



Solid phase extraction of lactic acid from fermentation broth by anion-exchangeable silica confined ionic liquids

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ABSTRACT

Three anion-exchangeable, silica-confined ionic liquids were synthesized for solid phase extraction of lactic acid from fermentation broth, followed by high-performance liquid chromatography coupled to ultraviolet detection. By comparing the adsorption isotherms of lactic acid on different silica-confined ionic liquids, interactions between the lactic acid and sorbents were investigated. The adsorbed amounts were then fitted into different adsorption isotherm equations; finally, the Langmuir equation was selected. Then the imidazolium silica with the highest adsorption capacity of lactic acid was packed into a cartridge for solid phase extraction. The loading volume of the cartridge was optimized by the Langmuir equation and geometry. After washing with distilled water and eluting with 0.25 mol L^{-1} of an HCl solution, the lactic acid was separated from interference with a recovery yield of 91.9%. Furthermore, this kind of anion-exchangeable material exhibited potential for industrial applications and separation of other anionic bioactive compounds.

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1. Introduction

Lactic acid (LA), as an important organic acid, is widely used in the food, pharmaceutical, leather and textile industries [1]. Recently, apart from previous applications, LA could be used as a raw material for the production of biodegradable and renewable plastics that have great potential for replacing petrochemical plastics [2]. Thus, LA has gained much interest and its requirement is thus, increasing.

LA can be produced either by chemical synthesis or through metabolism of living organisms, with the latter prevailing [3,4]. To recover the lactic acid from fermentation broths, several techniques have been developed including electrodialysis [5], distillation with an esterification reaction [2], ion exchange resins [6] and extraction [7], of which the ion exchange technique is most widely used. Several different ion exchangers, such as PVP [8], IRA-420 [9], and IRA-400 [10] have been studied in the past decades. However, the low compressive strength and capacity of the resins limit further applicability of the method [7]. Therefore, new materials should be developed to overcome such shortages.

Silica confined ionic liquids (Si-ILs) were already in use in chromatographic separations [11–16] due to their excellent physical and chemical properties. Although the interactions between target compounds and Si-ILs have been investigated and used for

separation of organic compounds, application of anion-exchange mechanism was relative few. Hence, the Si-ILs show a potential to be applied as a kind of anion-exchanged material, with solid-phase extraction (SPE) for the separation and determination of lactic acid in the fermentation broth.

Solid-phase extraction (SPE) has been developed as an acceptable alternative to liquid–liquid extraction for the separation, purification, and solvent exchange of solutes from a solution [17]. It typically includes loading, washing and elution steps; the conditions are optimized through experimental testing [18,19]. However, the loading volume of samples is always based on a rough determination. To obtain a more precise loading volume, certain theoretical investigations should be involved, such as adsorption isotherms and geometrical calculations.

The adsorption isotherm, a basic thermodynamic property of the separation process, reflects the interactions between sorbate and sorbent [20,21]. The parameters of the adsorption isotherm equations can be determined by fitting the various models to the experimental data. Using this method, it is possible to predict and optimize separation conditions. Therefore, the theoretical loading volume of the SPE cartridge (V_t) can be obtained by adsorption isotherm equations, and the maximum loading volume (V_m) calculated by geometrical method.

In this study, Si-ILs (Fig. 1) were synthesized and packed into cartridges for the SPE of LA from fermentation broth by an anion-exchanged mechanism. The interactions between LA and Si-ILs were investigated by adsorption isotherms, and a suitable adsorption isotherm equation was selected for optimizing the loading

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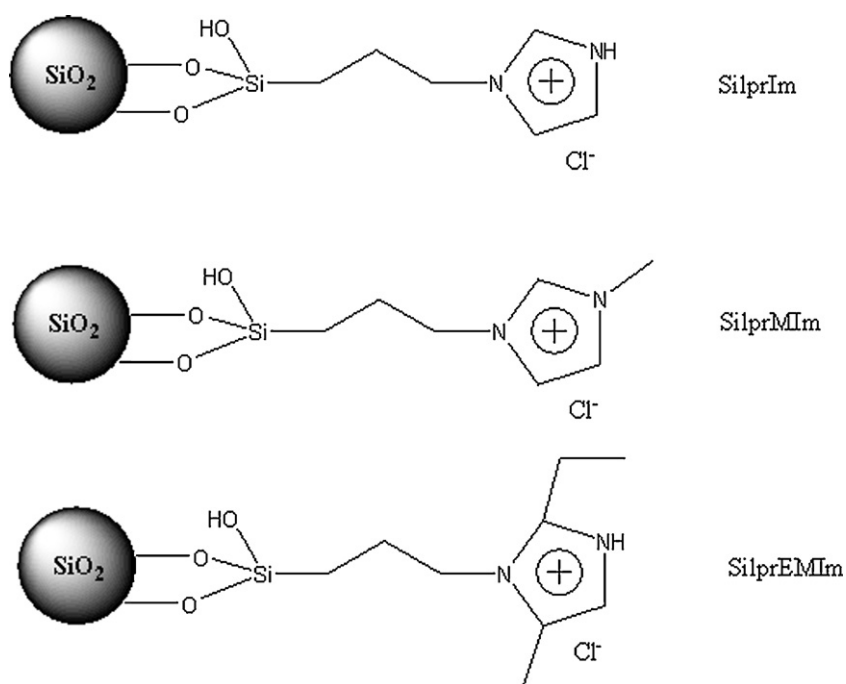


Fig. 1. Chemical structure of studied Si-ILs.

volume of the SPE. After that, the conditions of washing and elution steps were optimized through experimentation.

2. Experimental

2.1. Materials

(D,L)-Lactic acid (90%) was purchased from Fluka (Milwaukee, WI, USA), while imidazole (99%), 1-methylimidazole (99%), 2-ethyl-4-methylimidazole (95%) were obtained from Aldrich (Milwaukee, WI, USA). Methanol, acetonitrile, dichloromethane, *n*-heptane and hydrochloric acid (HCl) (35.0–37.9%) were from DUKSAN Pure Chemical CO., Ltd. (Ansan, Korea). Distilled water was filtered using a vacuum pump (Division of Millipore, Waters, USA) and a filter (HA-0.45, Division of Millipore, Waters, USA). All solvents used in the experiment were HPLC or analytical grade. All the samples were filtered by a filter (MFS-25, 0.2 μm TF, Whatman, USA) before injected into the HPLC system.

2.2. HPLC analysis

The HPLC system was comprised of a M930 solvent delivery pump (Young Lin Co., Korea), a UV detector (M 720 Absorbance Detector, Young-In Scientific Co., Korea) and an integrated data system (Autochromin, Ver. 1.42, Young Lin Co., Korea). Injection valves with 20 μL sample loops were used. The HPLC analysis was performed with a commercial C_{18} column (4.6 mm \times 250 mm, 5 μm) purchased from RStech Co. (Daejeon, Korea). The mobile phase was 1% ACN/99% 0.05 M NaH_2PO_4 , pH = 2.8 (adjusted by 1 mol L^{-1} H_3PO_4), the flow-rate was set at 0.5 mL min^{-1} , the UV wavelength was set at 210 nm, and the injection volume was 10 μL .

2.3. Preparation of Si-ILs

The synthesis procedure is the same as described in the literature [22,23]. Silica was firstly immersed in hydrochloric acid for 24 h and then washed with deionized water and dried at 100 $^\circ\text{C}$ for 8 h. The activated silica (6.0 g) was suspended in 60.0 mL of

dry toluene and then an excess of 3-chloropropyltriethoxysilane (6.0 mL) was added. The suspension was stirred and refluxed for 24 h. After refluxing, the reaction was stopped and the modified silica was cooled to room temperature, and washed with toluene, deionized water in turn and finally with methanol. Chloropropyl silica, SilprCl, was dried at 60 $^\circ\text{C}$ for 10 h.

Second, the chemically bonded chloropropyl group on the silica surface was reacted with imidazole, 1-methylimidazole and 2-ethyl-4-methylimidazole, respectively. In brief, 5.0 g of dry chloropropyl silica was placed in a reaction flask containing 50.0 mL of toluene and a large excess of imidazoles (5.0 g). The mixture was refluxed with stirring for 24 h. After refluxing, the reaction was stopped and the modified silica was cooled to room temperature, and washed with toluene, ethanol, and methanol in turn. The silica chemically bonded with imidazolium was dried at 60 $^\circ\text{C}$ for 10 h. The silica bonded with imidazole, 1-methylimidazole and 2-ethyl-4-methylimidazole were named as SilprIm, SilprMIm and SilprEMIm, respectively.

2.4. Adsorption isotherm

The stock standard aqueous solution with different of concentration of LA (5.0, 10.0, 15.0, 20.0, 25.0 30.0 and 35.0 mg mL^{-1}) were prepared in vials and stored at 4 $^\circ\text{C}$ in a refrigerator.

0.02 g Si-ILs and 1.0 mL LA standard aqueous solutions with different concentrations were added into vials with stirring at room temperature. When the equilibrium adsorptions were obtained, the amounts of adsorbed lactic acid on Si-ILs were calculated by subtracting the concentrations of unadsorbed lactic acid in solutions.

2.5. Pretreatment of LA fermentation broth

LA fermentation broth was supported by Biological Reaction Engineering Lab in Inha University. The fermentation broth was filtered and clarified by centrifugation at 10,000 rpm for 10 min at 4 $^\circ\text{C}$ to remove the insoluble proteins. Then the soluble proteins were precipitated by acetonitrile. After mixed and centrifugation, the supernatant was removed, diluted with water and

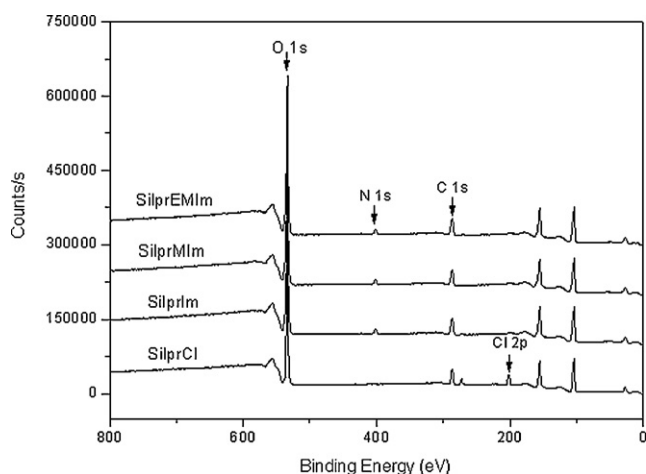


Fig. 2. ESCA spectra of the surface of SilprCl, SilprIm, SilprMIm and SilprEMIm.

kept at 4 °C in a refrigerator in darkness for further purification procedure.

2.6. Procedure of SPE

Si-ILs (0.3 g) were packed into empty polypropylene cartridges and preconditioned with 4.0 mL distilled water, ethanol and methanol in turn. Pretreated fermentation broth (0.5 mL) was loaded onto the SPE cartridges to obtain the adsorption equilibrium, and washed with different solvents such as water, methanol, acetonitrile, *n*-hexane and dichloromethane, to remove the interferences. Then, LA was eluted by different concentrations of HCl solution. The filtrate was evaporated to dryness and reconstituted in mobile phase for further HPLC analysis.

3. Results and discussion

3.1. Electron spectroscopy for chemical analysis

Fig. 2 shows the ESCA spectra of the surface of the SilprCl, SilprIm, SilprMIm and SilprEMIm. Existence of covalently bound chlorine atoms on the SilprCl silica surface was confirmed by the Cl 2p signal at a binding energy of 200 eV [24]. The peak at 401 eV was attributed to N 1s, indicating the linked imidazolium on the surface of SilprIm, SilprMIm and SilprEMIm. These spectra proved that immobilization occurred on the surface.

3.2. Elemental analysis

The elemental contents and surface coverage of the SilprCl, SilprIm, SilprMIm and SilprEMIm are listed in Table 1. According to the reference [25], the bonding density was determined at 5.75 $\mu\text{mol m}^{-2}$ for SilprCl based on the percentage amounts of carbon. The bonding densities were based on the nitrogen percentages and were 2.80, 2.29 and 1.27 $\mu\text{mol m}^{-2}$ for SilprIm, SilprMIm and SilprEMIm, respectively. The elemental analysis data proved that immobilization on the surface was successful. The bonding density of the imidazolium silica decreased with increasing imidazole alkyl

Table 1
Element analysis of silica-based ionic liquid stationary phases.

Materials	C (%)	H (%)	N (%)	Coverage ($\mu\text{mol m}^{-2}$)
SilprCl	9.84	2.05	–	5.75
SilprIm	11.46	1.87	3.52	2.80
SilprMIm	11.36	2.37	2.89	2.29
SilprEMIm	11.48	2.07	1.63	1.27

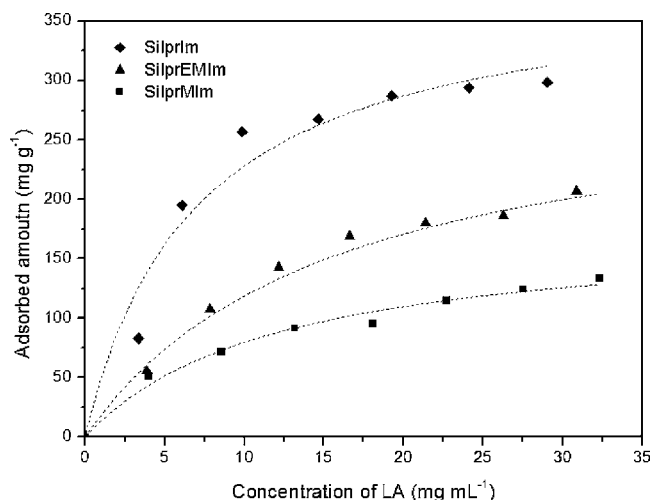


Fig. 3. Adsorbed amount of standard LA on three Si-ILs.

branches, which may be rationalized by steric hindrance from the alkyl chain. However, the separation of analytes was dominated by the influence of interactions between analyte and stationary phase, rather than the influence of bonding density [11].

3.3. Adsorption isotherm

The adsorption isotherms were introduced in order to investigate the interactions between LA and Si-ILs as well as choosing the suitable sorbent for SPE of LA from the fermentation broth. The adsorbed amounts (Q) of LA onto the three Si-ILs were determined as follow:

$$Q = \frac{(C_0 - C)V}{m} \quad (1)$$

where Q (mg g^{-1}) is the adsorbed amount, C_0 (mg mL^{-1}) is the initiator concentration, C (mg mL^{-1}) is the unadsorbed concentration, V (mL) is the volume of the sample solvent, and m (g) is the mass of the Si-ILs. The results of adsorbed amount are shown in Fig. 3.

According to the data, the adsorbed amounts of LA on different Si-ILs decreased in the order of: SilprIm > SilprEMIm > SilprMIm. This result can be attributed to the interactions between LA and Si-ILs. LA can be ionized in aqueous solution and anion-exchanged with imidazolium groups (Fig. 4). When the alkyl groups were increased on the imidazolium groups, the polarity of the ILs decreased with decreasing electrostatic interaction. Meanwhile, the extra alkyl groups generated steric hindrance. Therefore, the adsorbed amount of LA onto the SilprIm was higher than for others. However, the adsorbed amount of LA onto the SilprEMIm was higher than that on SilprMIm. This can be explained by the different positions of the alkyl groups. Methyl group was connected with nitrogen in the imidazole group of the SilprMIm, whereas the $-\text{NH}-$ group of the SilprEMIm was not covered by the alkyl groups and thus, the hydrogen bonding interactions remained. Hence, the SilprEMIm showed a stronger affinity to LA in comparison with SilprMIm. Comparing the adsorption isotherms of LA on the three Si-ILs, the SilprIm with the highest adsorbed capacity was selected as the sorbent for SPE of LA from the fermentation broth.

After that, this experiment data was fitted to the following adsorption isotherm equations [13,20,21]:

$$Q = aC_E + b \quad (2)$$

$$Q = \frac{aC_E}{1 + bC_E} \quad (3)$$

$$Q = aC_E^{1/b} \quad (4)$$

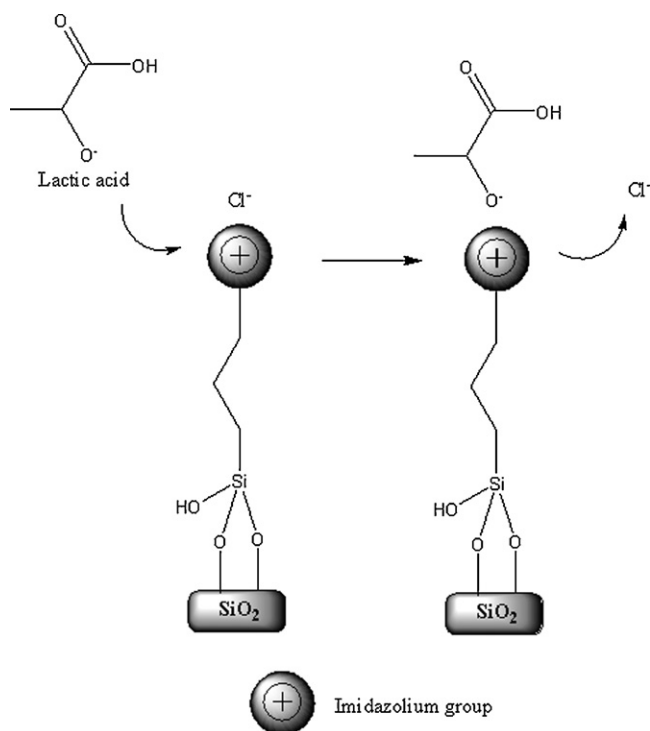


Fig. 4. Proposed scheme of anion exchange mechanism on Si-ILs.

where C_E (mg mL^{-1}) in the three equations is the equilibrium concentration of the solute in the liquid phase. a and b are the parameters. These adsorption isotherm equations are the linear (Eq. (2)), Langmuir (Eq. (3)) and Freundlich (Eq. (4)) equations, respectively. According to the regression coefficient (r^2) in Table 2, the Langmuir equation was evidently better than the others in this experiment.

It was known that adsorption of LA onto the sorbent was affected by salts in the fermentation broth. Therefore, a simulated fermentation broth (a mixture containing 1.0 mg mL^{-1} of $\text{NaCH}_3\text{COO}_3 \cdot \text{H}_2\text{O}$, 0.5 mg mL^{-1} of KH_2PO_4 , 0.2 mg mL^{-1} of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 mg mL^{-1} of K_2HPO_4 , 0.03 mg mL^{-1} of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 0.03 g L^{-1} of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used to investigate the influences [6]. Fig. 5 shows that the maximum Q for standard LA, with LA in the simulated fermentation broth near 298.4 and 269.1 mg g^{-1} , respectively. The difference in value between the Q was obviously due to the competitive adsorption of the LA and salts in the fermentation broth. The data was then fitted to a Langmuir equation with the adsorption isotherm equation of the LA in the simulated fermentation broth being $Q = 34.27C_E / (1 + 0.089C_E)$ ($r^2 = 0.992$).

Table 2
Parameters in adsorption isotherms of LA on different Si-ILs.

Sorbent	Equation	Parameter		r^2
		a	b	
SilprMIm	(2)	27.95	3.63	0.893
	(3)	14.45	0.08	0.985
	(4)	26.84	2.17	0.995
SilprEMIm	(2)	37.06	5.95	0.892
	(3)	19.53	0.06	0.996
	(4)	34.92	1.92	0.983
SilprIm	(2)	73.26	8.67	0.791
	(3)	40.27	0.09	0.977
	(4)	72.21	2.32	0.944

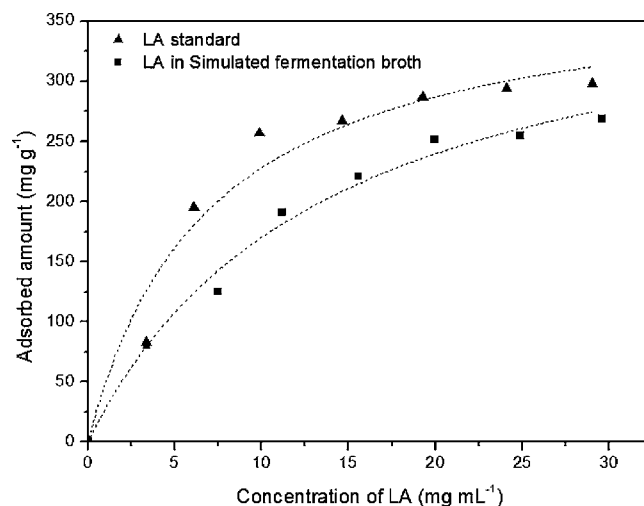


Fig. 5. Adsorbed amount of standard LA and LA in fermentation broth on SilprIm.

3.4. Optimization of SPE conditions

3.4.1. Loading step

The theoretically adsorbed amount could be determined by Eq. (5).

$$Q = \frac{34.27C_E}{1 + 0.089C_E} \quad (5)$$

C_E was considered as the concentration of LA in fermentation broth, which can be determined by HPLC. Thus, Q was obtained by substituting C_E into the equation.

$$Q_T = 0.3 \times Q \quad (6)$$

$$V_T = \frac{Q_T}{C_E} \quad (7)$$

Because 0.3 g Si-ILs was packed into the cartridge, the theoretically adsorbed amount (Q_T) was 69.39 mg g^{-1} (Eq. (6)). Then, the theoretical loading volume ($V_T = 28.09 \text{ mL}$) was calculated from Eq. (7).

The maximum loading volume (V_M) of LA fermentation broth on the SPE cartridge was calculated from

$$V_M = V_I + V_P \quad (8)$$

where V_I and V_P were the inter-particle and pore volume, respectively. The V_I could be firstly calculated by geometry. The diameter (D_C) and height (H_C) of the packed cartridge was 8.0 mm and 8.5 mm , respectively. The Si-IL particles were packed in the cartridge layer by layer (Fig. 6a); it could be supposed that eight particles constitute a cube (Fig. 6c and d) as the "unit cell in crystal structure". The length (L) of the cube was $15.0 \mu\text{m}$, and the diameter (d) of the Si-IL was $15.0 \mu\text{m}$. Thus, the inter-particle volume (v_I) in the cube was $1.61 \times 10^{-9} \text{ mL}$ (Eq. (9)).

$$v_I = L^3 - (4/3) \times \pi(d/2)^3 \quad (9)$$

$$V_I = N \times v_I \quad (10)$$

$$N = (D^2/d^2) \times (H/d) \quad (11)$$

Then the V_I could be calculated from Eq. (10), where N was the number of cubes in the cartridge. According to Fig. 6e, one cube occupied a whole Si-IL particle, and N equals the number of Si-IL particles in the cartridge. Because one layer contained 2.84×10^5 particles (D^2/d^2) (Fig. 6b) and 6.0×10^2 layer (H/d) was found in the cartridge, N could be calculated from Eq. (11). Therefore, V_I was 0.258 mL . After determination of the V_I , the V_P (0.75 – 0.95 mL g^{-1}) was determined by Brunauer Emmett Teller (BET, ASAP 2020, Micromeritics,

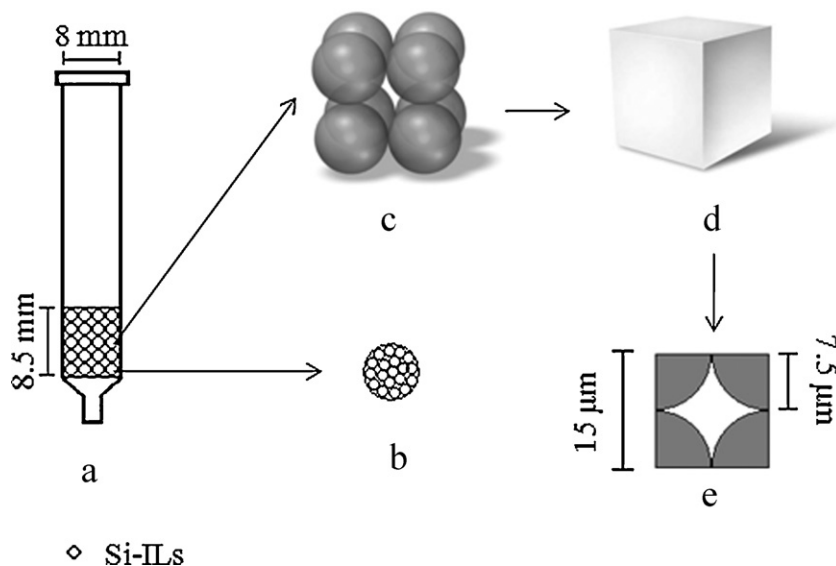


Fig. 6. Proposed geometric structure of Si-ILs packed SPE cartridge.

USA). Finally, the V_M was obtained in a range of 0.48–0.54 mL. Due to $V_M < V_T$, V_M was selected as the loading volume with full adsorption of LA onto the SPE cartridge. Accordingly, the exact loading volume was investigated from 0.48 to 0.54 mL, and 0.5 mL was selected without a leak.

3.4.2. Washing step

In order to remove interference from fermentation broth, different solvents (water, ethanol, methanol, acetonitrile, *n*-hexane, acetone) were applied to wash the loaded SPE cartridge. It was found that water could efficiently wash the interferences away. Then different volumes of the solvents (from 1.0 to 6.0 mL) were used to obtain the optimal volume. When the volume of the washing solvents was larger than 4.0 mL, the interference removal did not increase.

3.4.3. Elution step

For the sake of recycling, HCl solutions were selected as elution solvent. The solutions with different concentrations (from 0.1 to 1.0 mol L⁻¹) and volumes (from 0.2 to 1.4 mL) were used to obtain the optimal elution condition. As shown in Fig. 7, the recovery

yields of LA increased with increasing the HCl concentration below 0.25 mol L⁻¹. However, the recovery yield of LA was fixed at 91.9%, when a concentration larger than 0.25 mol L⁻¹ was used. Therefore, 0.25 mol L⁻¹ HCl solution was the optimal concentration. Where after, the volume of the HCl solution was investigated. It was found that the recovery yield of the LA increased with increasing volumes of 0.25 mol L⁻¹ HCl solutions in a range of 0.2–1.0 mL. Further increase in elution volume could not increase the recovery yield.

The previous optimization indicated the following steps to separate the target compounds and interferences. First, 0.5 mL fermentation broth was loaded onto a SilprIm-packed SPE cartridge. Then interferences were washed out using 4.0 mL water. Finally, 91.9% LA was eluted using 1.0 mL of 0.25 mol L⁻¹ HCl solution (Fig. 8).

3.5. Validation of proposed analytical method

The calibration curves were constructed using the chromatographic peak areas measured at seven increasing concentrations, ranging from 2.0 to 35.0 mg mL⁻¹. Each measurement was repeated three times with good linear correlation equations for LA: $Y = 440.82x + 30.93$ ($r^2 = 0.999$). The assays of repeatability were cal-

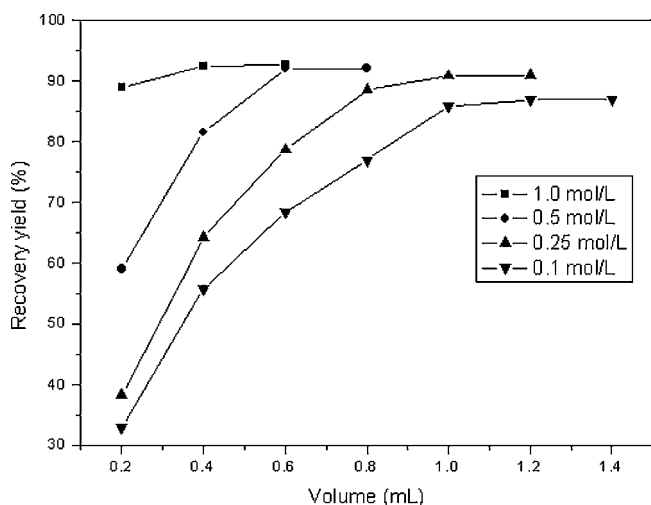


Fig. 7. Recovery yields of LA on SilprIm eluted by different volume of HCl solutions with different concentrations.

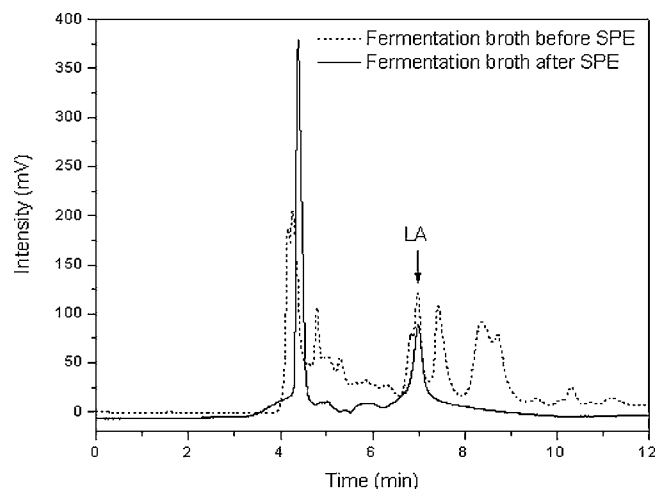


Fig. 8. Chromatogram of fermentation broth before and after SPE.

culated from the relative standard deviation (RSD), determined by injecting standard solutions of LA five times over a five-day period. The standard solutions of LA were diluted and injected until the limit of detection (LOD) was obtained at a signal-to-noise ratio of 3. The RSDs of the precision tests were from 0.31 to 2.76, and the LOD of the standard solutions was $2.25 \mu\text{g mL}^{-1}$ for LA, confirming that these values were of acceptable precision and accuracy.

3.6. Recycling of SilprIm in SPE

The recycling of SilprIm in the SPE cartridge was investigated. The recovery yields of the LA from fermentation broth within four recycles of SilprIm were from 91.9 to 85%. The recovery yields of LA exhibited little decrease, indicating that this sorbent possesses stable characteristics.

4. Conclusion

In this study, the anion-exchanged SilprIm was selected for the SPE of LA from fermentation broth. The Langmuir equation and geometry were introduced to optimize the loading volume of the SPE. By optimizing the loading volume (0.5 mL), washing (4.0 mL of distilled water) and elution solvent (1.0 mL of 0.25 mol L^{-1} HCl solution) for SPE, LA was successfully separated from interference with a recovery yield of 91.9%. Furthermore, the recycling of SilprIm during the extraction demonstrated the potential for economic industrial applications, this type of anion-exchangeable ionic liquid-modified sorbents exhibit a possibility for separation and purification of anionic bioactive compounds from natural plants extracts.

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