Enhanced separation performance of three-zone simulated moving bed chromatography with ModiCon strategy

Seoin Hwang^{*}, Jae-Ryoung Song^{*}, Ngoc Lan Mai^{**,†}, and Yoon-Mo Koo^{*,†}

*Department of Biological Engineering, Inha University, Incheon 22212, Korea **Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Vietnam (*Received 19 December 2019 • accepted 28 February 2020*)

Abstract-A three-zone simulated moving bed (SMB) chromatography using ModiCon strategy is proposed to enhance the separating performance. In this approach, three fold-concentrated feed and only desorbent are introduced during one-third and two-thirds of the switching time, respectively. The results showed that if the concentrated feed is introduced during the first and the last subsection of switching time, purity of extract and raffinate are improved, respectively, while recovery and other performance indices (i.e., solvent consumption and ratio of desorbent/feed) are slightly decreased. On the other hand, introduction of concentrated feed during the middle subsection of switching time results in an increase of both raffinate and extract purity, as well as the recovery yield. Other performance indices were comparable to those of three-zone SMB without ModiCon.

Keywords: ModiCon, Three-zone, Simulated Moving Bed (SMB)

INTRODUCTION

Chromatography is widely used for high purity separation, such as in the pharmaceutical industry, fine chemicals and biotechnology. Traditionally, liquid chromatography is a discontinuous batch process. In batch chromatography, the mixture interacts with the adsorbent packed in the column and moves at different rates within the column, which leads to material separation. Batch chromatography is generally expensive because of high solvent consumption and low productivity [1]. To alleviate these shortcomings, an alternative concept, SMB (Simulated Moving Bed), was developed that enables a continuous operation, patented by Universal Oil Products [2,3].

The conventional SMB device, shown in Fig. 1(a), consists of





[†]To whom correspondence should be addressed.

E-mail: maingoclan@tdtu.edu.vn, ymkoo@inha.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

four zones bounded by two inlets (feed, desorbent) and two outlets (raffinate and extract). Each zone consists of columns packed with adsorbent. The mixture to be separated is injected through the feed inlet, and the solvent is continuously introduced through the desorbent inlet. During the separation, high affinity substances with the adsorbent are recovered at the extract outlet, whereas low affinity substances with the adsorbent are recovered at the raffinate outlet.

One of the major factors affecting the design and operation of SMB devices is the number of valves and pumps in the system, which are directly related to the structure and operating costs of the SMB. Appropriate use of such equipment affects the flexibility, scalability, and operation mode of the SMB systems. However, having a considerable number of valves and pumps increases the feed line or the dead volume of the system thus affects the efficiency and operation cost of the SMB separation [4,5]. To reduce process costs while maintaining the high efficiency of the SMB, three-zone SMB has been proposed [6,7].

As shown in Fig. 1(b), the three-zone SMB does not have zone IV and has several advantages over conventional SMB [8]. First, the use of adsorbent can be reduced by reducing the number of columns. Second, the chance of failure is reduced by reducing the number of valves and pumps. Third, the cost of chromatography purification can be reduced by reducing columns, adsorbents, valves and pumps. However, the removal of zone IV results in the diluted raffinate product since the mobile phase is not recycled and is discharged entirely through the raffinate outlet.

To date, various driving strategies, such as Varicol [9,10], PowerFeed [11-13], and ModiCon [14,15], have been reported to increase the efficiency of the general SMB operation or to compensate for the disadvantages of conventional SMB. VariCol uses asynchronous switching with different switching times for each zone within one cycle, so that the length of each zone is flexible. This strategy improves the performance of the base SMB, but is limited by its ability to only improve the purity of the components [16]. Powerfeeds that change the feed flow rate are more likely to fail components in the mechanical plant and present a risk of shortening the life of the equipment [15]. Finally, ModiCon is based on changes in concentration in the SMB process during the exchange time. According to previous studies comparing the three SMB strategies, the ModiCon strategy showed the most improved separation performance [17]. Moreover, several strategies such as partial-feeding [18], port-location rearrangement [18,19], and three-zone SMB apparatus without zone I [20], have been proposed to improve the performance of three-zone SMB. However, publications regarding the application of ModiCon strategy in three-zone SMB were not found in the literature. Therefore, in this study, we applied the Modi-Con strategy to improve the performance of three-zone SMB, performed various case studies through computer simulation, and compared the results to confirm the effect of ModiCon on the process. The separation of succinic acid and lactic acid, which is considered as crucial process for the production of succinic acid by biotechnological pathway [21], was used as model solutes in this study.

EXPERIMENTAL METHODS

1. Design of Three-zone SMB with ModiCon

Fig. 1(b) represents the three-zone SMB design used in this study. Since zone IV is removed as compared to that of conventional SMB, the mobile phase is not recirculated. As a result, the raffinate product will be diluted with the mobile phase. To improve the performance of three-zone SMB, ModiCon was applied. The separation of binary solute model lactic acid (A) and succinic acid (B) was realized by using Amberchrom-CG300C as resin and pure water as desorbent. The adsorption isotherms of the solutes were obtained from previous studies [21].

Fig. 2 shows the three different ModiCon strategies used in this study. Feed solution with equal concentration of lactic acid and succinic acid was used. Concentrated feed was injected at different period of the switching time by dividing the switching time into three equal sections. For instance, feed solution (10 g/L, i.e., 5 g/L of each solute) was constantly injected during the whole switching time of 7.56 minutes in the conventional SMB and in three-zone SMB without ModiCon. Whereas, in three-zone SMB with Modi-Con, three-fold concentrated feed solution (30 g/L, i.e., 15 g/L of each solute) was introduced in only 2.52 minutes and desorbent



Concentrated feed (30 g/L) was injected during the first (a), middle (b) and last third (c) of the switching time. In the four-zone SMB and three-zone SMB without ModiCon, feed (10 g/L) was constantly injected during the whole switching time (7.56 minutes, dashed line), whereas in three-zone SMB with ModiCon, high concentrated (30 g/L) and desorbent was injected for 2.52 and 5.04 minutes, respectively, during the switching time (7.56 minutes).

Fig. 2. Definition of three ModiCon patterns of feed in three-zone SMB.

was injected in the remaining 5.04 minutes of switching time period. The total feed amount, feed flow rate, and column configuration of three-zone SMB were similar to that of conventional four-zone SMB.

2. SMB Modelling and Simulation

Computer simulations were performed using Aspen Chromatography V9 (Aspen Tech., USA) for the study of three-zone SMB with ModiCon strategy.

The equilibrium between solid and liquid phases is represented by linear adsorption isotherms and nonlinear Langmuir adsorption equations. First, in the case of linear, it is expressed as follows:

$$\mathbf{q}_i^* = \mathbf{H}_i \mathbf{C}_i \quad (\mathbf{i} = \mathbf{A}, \mathbf{B}) \tag{1}$$

where H_i is Henry's constant for component i and q_i is the adsorption concentration at equilibrium with liquid concentration C.

In the case of a nonlinear adsorption isotherm, there are various types but the Langmuir adsorption isotherm, the most common one, is represented as follows:

$$q_{i}^{*} = \frac{H_{i}C_{i}}{1 + K_{A}C_{A} + K_{B}C_{B}} \quad (i = A, B)$$
(2)

where K_i is the equilibrium constant for component i.

Successful operation of the SMB requires the proper determination of various variables. In particular, the flow rate has the greatest influence on the movement speed of the actual materials, so setting the proper flow rate is directly related to successful SMB operation. To this end, various flow rate determination methods for SMB have been studied. In this study, the operating conditions of SMB were determined using triangle theory [22], which is the most widely used flow rate determination method. In triangular theory, the variable m_j is expressed as Eq. (4) to derive the perfect separation region.

$$H_A < m_2 < m_3 < H_B$$
 (3)

$$m_{j} = \frac{Q^{SMB} t_{sw} - V \varepsilon^{*}}{V(1 - \varepsilon^{*})}$$
 (j: location of zone) (4)

 m_j is the dimensionless flow rate ratio and is defined as the ratio between the stationary and mobile phase flow rates in each zone. m_j is an important parameter that determines the flow rate in zone II and zone III where the actual separation is performed. Therefore, the conditions under which the two components can be completely separated in linear SMB chromatography can be carried out under the following boundary conditions [10]:

$$H_B < m_1 < \infty \tag{5}$$

$$H_A < m_2 < H_B \tag{6}$$

$$\mathbf{H}_{A} < \mathbf{m}_{3} < \mathbf{H}_{B} \tag{7}$$

$$\frac{-\varepsilon}{1-\varepsilon} < m_2 < H_B \tag{8}$$

Fig. 3 shows the boundary conditions shown in Eq. (5)-(8) in m_2 - m_3 chart. From this the criteria for determining the parameters required for SMB chromatography operating conditions are presented.

The internal flow rate of the column can be calculated from the material balance around the inlet and outlet nodes. The flow rate



Fig. 3. Divided plane (m₂, m₃) with different performance in terms of purity of the outlet stream with linear adsorption isotherm.

calculation methods for four-zone and three-zone SMB are different. This is because there is a recycle stream from zone IV to zone I in four-zone SMB, while there is no recycle from zone IV in the three-zone SMB. The following shows the flow rate calculations in the conventional four-zone and three-zone SMB.

• Conventional four-zone SMB:
Desorbent node:
$$Q_{IV}+Q_D=Q_I$$

Extract node: $Q_{II}-Q_E=Q_{II}$
Feed node: $Q_{II}+Q_F=Q_{III}$
Raffinate node: $Q_{II}-Q_R=Q_{IV}$ (9)
• Three-zone SMB:
Desorbent node: $Q_D=Q_I$
Extract node: $Q_I-Q_E=Q_{II}$
Feed node: $Q_{II}+Q_F=Q_{III}$
Raffinate node: $Q_R=Q_{III}$ (10)

where Q_b , Q_{Ib} , Q_{IIb} , Q_{IV} are the flow rates through the corresponding zones. Q_{D} , Q_B , Q_E , Q_R are the flow rates of desorbent, feed, extract and raffinate, respectively.

Purity, recovery yield, solvent consumption and desorbent/feed ratios were calculated to evaluate the performance of SMB.

When solute A is recovered from raffinate and solute B is recovered from extract in SMB, the purity of each substance is defined as Eq. (11). The numerator in Eq. (11) refers to the targeted material in the product, and the denominator is the sum of the two captured materials [23].

$$Purity_{RA} [\%] = \frac{C_R^A}{(C_R^A + C_R^B)} \times 100$$
$$Purity_{EB} [\%] = \frac{C_E^B}{(C_E^A + C_E^B)} \times 100$$
(11)

The recovery yield of the solute is an important variable of the separation process, and the recovery yield of solutes at raffinate and extract ports can be calculated by Eq. (12). The numerator refers to the amount of characteristic components in the product, and the denominator refers to the total amount of raw material [23]:

Korean J. Chem. Eng.(Vol. 37, No. 6)

$$\operatorname{Recovery}_{RA} [\%] = \frac{C_R^* \cdot Q_R}{C_F^A \cdot Q_F} \times 100$$

$$\operatorname{Recovery}_{EB} [\%] = \frac{C_E^A \cdot Q_E}{C_F^A \cdot Q_F} \times 100$$
(12)

One important measure of process performance is solvent consumption. Eq. (13) is defined as the flow rate of the solvent required to separate the raw material [23]:

Solvent Consumption_{*Raf*} [L/g] =
$$\frac{(Q_E + Q_F)}{(C_R^A Q_R)}$$

Solvent Consumption_{*Ext*} [L/g] = $\frac{(Q_E + Q_F)}{(C_E^B Q_E)}$ (13)

where C_k^i is concentration of solute i (A and B) in the stream k (F: feed, E: extract, R: raffinate).

The flow rate ratio of desorbent/feed ratio was used to determine the degree of dilution of raffinate in the three-zone SMB.

Flow rate ratio
$$\left(\frac{\text{Desorbent}}{\text{Feed}}\right) = \frac{Q_D}{Q_F}$$
 (14)

RESULTS AND DISCUSSION

The performance of conventional four-zone SMB, three-zone

Table 1. Model parameters used in SMB operations [21]



Fig. 4. Operating points in triangle with linear adsorption isotherm.

SMB with and without ModiCon was compared. The model parameters used in SMB, including column size, porosity, and transfer coefficients, are shown in Table 1. Both conventional and threezone SMB were operated in the same way. For the conventional SMB, eight columns were arranged in each zone with a configuration of 2/2/2/2 while six columns with a configuration of 2/2/2were arranged for three-zone SMB.

	Lactic acid (A)	Succinic acid (B)
Henry constant (H)	2.7343	6.9744
Molecular diffusivity (D_{∞}), cm ² /min	8.63×10^{-4}	7.30×10^{-4}
Intra-particle diffusivity (D_p) , cm ² /min	7.15×10^{-4}	6.45×10^{-4}
Axial dispersion coefficient (E_b) , cm ² /min	Chung and Wen correlation [24]	
Adsorbent particle diameter (d_p) , μm	120	
Column length (L _c), cm	15	
Column diameter (d _c), cm	2.5	
Inter-particle porosity (ε_b)	0.376	
Intra-particle porosity (ε_p)	0.723	

Table 2. Operating conditions in each operating point (Fig. 4)

Operating mode		(m ₂ , m ₃) [ml/min]	Q _I [ml/min]	Q _∏ [ml/min]	Q _{III} [ml/min]	Q _{IV} [ml/min]	Х	C_i^F [g/L]
	Conventional four-zone SMB	(2.73, 6.97)	8.92	6.23	8.39	6.01	2/2/2/2	10
Point 1	Three-zone SMB w/o ModiCon	(2.73, 6.97)	8.92	6.23	8.39	-	2/2/2	10
	Three-zone SMB with ModiCon	(2.73, 6.97)	8.92	6.23	8.39	-	2/2/2	30-0-0/0-30-0/0-0-30
	Conventional four-zone SMB	(3.26, 5.38)	8.92	6.50	7.58	6.01	2/2/2/2	10
Point 2	Three-zone SMB w/o ModiCon	(3.26, 5.38)	8.92	6.50	7.58	-	2/2/2	10
	Three-zone SMB with ModiCon	(3.26, 5.38)	8.92	6.50	7.58	-	2/2/2	30-0-0/0-30-0/0-0-30
Point 3	Conventional four-zone SMB	(3.79, 5.91)	8.92	6.77	7.85	6.01	2/2/2/2	10
	Three-zone SMB w/o ModiCon	(3.79, 5.91)	8.92	6.77	7.85	-	2/2/2	10
	Three-zone SMB with ModiCon	(3.79, 5.91)	8.92	6.77	7.85	-	2/2/2	30-0-0/0-30-0/0-0-30
Point 4	Conventional four-zone SMB	(4.32, 6.44)	8.92	7.09	8.12	6.01	2/2/2/2	10
	Three-zone SMB w/o ModiCon	(4.32, 6.44)	8.92	7.09	8.12	-	2/2/2	10
	Three-zone SMB with ModiCon	(4.32, 6.44)	8.92	7.09	8.12	-	2/2/2	30-0-0/0-30-0/0-0-30

1060

Operating mode		Purity [%]		Recovery [%]		Solvent consumption [L/g]		Desorbent/
		Raffinate	Extract	Raffinate	Extract	Raffinate	Extract	feed ratio
	Case1	84.25	86.45	82.98	77.97	0.27	0.29	1.34
	Case2	78.67	90.38	88.62	70.27	0.25	0.32	4.14
Point 1	Case3	66.01	99.85	98.69	48.49	0.23	0.52	4.14
	Case4	86.98	97.53	94.39	84.66	0.24	0.29	4.14
	Case5	90.76	90.77	72.77	87.56	0.31	0.26	4.14
	Case1	91.32	88.06	81.22	87.56	0.40	0.37	2.70
	Case2	85.67	92.96	89.08	77.58	0.36	0.42	8.28
Point 2	Case3	77.57	99.77	97.96	63.66	0.33	0.51	8.28
	Case4	91.95	97.51	92.86	82.87	0.35	0.39	8.28
	Case5	93.75	88.82	83.51	86.13	0.43	0.38	8.28
	Case1	90.79	91.50	86.18	83.12	0.35	0.36	2.70
	Case2	83.52	96.18	92.95	72.26	0.36	0.41	8.28
Point 3	Case3	72.92	99.94	98.44	54.28	0.30	0.55	8.28
	Case4	90.90	99.14	95.27	78.85	0.31	0.38	8.28
	Case5	92.89	92.64	85.14	84.71	0.35	0.35	8.28
	Case1	85.78	93.50	89.28	76.12	0.31	0.33	2.70
	Case2	79.03	98.01	94.99	65.68	0.29	0.42	8.28
Point 4	Case3	66.56	99.98	98.65	42.69	0.28	0.64	8.28
	Case4	86.48	99.72	96.33	71.94	0.29	0.38	8.28
	Case5	90.78	95.59	90.01	82.32	0.31	0.33	8.28

Table 3. SMB simulation results with linear adsorption isotherm

Case 1: Conventional four-zone SMB.

Case 2: Three-zone SMB without ModiCon.

Case 3-5: Three-zone SMB with ModiCon: concentrated feed at first (3), middle (4) and last third (5) of the switching time.

1. Separation with Linear Adsorption Isotherm

In the case of linear adsorption isothermal, the triangle theory is used to determine the operating range of the conventional and the three-zone SMB (Fig. 3). The operating points within the triangular region, where pure products can be obtained in both raffinate and extract, were employed. To find the efficient operating conditions, simulation was carried out for four points in the triangle as shown in Fig. 4. The operating conditions for each operating point are given in Table 2.

As in Table 3, the separation performance from point 1 to point 4 was similar among SMB operating modes. For instance, the lowest purity was observed at point 1, which is close to no pure zone, whereas the highest raffinate and extract purity were obtained at point 2 (close to pure raffinate), and point 4 (close to pure extract), respectively. Operating point 3 (located between point 2 and 4) was observed to be the optimal operating point since high purity of both raffinate and extract could be obtained. In addition, the raffinate was more diluted in three-zone SMB as compared to conventional SMB as the ratio of desorbent/feed of three-zone SMB (case 2-5) was at least three-times higher than that of conventional 4 zone SMB (case 1).

Among the three feeding time in three-zone SMB with Modi-Con, concentrated feed during the first third (case 3) could enhance the purity of extract but reduce the extract recovery and increase solvent consumption. Similarly, concentrated feed during the last third (case 5) resulted in higher raffinate purity but lower raffinate recovery and higher solvent consumption. Concentrated feed during the middle third (case 4) improved all the qualities of both raffinate and extract, i.e., purity, recovery and solvent consumption comparing to three-zone SMB without ModiCon (case 2). Particularly, in some cases the purity of both raffinate and extract of three-zone SMB with ModiCon were higher than that of the conventional four-zone SMB at all tested operating points (cases 4 and 5). At the operating point 3, the purity of raffinate and extract of three-zone SMB with ModiCon (case 4) increased by 7.38% and 2.96%, respectively, while the recovery yield increased by 2.32% and 6.59% for raffinate and extract, respectively, as compared to threezone SMB without ModiCon (case 2). In addition, the solvent consumption also decreased by 0.0409 L/g and 0.0325 L/g for raffinate and extract, respectively.

The concentration profile of conventional four-zone SMB (Fig. 5(a)) and three-zone SMB (Fig. 5(b)) indicates a clear separation between component A and B with linear isotherm. The concentration profile of three-zone SMB with ModiCon is shown in Fig. 6. When concentrated feed was introduced during the first third of switching time (Fig. 6(a)), it was fed into the rear part of the concentration profile of component B and pushed the profile to the right, resulting in broader B and sharper A concentration profile in zone III. As a result, raffinate (A) was contaminated by extract (B) while extract (B) became purer. On the other hand, when the concentrated feed was introduced during the last third of switching time (Fig. 6(c)), it was fed into the front part of the concentration profile of compo-



Fig. 5. Concentration profile of four-zone SMB (a) and three-zone SMB without ModiCon (b) with linear adsorption isotherm.

nent A and pushed the profile to the left. This movement resulted in a broader A and sharper B concentration profile in zone II. As a result, purer raffinate (A) was obtained as the front height of component A profile increased. When the concentrated feed was introduced in the middle third of the switching time (Fig. 6(b)), it went onto the middle of overlapping peaks, resulting in no shift of concentration profile. Both A and B showed sharper profiles due to the addition of feed onto the middle of overlapping peaks. As a result, purer product was obtained in both raffinate and extract.

The total amount of feed was identical between all SMB operation modes during one switching interval. Three-times concentrated feed was introduced only for one-third of the switching time in three-zone SMB with ModiCon. The results indicated the position of introducing concentrated feed during the switching time has a strong influence on the purity of product ports. This allows one to obtain desired product purity by appropriately selecting the position to introduce the concentrated feed during the switching time in operation of three-zone SMB with ModiCon.

2. Separation with Langmuir Adsorption Isotherm

In this study, the effects of adsorption isotherm parameters pro-



Concentrated feed at first third (a), middle third (b) and last third (c) of the switching time. The dashed line is concentration profile of three-zone SMB without ModiCon.

Fig. 6. Concentration profile of three-zone SMB with ModiCon with linear adsorption isotherm.

vided in the simulation program (i.e., linear or nonlinear/Langmuir) on the performance of SMB were also investigated. To do this, the simulations were carried by keeping all other parameter identical except the equation form of the adsorption isotherm in the simulation program. The SMB operating point (Fig. 7) was



Fig. 7. Operating point in triangle with Langmuir adsorption isotherm.

selected from the linear adsorption system (point 3, Fig. 4) as a reference for the SMB operation with Langmuir adsorption isotherm. The SMB column configuration, flow rate, switching time, and feed concentration were all identical to those of the linear adsorption case, except the adsorption isotherm. The operating conditions of SMB with Langmuir adsorption isotherm are summarized in Table 4.

The separation performance of SMB with the Langmuir adsorption is shown in Table 5. The performance of SMB with Langmuir adsorption isotherm was similar to that with the linear adsorption isotherm. For instance, reduced raffinate purity and increased raffinate dilution was observed in three-zone SMB compared to fourzone SMB. In addition, ModiCon could enhance the performance of three-zone SMB, and the tendency was similar to that with linear adsorption isotherm. For example, higher extract purity and lower solvent consumption but lower extract recovery were obtained when high concentration feed was injected during first third of switching time (case 3). Higher raffinate purity and lower solvent consumption but lower raffinate recovery were obtained when concentrated feed was introduced during last third of switching time (case 5) as compared to conventional four-zone SMB and three-zone SMB without ModiCon. The injection of concentrated feed during the middle third section (case 4) improved both purity and recovery of raffinate and extract and reduced the solvent consumption. For instance, the purity of raffinate and extract increased by 6.73% and 2.68%, respectively. Meanwhile, the recovery was increased by 2.06% and 4.54%, respectively, for raffinate and extract. Solvent consumption was decreased by 0.0069 L/g and 0.0277 L/g, respectively, for raffinate and extract.

The concentration profiles of four-zone SMB and three-zone SMB in case of Langmuir adsorption isotherm are shown in Fig. 8. The concentration profile of three-zone SMB with ModiCon is shown in Fig. 9. The Langmuir adsorption case also shows the same tendency as the linear adsorption isotherm: the feed moved much to the right when the concentrated feed was injected during the first third (Fig. 9(a)) causing higher peak of B and contaminating the raffinate in zone III, resulting in purer extract. On the other hand, feed was moved significantly to the left when concentrated feed was fed during the last third, causing narrower peak of B, result-

Table 4. Operating conditions of various SMB processes with Langmuir adsorption isotherm

1 0	1 0		
Operating conditions	Conventional four-zone SMB	Three-zone SMB w/o ModiCon	Three-zone SMB with ModiCon
Q _I (ml/min)	8.92	8.92	8.92
Q _{II} (ml/min)	6.77	6.77	6.77
Q _{III} (ml/min)	7.85	7.85	7.85
Q _{IV} (ml/min)	6.01	-	-
t _{su} , min	7.56	7.56	7.56
Column configuration	2/2/2/2	2/2/2	2/2/2
Feed concentration $(C_A^F + C_B^F)$, g/L	10	10	30-0-0/0-30-0/0-0-30
Adsorption isotherm		$q_A = \frac{2.73x}{1+0.01x}, q_B = \frac{6.97x}{1+0.01x}$	

Table 5. SMB simulation results of various SMB processes with Langmuir adsorption isotherm

Operating	Purity	r [%]	Recover	ry [%]	Solvent consu	mption [L/g]	n [L/g] Desorbent/	
mode	Raffinate	Extract	Raffinate	Extract	Raffinate	Extract	feed ratio	
Case1	86.19	91.36	86.51	77.28	0.35	0.39	2.70	
Case2	80.50	96.71	93.81	67.88	0.32	0.44	8.28	
Case3	66.49	99.95	98.56	41.96	0.30	0.68	8.28	
Case4	87.23	99.39	95.87	72.42	0.31	0.41	8.28	
Case5	92.61	93.75	87.64	84.31	0.34	0.36	8.28	

Case 1: Conventional four-zone SMB.

Case 2: Three-zone SMB without ModiCon.

Case 3-5: Three-zone SMB with ModiCon: concentrated feed at first (3), middle (4) and last third (5) of the switching time.

16

14

12

10

8

6

4

2

(a)

Concentration (g/L)

Ι



Fig. 8. Concentration profile of four-zone (a) and three-zone SMB without ModiCon (b) with Langmuir adsorption isotherm.

ing in purer raffinate. When concentrated feed was injected during the middle third, both A and B peaks became sharper, and purer extract and raffinate were obtained.

CONCLUSIONS

The SMB process is a continuous process that can satisfy high purity and recovery at the same time as compared to batch chromatography. Three-zone SMB derived from conventional four-zone SMB by eliminating zone IV could reduce the amount of adsorbent, valves and pumps, and thus the purification cost and risk of failure of SMB chromatography.

In this study, the ModiCon strategy was applied to improve the performance of three-zone SMB, and the results were compared through simulations in various situation using Aspen chromatograph. The ModiCon strategy divides the switching time into three subsections, injecting three-fold concentrated feed during one third, and only desorbent for two-thirds without injection of the target material. This operation was performed assuming linear or Langmuir adsorption isotherm. As a result, it was best to introduce concentrated feed during the middle third for both cases of



² (c)

0

Desorbent

Column number Concentrated feed at first (a), middle (b) and last third (c) of the switching time. The dashed line is concentration profile of three-zone SMB without ModiCon.

30 ↓ E×tr П

В

60

† Feed

60

↑ Feed

60 ↑ Feed Ш

Α

90

1

90 ↓ ate

Raff

Raffi

Ш

Α

Π

Δ

90

Fig. 9. Concentration profile of three-zone SMB with ModiCon with Langmuir adsorption isotherm.

adsorption isotherm. Introduction of concentrated feed during the middle third enhanced purity and recovery of both raffinate and extract, and decreased the solvent consumption.

In particular, the characteristics of the ModiCon process could be confirmed through various types of simulation results. As the purity changes depending on the timing of introducing concentrated feed, this modified process can be used to increase specific target material. For example, it is advantageous to inject concentrated feed during the first third to increase the purity of the extract. Conversely, it is recommended to introduce the concentrated feed during the last third to obtain purer raffinate.

The ModiCon strategy is useful in reducing capital and operating costs through the less use of equipment and solvents without sacrificing quality and quantity of products compared to three-zone SMB operations. The proposed strategy could also be applied to industrial-scale SMB with different sorbent types to handle the feed of high concentration.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (2016R1A2B2014099).

REFERENCES

- 1. L. Miller, C. Grill, T. Yan, O. Dapremont, E. Huthmann and M. Juza, *J. Chromatogr. A*, **1006**, 267 (2003).
- 2. D. B. Broughton and C. G. Gerhold, U.S. Patent, 2,985,589 (1961).
- 3. D. B. Broughton, Chem. Eng. Prog., 66, 70 (1970).
- 4. P. Sá Gomes and A. E. Rodrigues, *Chem. Eng. Technol.*, 35, 17 (2012).
- 5. R. P. V. Faria and A. E. Rodrigues, J. Chromatogr. A, 1421, 82 (2015).
- K. Hashimoto, M. Yamada, S. Adachi and Y. Shirai, J. Chem. Eng. Jpn., 22, 432 (1989).
- 7. Y. Zang and P. C. Wankat, Ind. Eng. Chem. Res., 41, 5283 (2002).

- 8. C. Y. Chin and N. H. L. Wang, Sep. Purif. Rev., 33, 77 (2004).
- 9. O. Ludemann-Hombourger, R. M. Nicoud and M. Bailly, Sep. Sci. Technol., 35, 1829 (2000).
- O. Ludemann-Hombourger, G. Pigorini, R. M. Nicoud, D. S. Ross and G. Terfloth, *J. Chromatogr. A*, 947, 59 (2002).
- 11. Y. Zang and P. C. Wankat, Ind. Eng. Chem. Res., 41, 5283 (2002).
- Z. Zhang, M. Mazzotti and M. Morbidelli, J. Chromatogr. A, 1006, 87 (2003).
- 13. Z. Zhang, M. Morbidelli and M. Mazzotti, AIChE J., 50, 625 (2004).
- H. Schramm, A. Kienle, M. Kaspereit and A. Seidel-Morgenstern, Chem. Eng. Sci., 58, 5217 (2003).
- 15. H. Schramm, M. Kaspereit, A. Kienle and A. Seidel-Morgenstern, *J. Chromatogr. A*, **1006**, 77 (2003).
- 16. Y. Yu, K. R. Wood and Y. A. Liu, Ind. Eng. Chem. Res., 54, 11576 (2015).
- Z. Zhang, M. Mazzotti and M. Morbidelli, *Korean J. Chem. Eng.*, 21, 454 (2004).
- 18. S. Mun, J. Chromatogr. A, 1341, 8 (2014).
- 19. P. Tangpromphan, H. Budman and A. Jaree, *Chem. Eng. Process. -Process Intensification*, **126**, 23 (2018).
- B. Shen, M. Chen, H. Jiang, Y. Zhao and F. Wei, Sep. Sci. Technol., 46, 695 (2011).
- 21. H.-G. Nam, C. Park, S.-H. Jo, Y.-W. Suh and S. Mun, *Process Biochem.*, 47, 2418 (2012).
- G. Storti, M. Mazzotti, M. Morbidelli and S. Carrà, AIChE J., 39, 471 (1993).
- 23. I. M. Aroso, R. Craveiro, Â. Rocha, M. Dionísio, S. Barreiros, R. L. Reis, A. Paiva and A. R. C. Duarte, *Int. J. Pharm.*, **492**, 73 (2015).
- 24. E. J. Wilson and C. J. Geankoplis, *Ind. Eng. Chem. Fundam.*, 5, 9 (1966).