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A biologically-derived 1,3-propanediol recovery from fermentation broth using preparative liquid chromatography

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ABSTRACT

This work studies the process development for the purification of 1,3-propanediol by batch preparative chromatography. The strongly acidic cation exchangers in hydrogen and sodium form were used as the stationary phases. The equilibrium adsorption of 1,3-propanediol and glycerol onto two polymeric resins were investigated and the model parameters were experimentally determined to process simulation. The work has proven that 1,3-propanediol can be isolated from the fermentation broth with high efficiency. The obtained results show that the Equilibrium-Dispersive model can be applied to simulation experiments and scale-up designs of chromatographic processes.

1. Introduction

1,3-propanediol (1,3PD) is a diol which has a wide range of applications in the production of cosmetics, adhesives, lubricants and polymers such as polyesters, polyethers and polyurethanes synthesis [1–3]. 1,3PD can be produced via chemical or microbiological processes [2,3]. The chemical route using either acrolein or ethylene oxide is environmentally unfriendly and produces toxic intermediates [4,5]. Due to the environmental advantages, production of a biologically-derived 1,3PD can be considered as a promising green technology [6,7]. The biologically-derived 1,3PD is produced by microorganisms during the fermentation of a carbon source such as a glycerol or glucose. The microbial production of 1,3PD from renewable biomass is currently the subject of many studies focused on the fermentation conditions and kind of bacteria or fungal strains including *Clostridium butyricum* [8,9], *Clostridium perfringens* [10], [11], *Citrobacter freundii* [12], *Lactobacillus reuteri* [13], *Lactobacillus brevis* [14] and *Saccharomyces cerevisiae* [15]. Apart from fermentation, there are many separation and purification challenges associated with pollutants present in the fermentation broth and the low concentration of the final product. The 1,3PD fermentation broth contains many components, including biomass, residual glycerol, inorganic salts as well as organic acid by-products. Therefore, economical and efficient downstream processing of 1,3PD fermentation broth is essential. Several separation methods have been reported to purify 1,3PD, including liquid-liquid extraction [16–18], aqueous two-phase extraction [19–24], chemical reaction methods [25–29], adsorption and chromatographic methods [30–33], distillation [34,35], and membrane methods [36–39].

The aim of this work is to present the developed process of the purification of 1,3PD using a chromatographic technique with polymer resins as a stationary phase. The paper presents the results of the experimental studies obtained for the model solutions and for the fermentation broths, as well as the simulation studies using mathematical modeling of liquid chromatography.

2. Theory of chromatography

Different kinds of mathematical models of preparative liquid chromatography have been developed with varying complexity and assumptions [40]. The theory of chromatographic models has been thoroughly described in many papers [41–43]. In this work the Equilibrium-Dispersive (ED) model was applied to model the mass balance of the solutes in the chromatographic column:

$$\frac{\partial C_i}{\partial t} + \frac{u}{\varepsilon_t}\frac{\partial C_i}{\partial x} + \frac{(1-\varepsilon_t)}{\varepsilon_t}\frac{\partial q_i}{\partial t} = D_a\frac{\partial^2 C_i}{\partial x^2},$$

where C_i and q_i are the solute concentration in the mobile and stationary phase, respectively, ε_t is the total porosity, u is the linear velocity, D_a is the apparent dispersion coefficient, t is the time, and x is the distance along the column.C_i and q_i values are correlated by the adsorption isotherm equation [44]. The ED model can be used when the mass transfer kinetics is fast but not infinitely fast [45]. The model is completed by appropriate initial and boundary conditions. For t = 0 (0 < x < L, where L is column length), the initial concentrations are:

$$C_i(0, x) = 0 \quad \text{and} \quad q_i(0, x) = 0,$$

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so the column is filled with a pure mobile phase. The boundary conditions (the Danckwerts-type boundary conditions) are:

at the column inlet (t > 0, x = 0),

$$u(C_{0i}(t) - C_i(t, 0)) = -\varepsilon_t D_a \frac{\partial C_i(t, 0)}{\partial x},$$

at the column outlet (t > 0, x = L),

$$\frac{\partial C_i(t, L)}{\partial x} = 0$$

where C_{0i} is the injection concentration of the sample [46,47].

The equilibrium-dispersive model is widely applied in liquid chromatography and has been successfully employed in chemical engineering for simulation of substance separation.

3. Materials and methods

3.1. Materials

1,3-propanediol (99%, 1,3PD), acetic acid (99.5%, AA), and butyric acid (99%, BA) were purchased from Sigma-Aldrich Corporation. Glycerol (98%, Gly), lactic acid (88%, LA), and sodium chloride (99.8%, Salt) were purchased from Avantor Corporation. Chromatographic separation experiments were carried out using two types of monospheric ion exchange resins based on a styrene-divinylbenzene copolymer: strongly acidic cation exchange in hydrogen form (Spectra/Gel Ion Exchange 50 × 8, Spectrum, 40–75 and 75–150 μm) and strongly acidic cation exchange in sodium form (Lewatit S1567, 0.6 mm and Amberjet 1200Na, 0.6 mm). The microscopy images of the dry bead in hydrogen form are shown in Fig. 1. The feed solution of 1,3-PD fermentation broth was composed of 37.7 g/L 1,3PD, 5.0 g/L Gly and LA, 6.0 g/L BA, 2.5 g/L AA, and 5.5 g/L inorganic salts (mainly sodium chloride).

3.2. Analytical method

An HPLC system with RI detector was used to measure the concentration of 1,3PD, Gly, acids and inorganic salts in the diluted solutions and fermentation broths. Rezex-ROA Organic Acid column (4.6 mm × 250 mm, Phenomenex) was used as a HPLC analytic column and 5 mM H_2SO_4 as a mobile phase. The flow rate of the mobile phase was maintained at 0.4 mL/min with a column temperature of 50 °C. The analysis of concentrated final product was performed on a HP5890 series II gas chromatography (Hewlett Packard) equipped with a FID detector and Permabond CW20M column (30 m × 0.53 mm, Macherey-Nagel). On-line measurements were performed using a multifunction meter (Elmetron) measuring the pH, temperature and conductivity of working solutions.

3.3. Chromatographic separation step

The selection of an appropriate sorbent is an important factor for the efficient separation of 1,3PD from the aqueous solution. The selection of the resin was conducted on the basis of literature review. In the previous work the separation efficiency for different ionic forms of resin was investigated [48]. Based on previous studies, ion exchange resins in hydrogen and sodium form were used for preparative liquid affinity chromatography and ion exclusion chromatography, respectively.

The preparative chromatography system was composed of a pump, a chromatographic column (length 90 cm^3 and 530 cm^3 with bed height 35 cm and 100 cm, respectively) and fraction collector. Experiments were conducted for model aqueous solutions and for the fermentation broths. The feed solution was loaded into the packed column with amount converted into the column capacity (20–35% of the total bed volume). Distilled water was used as a mobile phase with space velocity of 1–2 h^{-1} (ratio of flow rate of the mobile phase to the total bed volume). Fractions from the column were collected and analyzed using the HPLC system.

3.4. Model parameters

In order to determine the column porosity, the column dead time t_{r0} was evaluated using aqueous solutions of sulfuric (VI) acid and sodium chloride (concentration in the range of 0.1–1.0%) as inert solutions. The bed porosities were measured in a small column with different length in the range of 10–20 cm (7 mm I.D.). Bed porosity is highly sensitive to the packing of the bed, therefore it is important to take into account the standard errors considered in this analysis. For each measurement, the column was filled with another portion of resin. The obtained results were similar and therefore the paper presents the average results for a 6 cm^3 column. The total porosity ε_t was calculated according to equation:

$$\varepsilon_t = \frac{t_{r0}\dot{V}}{V_B},$$

where $\dot{V}$ is a flow rate of the mobile phase [40,49].

The bed porosities were not measured with each column used in the separation experiments. The total porosity of the corresponding bed was determined independently of the separation conditions, which allows the use of this experimental data to simulate the process with different column volumes.

The apparent dispersion coefficient D_a was determined based on the chromatographic column efficiency N in accordance with the equation:

$$D_a = \frac{HETP * u}{2\varepsilon_t} = \frac{L * u}{N * 2\varepsilon_t}.$$

The number of theoretical plates N was calculated from the half-height peak width $w_{1/2}$ [50]:

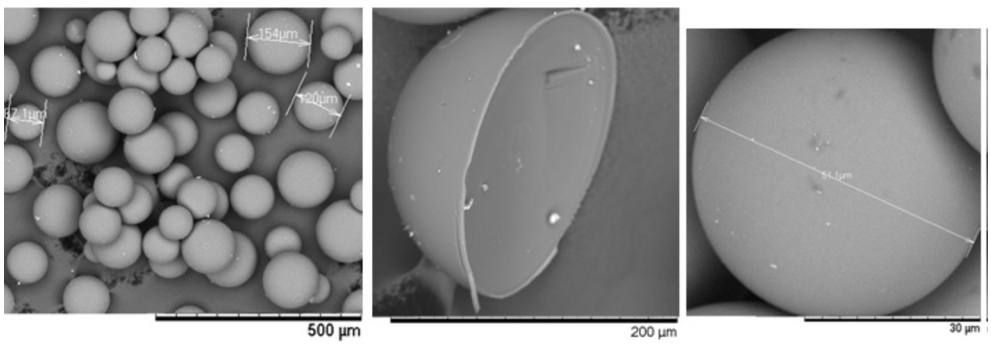

Fig. 1. Strongly acidic cation exchange bead in hydrogen form-dry form of the resin (Scanning electron microscopy TM-3030, Hitachi).