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Model-based design of an intermittent simulated moving bed process for recovering lactic acid from ternary mixture

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ABSTRACT

An intermittent simulated moving bed (3F-ISMB) operation scheme, the extension of the 3W-ISMB to the non-linear adsorption region, has been introduced for separation of glucose, lactic acid and acetic acid ternary-mixture. This work focuses on exploring the feasibility of the proposed process theoretically and experimentally. Firstly, the real 3F-ISMB model coupled with the transport dispersive model (TDM) and the Modified-Langmuir isotherm was established to build up the separation parameter plane. Subsequently, three operating conditions were selected from the plane to run the 3F-ISMB unit. The experimental results were used to verify the model. Afterwards, the influences of the various flow rates on the separation performances were investigated systematically by means of the validated 3F-ISMB model. The intermittent-retained component lactic acid was finally obtained with the purity of 98.5%, recovery of 95.5% and the average concentration of 38 g/L. The proposed 3F-ISMB process can efficiently separate the mixture with low selectivity into three fractions.

1. Introduction

Simulated moving bed (SMB) technology was first developed by Universal Oil Products (UOP) as the Sorbex process [1], which was applied to the petrochemical and then to the sugar industry successfully. Later on its application scope was extended to the pharmaceutical industry for manufacturing chiral and biological drugs [2]. This process allows for both continuous feeding and withdrawal of purified extract and raffinate products. The conventional SMB processes, however, can only separate binary mixture, thus limiting their applicability to the case of the purification of biological compounds.

Recently a number of research groups have been addressing this issue with the aim of developing multicolumn processes that allow for ternary or even quaternary separations. Using such a process, not only ternary mixtures can be treated, but also a certain target component out of a pseudo-ternary mixture can be isolated. A so-called center cut separation for ternary separations has been reviewed by Seidel-Morgenstern and Lee et al. in the latest publication [3]. Different configurations can be found for solving this difficult problem. Among them, the SMB cascade [4], 8ZSMB-IR [5], MCSGP [6], JO [7], and Intermittent-SMB (3S/W-ISMB) [8,9] process schemes proposed so far are worth discussing in more detail. The SMB cascade scheme consists of two 4-zone SMB units connected through the raffinate or extract port. It is a straightforward solution to achieve ternary separation. This system, however, is not completely integrated due to different switching time between the coupled units and independent circulation of the mobile phase. Therefore, the concept of a fully integrated 8-zone SMB with internal recycle (8ZSMB-IR) has been investigated, and further theoretically as well as experimentally realized by coupling two classical SMB systems into a single device. Compared to the SMB cascade scheme, this process maintains the continuous feeding and withdrawal characteristics with higher productivities and better solvent usage. However, they involve higher operation and maintenance costs compared to a single SMB unit and their operation is inflexible. Another useful scheme is the multicolumn countercur-

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rent solvent gradient purification process (MCSGP), which allows to perform solvent gradient elution to a continuous countercurrent unit. High yields and purities of the purified product can be achieved in this operation mode. This method is often used for analysis and separation of complex mixtures, e.g., extracts in natural sources and reaction products. The JO process, one of the most important semi-continuous operation modes, is used to separate intermediate component. This SMB-like process exploits batch chromatography followed by the SMB operation without feed stream. This process is only feasible, when the selectivity between the intermediate component and the most retained one is rather high. Furthermore, a promising semi-continuous chromatographic process Intermittent-SMB (I-SMB) has been applied in the sugar industry with a high productivity. Similar to standard SMB, the I-SMB unit consists of four zones and two product streams; however, in contrast to SMB the switch period is divided into two substeps. In substep I the unit is operated as an SMB without flow in Section 4; in substep II all inlet and outlet ports are closed, and the fluid is just circulated through the column train in order to adjust the relative position of the concentration profiles. It has been shown higher productivity and more flexible than standard SMB whilst fulfilling high-purity specifications. Later on, a new approach based on I-SMB, so called 3S/W-ISMB process, has been developed by Mazzotti research groups for separating multi-component mixtures into three fractions [9]. The third species, either the strongest component (C, 3S-ISMB) or the weakest component (A, 3W-ISMB) is withdrawn during the second substep to realize the separation of three species, A, B and C in a feed. In both 3S/W-ISMB operation modes, four chromatographic columns are used. The strongest component C is obtained in the 3S-ISMB process while the weakest component A in the 3W-ISMB process. The purity constraints for 3S/W-ISMB depend on the reduced Henry's constants of species adsorption on the resin. All these process schemes, however, are basically investigated theoretically under low-concentration linear conditions. Interestingly reports about experimental studies under non-linear conditions on these three-fraction SMB-like processes are rather rare in the open literature.

Lactic acid, as a natural organic acid, can be involved in many chemical reactions with the hydroxyl and carboxylic acid groups. It is used in many aspects, such as, the food industry as a pH regulator, flavoring agent, the cosmetic industry for skin lightening, skin hydration, and the pharmaceutical industry as a component in tablets, prostheses, surgical sutures and drug delivery systems [10]. In recent years, lactic acid has been polymerized into biodegradable plastics as an important monomer in the polymer industry. Polylactic acid (PLLA) is considered as a potential material to replace traditional plastics from fossil fuels. The global lactic acid market is expected to reach around 1960 kilo tons by 2020 due to the increasing PLLA demand [11]. As an important step of the product quality, the issue of separating lactic acid in a continuous mode has been a major concern in the biotechnological process for industrial production. Lee et al. [12] separated a mixture of lactic acid and acetic acid based on a traditional four-zone SMB unit with a PVP resin. They obtained a high lactic acid purity of 99% in the end. But the concentration of lactic acid in the extract was only 6 g/L, which was highly diluted compared with the actual feed concentrations (lactic acid of 100 g/L–200 g/L) in the fermentation broth. Moreover, besides lactic acid and acetic acid, there is residual sugar involved in the fermentation broth as well. Therefore, it is necessary to develop a ternary-mixture separation process for recovery of lactic acid from its fermentation broth. In our previous work [13], a hyper-crossed linked resin was used to separate glucose, lactic acid and acetic acid ternary-mixture from the fermentation broth with good separation performance. The transport dispersive model (TDM) was selected as a suitable model to describe the adsorption behaviors.

In this paper we present a six-column intermittent SMB scheme for three fractions (3F-ISMB), the extension of the semi-continuous 3W-ISMB process to the non-linear adsorption region. Moreover we also explore the feasibility of the new process scheme experimentally for the separation of lactic acid from ternary mixture (glucose, lactic acid and acetic acid) existing in the fermentation broth. The separation requirement are minimum 98% lactic acid purity and 90% lactic acid recovery in the intermediate stream. Due to the reduced lactic acid recovery requirement and the high ratio between lactic acid and citric acid in the feed stream, the net flow rates in all four 3F-ISMB section were considered in the unit design. The operating parameter plane was obtained subsequently based on the real 3F-ISMB model coupled with TDM model and the Modified-Langmuir adsorption isotherm under the reduced-recovery of lactic acid conditions. Afterwards the influence of operating parameters on the separation performance was investigated systematically based on the model. Simultaneously the feasibility of the separation region was verified by several experiments.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

All the chemicals used in this work were A.R. Grade reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The glass chromatography column was brought from JinZheng instrument factory Co., Ltd. (Nanjing, China). The fraction collector (BSZ-100) was purchased from HUXI analysis instrument factory Co., Ltd. (Shanghai, China). The peristaltic pump (BT00-300 M) was purchased from LongerPump (Hebei, China).

2.1.2. Resin

The adsorbent used in this work is a kind of hyper-cross-linked polystyrene divinylbenzene polymeric resin with meso/micro porous structure. The resin was pretreated by firstly soaked in ethanol for 5 h and then packed in the column. Afterwards ethanol was removed from the column rinsing with deionized water until the colorless solution became transparent. The detailed pretreat method can be seen in our previous work [13].

2.2. Experimental methods

2.2.1. Competitive adsorption equilibrium experiments

A series of mixed samples with different concentrations of glucose: 0.45, 0.90, 1.80, 3.60, 5.20, 7.20, 10.41, 14.41, 20.83 g/L, the concentrations of lactic acid: 5.4, 10.8, 21, 43.0, 62.5, 86.5, 125.0, 173.0 and 250.0 g/L; the concentrations of acetic acid: 0.13, 0.27, 0.54, 1.08, 1.56, 2.16, 3.12, 4.32, 6.25 g/L; were prepared in vials. Then, the adsorbent of 1 g was added into each vial with a solution of 10 ml. Later, all the vials were shaken for 24 h in a shaking water bath at 150 rpm at 25 °C to attain equilibrium. Finally, a sample was collected from the supernatant fluid with a syringe and was diluted to the appropriate concentration. The residual concentrations of lactic acid, glucose and acetic acid in the solutions were determined by HPLC. The amount of adsorbed solutes per gram resin was calculated with the following Eq. (1):

$$q_{i,e} = \frac{V(c_{i,0} - c_{i,e})}{m}, \quad (1)$$

where $c_{i,0}$ and $c_{i,e}$ represent the initial and equilibrium aqueous concentration of the solutes, respectively, V is the volume of the solution and m is the mass of the used resin in the each vial.

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