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Recovery of ionic liquid and sugars from hydrolyzed biomass using ion exclusion simulated moving bed chromatography

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ABSTRACT

Efficient recovery of ionic liquid (IL) from aqueous mixture of ILs and sugars (which derived from enzymatic or chemical catalyzed hydrolysis of ILs-pretreated biomass) is a major drawback for commercialization of biofuel and platform chemicals production from biomass utilized ILs as pretreatment solvent. In this study, simulated moving bed (SMB) chromatography equipped with ion exclusion column (containing $[Emim]^+$ cation) was investigated to separate sugars (glucose and xylose) which are the main products from biomass hydrolysate and 1-Ethyl-3-methylimidazolium acetate (EmimAc) which is the ILs used for biomass pretreatment. A four-zone SMB system with a configuration of 2-2-2-2 (2 ion exclusion columns in each zone) was used to recover glucose, xylose and EmimAc from their aqueous mixture with yield of 71.38, 99.37 and 98.92%, respectively. Moreover, the optimization of SMB zone configuration by simulation results in a complete recovery of ILs. This result indicates that for the first time, ion exclusion SMB chromatography could be used for complete recovery of ILs from aqueous sugar mixture.

1. Introduction

The use of fossil fuels causes a considerable risk to the global climate and energy security. Renewable and sustainable energy production is an alternative method for dependent energy challenges. Cellulose is the most abundant biological material on earth. It has been considered as a sustainable source of raw material for the production of biofuels and platform chemicals [1]. Cellulose has a high crystalline structure and in nature, it is tangled with hemicelluloses and lignin. Therefore, lignocelluloses are highly resistant to hydrolysis. Pretreatment of raw materials is a prerequisite step to facilitate resistant cellulosic biomass more accessible to enzymatic hydrolysis [2]. Several methods for pretreatment have been proposed including biological, physical, physicochemical and chemical processes [3,4]. However, these methods have some disadvantages leading to the inefficient production of biofuels and chemicals from lignocellulosic materials.

Recently, ionic liquids (ILs), consisting entirely of ions and melting below 100 °C, has shown great promise for use in the pretreatment of biomass. Several types of ILs are able to dissolve crystalline cellulose and biomass under mild condition resulting polysaccharides that can be easily hydrolyzed using cellulolytic enzymes [5–8]. Moreover, cellulose dissolved in ILs could be efficiently converted into fermentable sugars (mostly glucose and xylose) by (solid) acid catalysts [9,10]. However, both of the processes rely on the recovery of ILs from aqueous sugar solution. Many attempts have been used to recover ILs from aqueous sugar mixtures. Binder and Raines [11] used ion exclusion chromatography in batch operation to recover ILs, glucose and xylose with yield >95, 94 and 88%, respectively. In addition, solvent extraction technique based on chemical affinity of borate for sugars was applied to extract of glucose, xylose and cellobiose from aqueous mixture of ILs with yield up to 90%. This result in fermentable sugars solution and facilitate the recovery of ILs [12]. ILs are expensive and complete recovery will be required to make biomass processing with ILs economical.

Simulated moving bed (SMB) chromatography, known as a powerful tool for the continuous counter-current separation of binary mixtures, was originally developed by Universal Oil Products (UOP). Compared with batch chromatographic process, SMB chromatography exhibits a number of advantages such as higher productivity and lower solvent consumption. SMB chromatography has been widely applied in sugar, pharmaceutical, oil and gas industries [13–17].

In this study, SMB chromatography equipped with ion exclusion column was investigated to separate ILs, glucose and xylose from their aqueous solution. Effect of SMB zone flow rate and zone

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configuration on the separation of ternary mixture of sugars and ILs was also investigated.

2. Materials and methods

2.1. Materials

1-Ethyl-3-methylimidazolium acetate (EmimAc), glucose, xylose, 3,5-Dinitrosalicylic acid (DNS), Dowex 99Ca/320 (Ca^{2+} form) and Dowex 50WX4-400 (H^+ form) cation exchanger resin were obtained from Sigma–Aldrich. All reagents were used without further purification. Distilled and deionized water (DDW) as the mobile phase was obtained from Milli-Q system (Millipore, USA). Jacketed glass columns (30 cm × 1.1 cm) were used as column for determining adsorption isotherm of solutes and SMB operation.

2.2. Preparation of ion exclusion column

Solution of Dowex 99Ca/320 (Ca^{2+} form) or Dowex 50WX4-400 (H^+ form) with DDW was packed in a jacketed glass column (30 cm × 1.1 cm) by slurry method. The functional group Ca^{2+}/H^+ of resin was exchanged with $[Emim]^+$ of EmimAc by passing 10 column volume (CV) of EmimAc in water through the column with ÄKTA FPLC system (GE Healthcare, USA). The cation exchange was performed at 50 °C. Conductivity detector was used to monitor the outlet stream during the process. The cation exchange process was completed when the conductivity signal (mS/cm) was stable for more than 5 CV (Fig. 1a). It implied that the column was fully saturated and completed exchange of Ca^{2+}/H^+ by $[Emim]^+$. Degassed and deionized water was then passed through the column to remove any contaminant solutes.

The performance of this column was confirmed by loading 100 μL of 2% EmimAc solution at flow rate of 1 mL/min into the column. In ion exclusion chromatography, charge species such as ionic liquid are excluded from the charged resin while nonelectrolytes such as sugars are retained [18]. Since EmimAc was not retained and diffused through inter and intra-particle pores of the resin (Fig. 1b), the retention volume of EmimAc was used to determine the total column porosity. Total porosity of this column was 0.35.

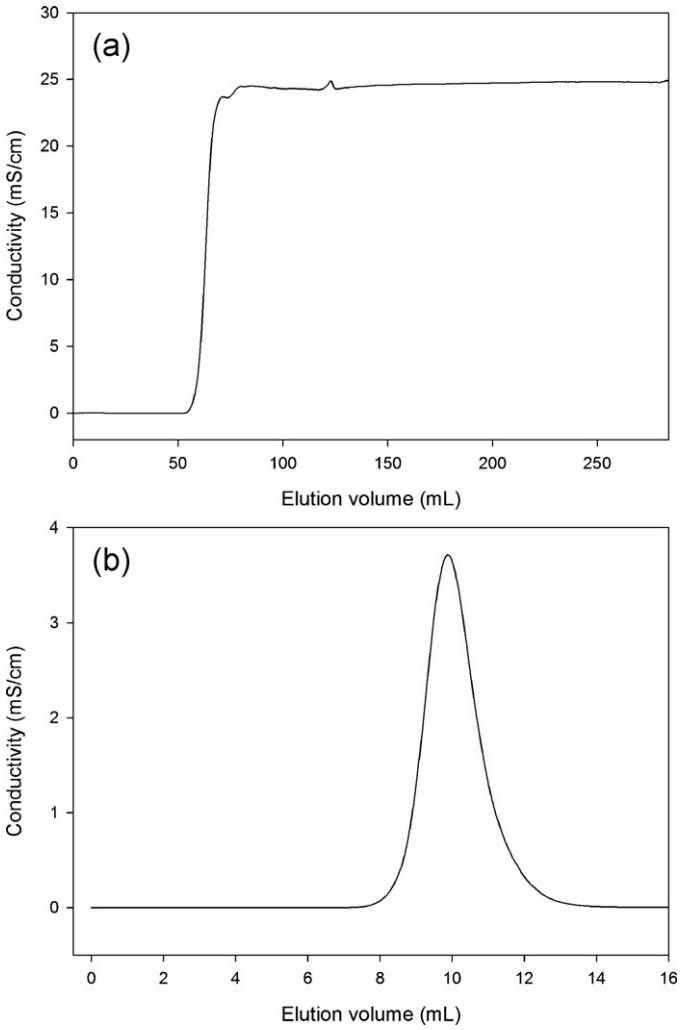

Fig. 1. Conductivity of Dowex 99Ca/320 (Ca^{2+} form) packed column during cation exchange process with EmimAc (a) and $[Emim]^+$ exchanged column with EmimAc injection (b).

2.3. Single component frontal analysis

Although there were many chromatographic methods available to determine single-component isotherms, frontal analysis (FA) exhibited the most efficient due to its accuracy and simplicity [19,20]. The FA method was used to determine the adsorption equilibrium isotherm of glucose, xylose and EmimAc on the ion exclusion Dowex-$[Emim]^+$ column.

The adsorption isotherms of glucose, xylose and EmimAc were carried out at 50 °C. Deionized water was used as the mobile phase with a flow rate of 1.5 mL/min. In this experiment, four different concentrations were used for each sugars and EmimAc in ranges of 5–20 g/L. Every 1.5 mL of effluent was fractioned and their concentration was determined. Glucose and xylose concentrations were determined by DNS method [21], while EmimAc concentration was analyzed by HPLC method.

2.4. SMB system for recovery of ionic liquid and sugars

Four-zone SMB system with eight columns connected in series, was constructed at SMB laboratory, Inha University for the experiment. This is a continuous chromatographic system composed of two columns in each zone. The jacketed glass columns (1.1 cm/ID × 30 cm height) were packed with Dowex 99Ca/320 (Ca^{2+} form was exchanged with $[Emim]^+$). Each column is connected with four ports including desorbent, feed, extract and raffinate ports via a 4-way connector. Two ECMT 16-port valves and four M50 pumps (Valco Instrument Inc. Co., USA) were installed for SMB system in order to control the direction of flow and zone flow rate, respectively. The system temperature was maintained at 50 °C by a circulating bath (WCR-P22, Daihan, Korea). Extract and raffinate streams were collected by Foxy 200 fraction collector (Teledyne Isco, USA), and SMB system was controlled by the software which was made by the Inha SMB laboratory.

2.5. Analytical methods

The concentration of glucose, xylose and EmimAc in ternary mixture was determined by HPLC analysis. HPLC system composed of a LC-10AD pump (Shimadzu, Japan), two detectors: RI detector (for sugars analysis) and UV detector (for ionic liquid detection) and a jacketed glass column (30 cm × 1.1 cm) packed with Dowex50WX4-400 cation exchanger resin (H^+ form which was exchanged with $[Emim]^+$) were used. Degassed and deionized water was used as mobile phase at flow rate of 1.5 mL/min. The analysis was performed at 65 °C.

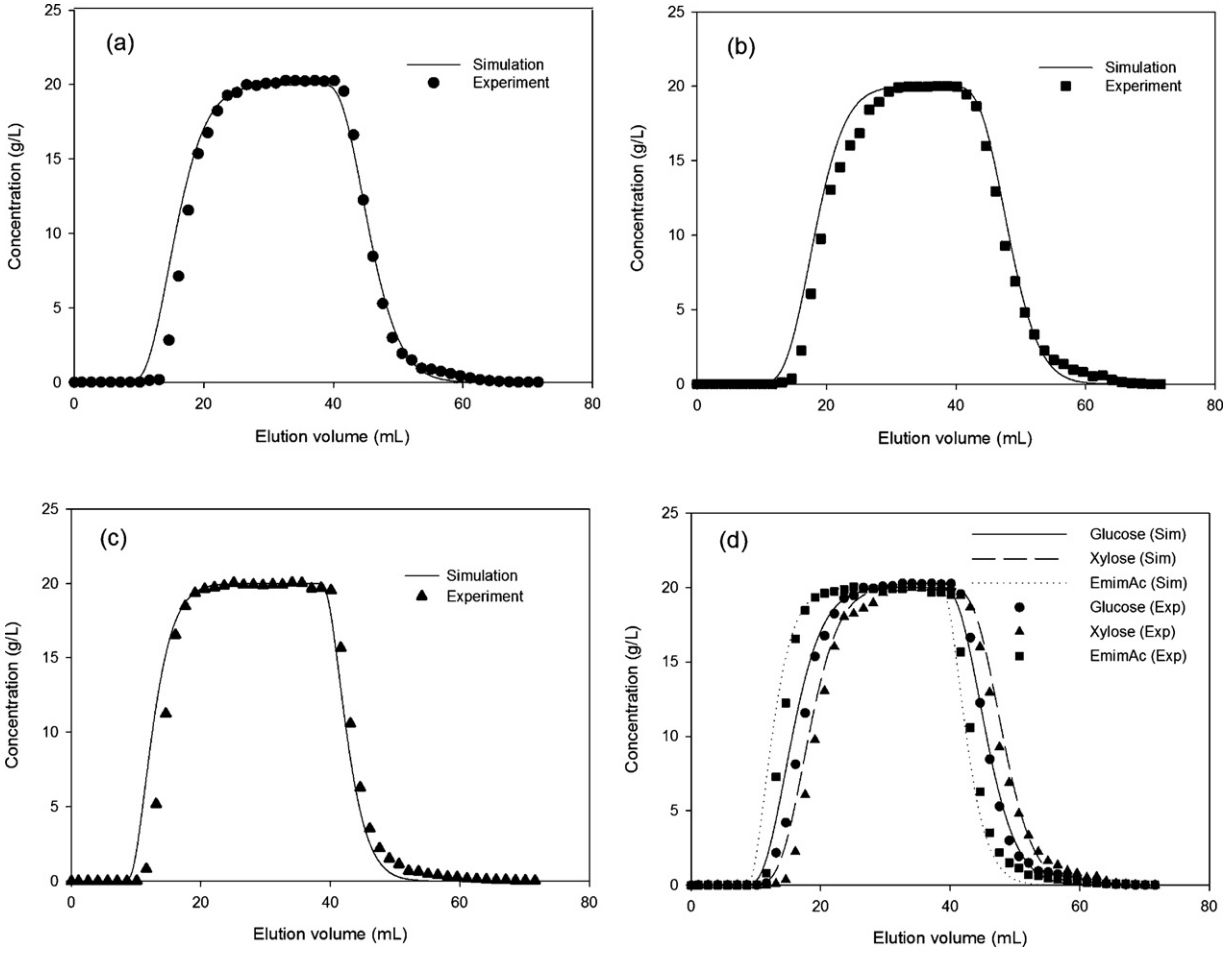

Fig. 2. Comparisons of experimental and simulated elution profile of glucose (a), xylose (b), EmimAc (c) and their ternary mixture (d).

3. Results and discussion

3.1. Adsorption isotherm of sugars and ionic liquid in ion exclusion column

Fig. 2 shows the elution profile of single frontal analysis of glucose, xylose and EmimAc. The elution profile of solutes was confirmed by using Aspen chromatography 2008™ software. If the simulated performances are well fitting with experimental results, simulations would give reliable predictions for SMB experiment results relating to column profiles, effluent histories, product purity and yield. The adsorption behaviors of glucose, xylose and EmimAc are obtained as linear isotherm within the concentration from 5 g/L to 20 g/L (Fig. 3). According to linear regression, Henry's constants of glucose, xylose and EmimAc were determined as 0.3388, 0.4683 and 0.1699, respectively. From the adsorption isotherms, it is observed that xylose is the most retained component while EmimAc is the least adsorbed solute. Because EmimAc is the charge molecule, it is excluded from the ion exclusion column while nonelectrolytes such as glucose and xylose are more retained in column. Moreover, the elution profile of sugars and IL mixture showed that these solutes were not interacted and eluted independently (Fig. 2).

3.2. Effect of zone flow rate on the separation

The triangle design method is widely applied for determining the operating conditions of SMB process. Based on this method, the separation zone is drawn into four distinguishing areas including pure extract and raffinate, pure extract, pure raffinate and no pure outlet [13]. The separation region for two sugars and IL is shown in Fig. 4. It is observed from the graph that EmimAc is the least retained solute. Therefore it is collected at the raffinate port. On the contrary, glucose and xylose are more retained than IL in the column and is collected at extract port of SMB system. Consequently, we decided to collect both glucose and xylose in the extract port. In this study, moreover, we focused on maximizing the recovery of

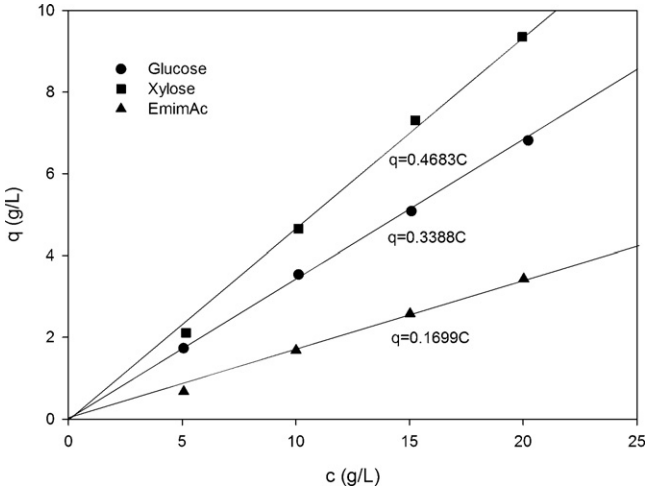

Fig. 3. Adsorption isotherm of glucose, xylose and EmimAc with linear fitting curves.

Table 1
Effect of zone II and zone III flow rate on the separation of sugars and IL.

Run	Zone II (mL/min)	Zone III (mL/min)	Purity (%)			Yield (%)		
			Glucose	Xylose	EmimAc	Glucose	Xylose	EmimAc
1	2.40	2.90	50.04	44.59	60.09	72.50	65.67	92.22
2	2.43	2.93	49.22	47.07	57.60	67.77	62.71	93.47
3	2.47	2.97	49.43	46.20	55.11	62.64	59.53	94.48
4	2.50	3.00	48.83	47.11	52.66	57.26	56.18	95.27

Simulation condition: zone configuration: 2-2-2-2; feed concentration 20 g/L; feed, desorbent, zone I and zone IV flow rate (mL/min) were of 0.5, 0.56, 2.87, and 2.31, respectively. Switching time was of 5.65 min. The results of purity and yield were of 12 cycles.

Table 2
Effect of zone I and zone IV flow rate on the separation of sugars and IL.

Run	Zone I up (%)	Zone IV down (%)	Purity (%)			Yield (%)		
			Glucose	Xylose	EmimAc	Glucose	Xylose	EmimAc
1	0	0	48.83	47.11	52.66	57.25	56.18	95.27
2	10	10	43.37	56.22	66.42	65.08	84.61	99.39
3	20	10	40.28	59.29	72.91	65.99	97.11	99.31
4	30	10	39.84	59.70	74.00	66.11	99.03	99.25
5	40	10	39.79	59.73	74.13	66.14	99.24	99.21
6	20	0	38.99	57.23	72.16	66.42	97.48	93.58
7	20	5	40.14	59.00	72.97	66.19	97.28	98.60
8	20	20	40.24	59.33	72.58	65.67	96.81	99.33

Simulation condition: zone configuration: 2-2-2-2; feed concentration 20 g/L; inlet, outlet and zone flow rate of run 1 was identical to those of run 4 in Table 1. Switching time was of 5.65 min. The results of purity and yield were of 12 cycles.

IL due to the expensive cost of it. Furthermore, the contaminated sugars in raffinate or recovered ILs stream might not be problem since their existences not affect the biomass pretreatment ability of ionic liquid [11]. Keeping these points in mind, the operating point was chosen in pure extract region. In addition, the SMB system is rather sensitive to some disturbances such as change in flow rate or feed concentration, temperature fluctuation and changes in adsorption isotherm. Therefore, the actual operating point for SMB system should be chosen at a reasonable distance from the optimal operating condition to guarantee a robust separation process [13]. In this experiment, we drew a straight line with a 10% safety margin from the vertex point to determine the operating point for SMB process (Fig. 4). SMB simulation shows that the higher recovery yield of IL could be obtained as the operating point moved up-right or the zone II and zone III flow rate were increasing (Table 1).

In SMB process, each zone plays a specific role for the separation performance. Zones II and III exhibit the key role in the startup and steady state behaviors of SMB compared with zone I and zone IV in four-zone SMB system [22]. However, modifying the flow rate of zone I and IV could lead to a change in SMB performances without any adjustments to the startup period [23]. In this experiment, we increased zone I and decreased zone IV flow rate simultaneously to limit the contamination of EmimAc to extract port. The SMB simulation shows that increasing 30% zone 1 while decreasing 10% zone 4 flow rates showed an acceptable EmimAc recovery yield (Table 2). Hence, these modification parameters were used for real SMB running (Table 3).

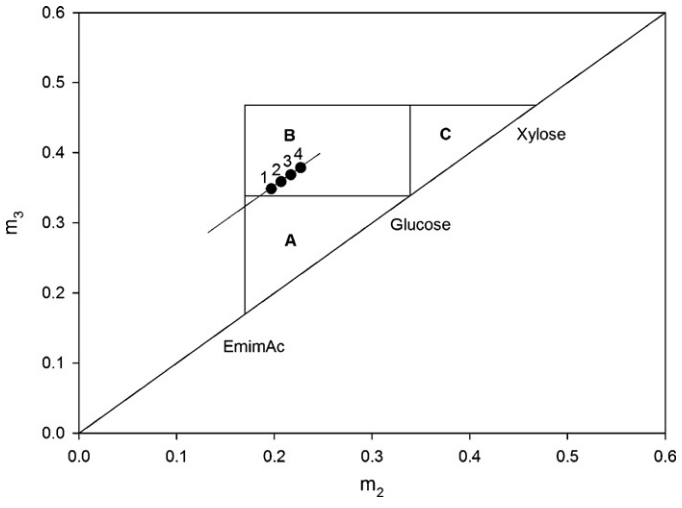

Fig. 4. Separation region of sugars and EmimAc. Circle symbol is the operating point for SMB running. The simulation results of point 1–4 were shown in Table 1 (run 1–4).

3.3. SMB operation strategy and experimental results

The SMB experiment to recover sugars and EmimAc was operated during twelve cycles. The history and elution profiles in SMB simulation and experiment are shown in Figs. 5 and 6, respectively. It is observed from the results that the simulated history profiles had a good agreement with the experimental history. However, the concentration history of products was not stable during the

Table 3
Operating conditions of SMB experiment.

Parameter	Value
Column properties	
Size L (cm) × ID (cm)	30 × 1.1
Total porosity	0.35
Temperature (°C)	50
Zone configuration	2-2-2-2
Feed concentration (g/L)	20
Inlet and outlet flow rate (mL/min)	
Feed	0.5
Desorbent	1.65
Raffinate	0.92
Extract	1.23
Recycle	2.08
Zone flow rate (mL/min)	
Zone I	3.73
Zone II	2.50
Zone III	3.00
Zone IV	2.08
Switching time (min)	5.65

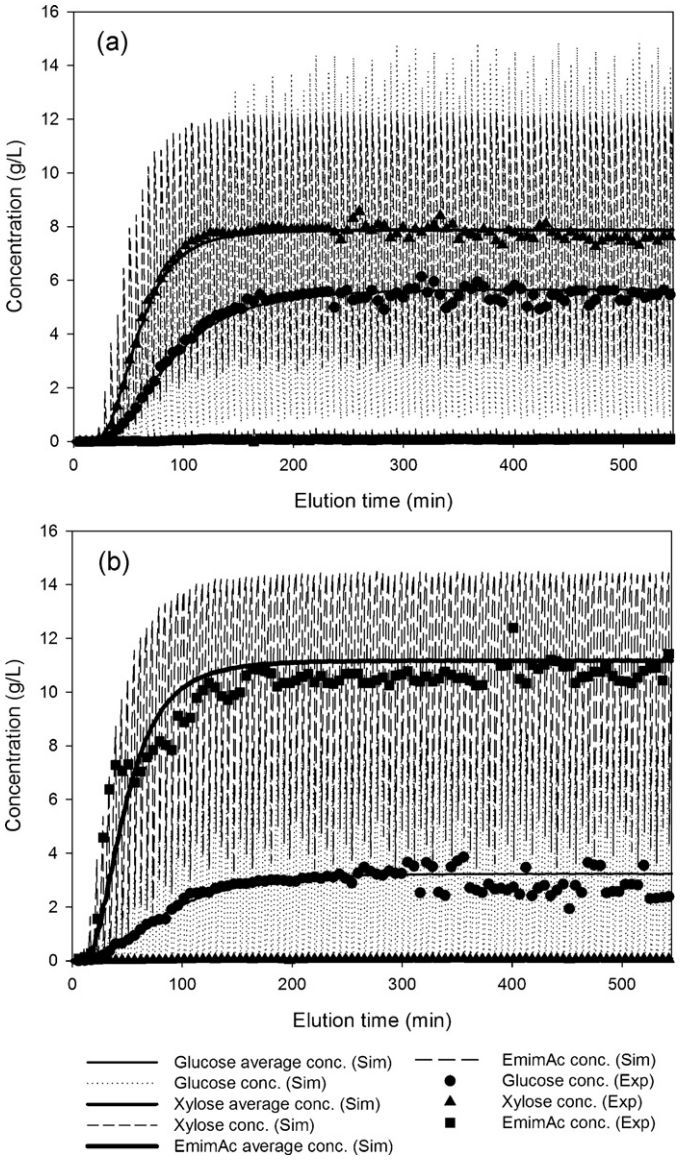

Fig. 5. History profiles of extract (a) and raffinate (b) in SMB experiment.

steady-state. It might be due to the pumps performance in the experiment. In some cases of switching time, the pumps could not deliver exact amount of required zone flow rates. However, the recovery yield and purity of experimental results were almost similar with simulation (Table 4). At steady-state, 71.38 and 99.44% of glucose and xylose were recovered at extract port, respectively, while 98.86% of EmimAc was obtained at raffinate port.

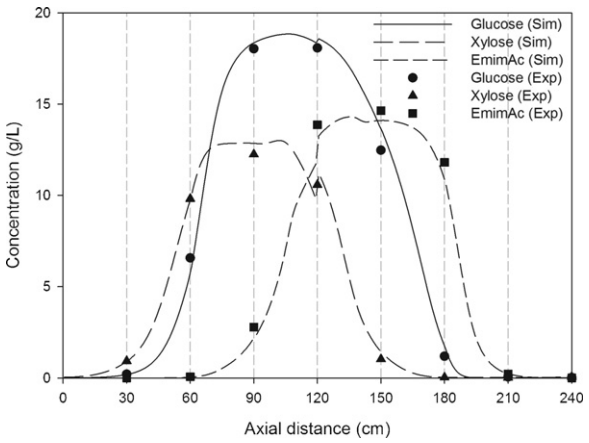

Fig. 6. Elution profiles of SMB experiment.

3.4. SMB zone configuration optimization

Pretreatment of lignocellulosic materials using ILs is still an unpractical application in industry due to high cost of ILs. Hence, the process should be optimized by maximizing the yield of IL at raffinate port in SMB system. Various simulation runs were performed in order to find the best condition for recovery of IL and sugars (Table 2). It is observed that increasing 20% of zone I while decreasing 10% of zone IV flow rate exhibited the good performance to recover not only EmimAc but also sugars. This condition was chosen for further optimization of SMB zone configuration (Table 5). The results show that by increasing the number of columns in each zone, the higher purity/yield, but lower productivity of glucose, xylose and EmimAc were obtained. Since the ultimate goal of this separation process is to completely recover ILs from its aqueous mixture with sugars, an optimized SMB configuration with 5 columns per zone could recover glucose, xylose and EmimAc with yield of 69.95, 99.93 and 100%, respectively. However, the feasibility of this configuration need to be verified by experimental since the pressure loses might occur as increased number of column and this affect the operation of SMB system.

Table 4
Result of SMB experiment and its corresponding simulation.

	Purity (%)	Yield (%)	Enrichment (%)
Simulation			
Glucose	41.54	71.39	28.28
Xylose	57.83	99.38	39.37
EmimAc	77.13	98.93	55.85
Experiment			
Glucose	41.47	74.43	27.30
Xylose	57.87	99.44	37.63
EmimAc	79.64	98.86	53.60

Table 5
SMB zone configuration optimization.

Case	Zone configuration	Purity (%)			Yield (%)			Productivity (10^3 g/L/h)		
		Glucose	Xylose	EmimAc	Glucose	Xylose	EmimAc	Glucose	Xylose	EmimAc
1	2-2-2-2	40.28	59.29	72.91	65.99	97.11	99.31	0.48	0.71	0.73
2	2-3-3-2	41.12	58.81	74.66	68.33	97.74	99.90	0.40	0.57	0.58
3	3-3-3-3	40.81	59.13	75.64	68.54	99.29	99.92	0.33	0.48	0.49
4	2-4-4-2	41.41	58.57	75.32	69.36	97.80	99.98	0.34	0.48	2.15
5	4-4-4-4	41.00	58.99	76.45	69.39	99.79	99.99	0.84	1.21	0.37
6	5-5-5-5	41.07	58.92	76.69	69.65	99.93	100	0.20	0.29	0.29

Simulation condition: feed concentration 20 g/L; feed, desorbent, raffinate, extract, recycle, and zone I–IV flow rate (mL/min) were of 0.5, 1.36, 0.92, 0.94, 2.08, 3.44, 2.50, 3.00, 2.08, respectively. Switching time was of 5.65 min. The results of purity, yield and productivity were of 12 cycles of SMB operation. The productivity was calculated as [(g of purified product)/(volume of stationary phase)/(operating time)].

4. Conclusions

Ion exclusion mechanism was proved the possibility to recover IL and sugars from their aqueous solution. Charged solute such as IL was eluted from the column, while nonelectrolyte components such as glucose and xylose were more retained which result in the separation of these solutes from their mixture. Recovery of EmimAc and sugars from ternary mixture was successfully performed by using ion exclusion SMB chromatography system. Glucose, xylose and EmimAc could be recovered with yield of 71.38, 99.37 and 98.92%, respectively from aqueous mixture of 20 g/L at the steady-state of 4 zone SMB operation with configuration of 2-2-2-2. A complete recovery of IL could be obtained by optimized SMB zone configuration (5-5-5-5).

Further studies exploiting series (or cascade) SMB [24] and pseudo-SMB [25] might demonstrate the practical and economic feasibility of ion exclusion SMB chromatography for the separation of sugars and ionic liquids from biomass hydrolysate.

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