspended in phosphate buffer and re-centrifuged. After cleaning, the activated cells were inoculated into the culture medium (250 mL) in 500-mL Erlenmeyer flasks to give an initial