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ScienceDirect
Powder Technology 169 (2006) 61 – 70
POWDER TECHNOLOGY
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Continuous enzymatic polymerization of phenol in a liquid–solid circulating fluidized bed

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Received 31 August 2005; received in revised form 1 August 2006; accepted 4 August 2006
Available online 18 September 2006

Abstract

A liquid–solid circulating fluidized bed (LSCFB) system consisting of 3.8 cm I.D. and 4 m high riser and 12 cm I.D. and 3.5 m high down-comer was investigated in this study for the continuous polymerization of phenol. Approximately 8.5 kg immobilized particles containing soybean seed hull peroxidase enzymes were applied in the LSCFB system. The continuous enzymatic polymerization was carried out in the riser section by introducing phenol and hydrogen peroxide at the entrance of the riser. Under optimized hydrodynamic conditions and by keeping the molar concentration ratio of phenol to H_2O_2 of 1:2, 54% conversion of phenol was achieved. The down-comer of the LSCFB was utilized for the regeneration of the coated immobilized enzyme particles. The effect of the superficial liquid velocity and an initial substrate concentration was studied. Our experimental results show that an enzymatic reaction and the regeneration of the biocatalysts can be carried out simultaneously and independently in the LSCFB system. Furthermore, this work opens the possibilities for many bioprocesses where the deactivation of the biocatalysts is a major problem and the regeneration of the biocatalysts is required.

Keywords: Liquid–solid circulating fluidized bed (LSCFB); Biocatalysts; Enzymatic reaction; Regeneration; Continuous system

1. Introduction

In industrial scale bio-refining processes, continuous reactors are preferred over the batch reactors where the proteins or enzymes act as catalysts to produce wide ranges of specialty to commodity products. To keep the enzymes inside the reactor, practically it is important to entrap them within the porous supports with a high area to volume ratio. Upon entrapment, the biomolecules possess more stable conformation, allow repetitive usage, increase the bio-volumetric activity of the process, and the downstream operations become cheaper [1]. Continuous processes with immobilized enzymes can be carried out in different types of reactor. Among them, fluidized bed reactors (FBRs) have several advantages over traditional fixed-bed and stirred-tank reactors. FBRs are preferable due to their hydrodynamic advantages like less pressure drop and a more uniform flow distribution in an axial direction of the reactor. The mechanical stirring is also not required in FBRs; hence the carrier material is not damaged by the impeller.

Many enzyme-catalyzed reactions have been investigated recently, only a few are in use. One of the reasons is complex kinetics of the process that includes substrate or product inhibition within the biocatalysts [2]. In case of inhibition, the choice is limited to either replacement or regeneration. Replacement is an expensive option when using immobilized catalysts and regeneration of the biocatalysts is the better choice. However this is usually a cyclic operation. An alternative approach with potential benefits is the liquid–solid circulating fluidized bed (LSCFB) system is for the simultaneous reaction and regeneration of the biocatalyst particles.

The LSCFB consists of two columns; the riser and the down-comer, and is described in detail later. The riser operates at high liquid velocity (higher than the terminal velocity of the particles) and the biocatalyst particles are carried up the riser column. The entrained particles are collected at the top and re-circulated to the bottom of the riser column through a down-comer to maintain the required biocatalyst hold-up in the riser [3].

The principal interest in the LSCFB system is; it can handle reaction and regeneration simultaneously by keeping the two process streams of different properties separate from each other without mixing. Previously, Lan et al. have successfully

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doi:10.1016/j.powtec.2006.08.001

demonstrated the LSCFB system for a continuous recovery of protein from the cheese whey [4,5,P-1]. The ion exchange particles were used for a continuous adsorption and desorption in this process [P-2]. Recently, Cui et al. have demonstrated the LSCFB system for simultaneous removal of carbon, nitrogen and phosphorus from the municipal wastewater treatment [6]. The LSCFB system provides an aerobic, an anaerobic and an anoxic zone to satisfy the process requirement. Compared to the conventional FBRs, the LSCFBs have specific advantages, such as higher throughput, less back-mixing, more efficient inter-phase contact area, and improved heat and mass transfer performance [3–9]. The hydrodynamics of the LSCFB system have also been investigated by many researchers [7–11].

The main objective of this study was to investigate the LSCFB system as an immobilized bioreactor system, where the reaction and the regeneration of the biocatalysts can be performed simultaneously and independently in the two inter-connected FBRs. The biocatalyst particles were soybean peroxidase (SBP) enzyme extracted from the soybean seed hulls and entrapped within a mixture of a silica sol-gel and calcium-alginate. The enzymatic properties of the SBP enzymes were investigated by many researchers and successfully demonstrated to treat phenolic pollutants in presence of a reactant hydrogen peroxide (H_2O_2) [12–17] and to synthesis the functional polymeric materials via nonbiosynthetic pathways [18–21]. The produced polymer shows a better thermal and conductive property than PF (phenol-formaldehyde) resins [18–21].

2. Experimental

2.1. Materials

The raw soybean seed hulls were donated by ADM Agri-Industries, Windsor, Ontario, Canada. A diluted phenolic solution was prepared by dissolving an analytical grade phenol (Sigma-Aldrich, Canada) into distilled water. A 30% hydrogen peroxide solution was purchased from Sigma-Aldrich, Canada. A 1:2 molar ratio of phenol to hydrogen peroxide was maintained in the riser. The soybean peroxidase enzymes were entrapped into a mixture of silica sol-gel/Ca^{+2}-alginate [22,23]. A colloidal silica solution (LUDOX TM-50) and a diluted potassium silicate (KASIL) solution were used as silica sol-gel precursors. A potassium silicate was obtained from PQ Corporation, PA, U.S.A. An alginic acid sodium salt was used as a supportive material to entrap the SBP enzymes, and it was obtained from Sigma-Aldrich, Canada. A 0.1 M solution of calcium chloride solution was used as a hardening solution. It was prepared by dissolving calcium chloride dehydrate powder into a distilled water to fabricate the peroxidase particles. A 5% (v/v) ethanol was optimized as a regeneration solution in the down-comer.

2.2. Liquid–solid circulating fluidized beds (LSCFB) system

As shown in the Fig. 1, a liquid–solid circulating fluidized beds (LSCFB) system is composed of two interconnected fluidized beds, namely, a riser and a down-comer. The other important components of the LSCFB involves a liquid–solid separator, a top particles returning pipe from riser to the down-comer, a bottom particles returning pipe from down-comer to the riser, a top washing section and a bottom washing section. In this study, the height of the riser was 4.0 m and 38 mm in a diameter. The down-comer was 3.5 m high and 120 mm in a diameter. The ratio of the cross sectional area of riser to down-comer was 10.

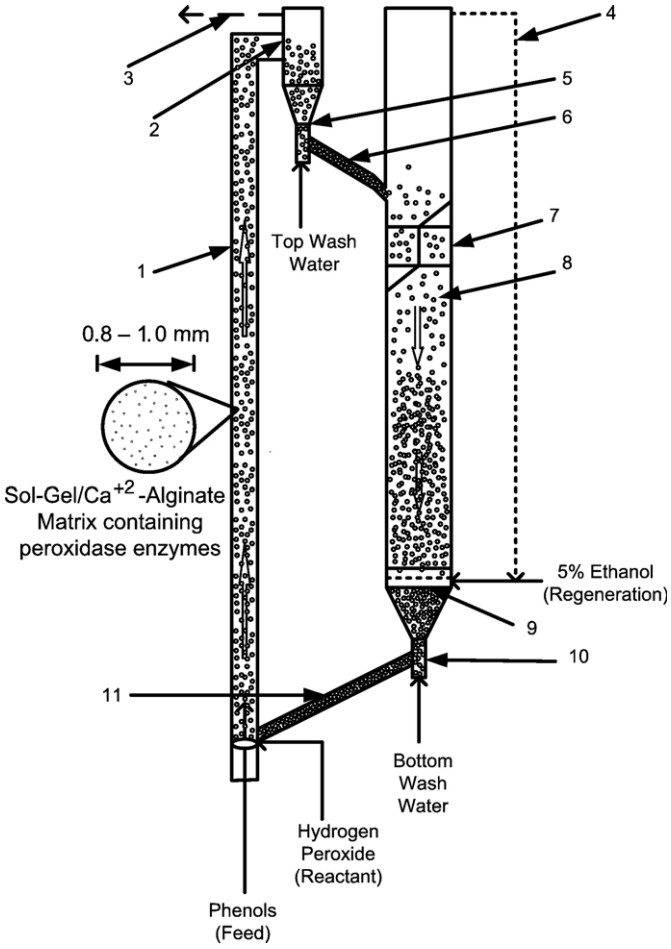

Fig. 1. Schematic of a liquid–solid circulating fluidized bed bioreactor system containing entrapped soybean seed hull peroxidase enzymes within the sol-gel/calcium-alginate matrices.

In the present investigation of the continuous enzymatic polymerization of phenols to polymeric resins, the soybean seed hull peroxidase (SBP) enzymes are entrapped into silica sol-gel/Ca^{+2}-alginate particles. The fabricated biocatalysts (porous particles containing SBP enzymes) had an average size of 0.8 mm (diameter) and were applied in the LSCFB system. A continuous phenol polymerization was carried out with the riser as the reaction vessel and the down-comer utilized for the regeneration of the biocatalysts. In this system, a riser was a fast fluidization vessel. In the riser, the particles containing SBP enzymes were carried in a co-current fashion by the combination of the main liquid stream (phenol) and an auxiliary liquid stream (H_2O_2). The proposed enzymatic polymerization of phenol falls in ping-pong reaction mechanism as the two substrates, phenol and H_2O_2, both are equally responsible for enhancing the enzymatic rate of reaction. The enzymatic rate of