Kinetics, Isotherm, and Thermodynamics of Adsorption of Sterol on Strong Acid Ion Exchange Resin

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Kinetics, isotherm and thermodynamics of sterol adsorption on styrene-divinylbenzene based ion-exchange resin with strong acid was investigated at temperature in the range of 298 to 313 K using a model solution of stigmasterol in n-heptane with initial concentration in the range of 0.3×10^{-3} to 1.8×10^{-3} kg/kg-solution. Adsorbent (5 wt%) was added to the model solution and isothermal adsorption was performed at 3.33 rps for 7.2×10^3 s. Kinetics of sterol adsorption was analysed based on pseudo-first-order and pseudo-second-order models. The results revealed that pseudo-second-order model agreed with the experimental data, much better than pseudo-first-order model. At the equilibrium of adsorption, adsorption capacity (q_e) decreased when the temperature was increased. This result indicated that sterol adsorption was exothermic. Analysis of adsorption isotherm data based on Langmuir, Freundlich and linear models showed that Freundlich was the best model that could predict the adsorption isotherm data. Adsorption equilibrium constants calculated based on Freundlich model at various temperatures were used to calculate Gibb's free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The increase of ΔG with respect to temperature indicated that the adsorption was more favourable at lower temperatures. The negative value of ΔH indicated that the adsorption was exothermic and agreed well with the effect of temperature on adsorption capacity. The negative value of ΔS indicated associative adsorption and decrease of the randomness between the solid/liquid interfaces due to the adsorption.

1. Introduction

Sterols have several beneficial bioactivities such as anti-cancer and decrease the risk of coronary heart disease. They have been widely used as starting material in food, cosmetics and pharmaceutical industries (Fernandes and Cabral, 2007). Over the past several decades, deodorizer distillate (DD) which is a by-product in a vegetable refinery plant became one of the most important sources of natural sterols. DD contains free fatty acids (FFA), monoglycerides (MG), diglycerides (DG), triglycerides (TG) and small amount of some bioactive compounds (Verleyen et al., 2001). Sterols have been successfully recovered from DD by two main methods. These methods were designed to remove undesired compounds (FFA and glycerides) from DD, followed by sterols separation. In one method, FFA in DD was saponified and then the resulted soap was removed from the mixture by simple solid-liquid separation. After that, sterols were separated from the resulted concentrate mixture by crystallization (Khatoon et al., 2010) or vacuum distillation (Rohr, 2003). The another method, FFA and other glycerides were transformed to fatty acid alkyl ester (FAAE) by esterification (Moreira and Baltanás, 2004) or esterification followed by transesterification (Wollmann et al., 2005). In the sterols preconcentration step, FAAE fraction was removed by vacuum distillation to obtain high yield of sterols. Similar to the former method, crystallization was applied as the last step for sterols separation. Although these methods have been

successfully applied to recover sterols from DDs, they require large energy consumption. In general, vacuum distillation is operated at 100 to 133.32 Pa and 453 to 473 K to remove undesired compounds in the resulted mixture from chemical treatment, and cold crystallization was used to separate sterols from the remaining mixture at low temperature (253 to 288 K). A simple, efficient, and economical method should be developed to serve the growth of sterols demand. Adsorption is widely used in separation of minor components from liquid mixture under mild conditions. The use of adsorbent is the basis of all adsorption techniques. Polymeric resins have been widely used to remove pollutants such as phenol (Victor-Ortega et al., 2016) or polyphenols (Njimou et al., 2017) from aqueous solutions because of low cost and high abundance. Based on chemical resistance and simplicity of operation, styrene-divinylbenzene based ion-exchange resin with strong acid (SA-R) was considered as attractive adsorbent in the sterol recovery process. The objective of this study was to investigate behavior of sterol adsorption on SA-R. Isothermal batch adsorption was performed using a model solution of stigmasterol in n-heptane to evaluate adsorption capacity. Kinetics of sterol adsorption was evaluated based on pseudo-first-order and pseudo-second-order models. Adsorption data at equilibrium were analyzed based on Langmuir, Freundlich and linear isotherms and three important thermodynamics parameters (i.e. Gibb's free energy change: ΔG, enthalpy change: ΔH and entropy change: ΔS) were calculated and the adsorption behavior was discussed based on the calculated thermodynamics parameters.

2. Materials and methods

2.1 Materials

Styrene-divinylbenzene copolymer cation-exchange resin (Lewatit® Monoplus SP 112H) with sulfonic acid group and mean bead size of $6.7 \times 10^{-4} \pm 0.5 \times 10^{-4}$ m (Lanxess, Germany) was selected as representative of a strong acid cation exchange resin (SA-R). SA-R was dried in an oven at 383 K under vacuum for 2.16×10^4 s and stored in a desiccator before being used in adsorption experiment. Prior to the adsorption experiment, SA-R was washed with methanol, n-propanol and n-hexane. Stigmasterol (Tama Biochemical Co. Ltd.) and n-heptane (AR grade, Apex Chemicals Co. Ltd.) were used in preparation of a model solution of sterol containing mixture. Cholesterol (Sigma-Aldrich Inc.) was used as an internal standard (ISTD) in quantitative analysis of stigmasterol. HPLC grade organic solvents (methanol, acetonitrile and water from RCI Labscan Ltd. and acetic acid from Merck Ltd.) were used in the quantification of stigmasterol.

2.2 Batch adsorption

To study kinetics, isotherm and thermodynamics of stigmasterol adsorptions on SA-R, isothermal batch adsorption was performed using a model solution of stigmasterol in n-heptane. This nonpolar solvent, n-heptane, was used in this experiment to avoid competitive adsorptions of stigmasterol and solvent in the adsorption system. Adsorption temperature and stigmasterol concentration were varied in the ranges of 298 – 313 K and 0.3×10^{-3} to 1.8×10^{-3} kg/kg-solution, respectively. The model solution (5.0×10^{-5} m^3) and the adsorbent (5 wt%) were heated and shaken in an orbital shaker (4000ic; IKA) at 3.33 rps for 7.2×10^3 s. Before and after the adsorption, samples (2.0×10^{-7} m^3) were taken and filtered through a 4.5×10^{-7} m nylon filter and used for the quantitative analysis of stigmasterol content.

2.3 Quantitative analysis

The content of stigmasterol in the sample was analyzed using a high-performance liquid chromatography (HPLC) connected with a UV detector. An injection valve connected with a 2.0×10^{-8} m^3 of sample loop was used to introduce the sample into the HPLC. Peak separation was achieved using a reverse-phase column (Inertsil C8-3; 5.0×10^{-6} m particle diameter, 0.25 m length, 4.6×10^3 m i.d., GL Sciences Inc, Japan). Composition of mobile phase and condition of analysis were adapted from the work reported by Chang et al. (2000). Mobile phase was a mixture of acetonitrile (85 %), methanol (5 %), and water containing 1% of acetic acid (10 %) and flowed at the rate of 2.16×10^{-8} m^3/s, the analysis was performed at the wavelength of 2.1×10^{-7} m. Since the sample was not dissolved well in the mobile phase, n-heptane in the sample was removed and an appropriate solvent was added to the solid sample as a solvent in the quantitative analysis. The solvent exchange was performed as follows; n-heptane was completely removed from the sample by evaporation at room temperature, methanol (8.0×10^{-7} m^3) was then added and the mixture was shaken in the orbital shaker at 3.33 rps for 3.6×10^3 s. As an internal standard, cholesterol in methanol (4.0×10^{-3} kg/kg-solution, 2.0×10^{-7} m^3) was added in the sample. Amount of stigmasterol adsorbed on the adsorbent at time "t" (q_t) was calculated according to Eq(1).

$$q_t = \frac{(C_0 - C_t)W_{sol}}{W_{ads}}$$

(1)

where C_0 and C_t are liquid-phase concentration of stigmasterol at initial and at time t, respectively. W_{sol} is the weight of the solution and W_{ads} is the weight of adsorbent used.

3. Results and discussion

3.1 Adsorption capacity

Figure 1 shows the time dependence of adsorption capacity of SA-R at various initial concentrations of stigmasterol. The adsorption capacity increased with time until equilibrium was reached within 1.8×10^3 s. Comparison of the profiles obtained at different initial concentrations revealed that the rates of adsorption on SA-R increased with the increase of concentration of stigmasterol. This is general behaviour of a process with positive order rate equation. The adsorption capacity at the equilibrium (q_e) increased from 2.4×10^{-3} to 9.2×10^{-3} kg/kg-adsorbent by increasing the initial concentration from 0.3×10^{-3} to 1.8×10^{-3} kg/kg-solution. In addition, the adsorption efficiency of SA-R was found in the range of 25 - 35 %, being higher at lower initial concentration.
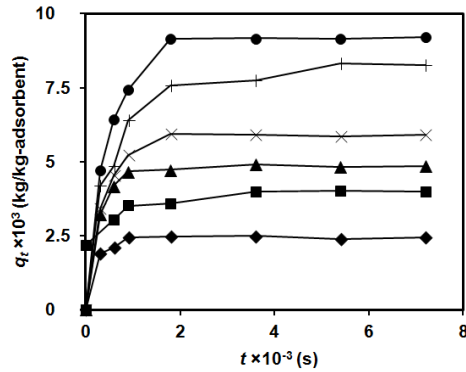

Figure 1: Capacities of SA-R for stigmasterol adsorption at various initial concentrations: (◆) 0.3×10^{-3}, (■) 0.6×10^{-3}, (▲) 0.9×10^{-3}, (✕) 1.2×10^{-3}, (+) 1.5×10^{-3}, (●) 1.8×10^{-3} kg/kg-solution; at 303 K and 5 wt% SA-R

3.2 Adsorption kinetics

To study the kinetics of adsorption, the experimental data were comparatively analyzed based on pseudo-first-order and pseudo-second-order models which are expressed as Eq(2) and Eq(3).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Where q_e and q_t are the amounts of stigmasterol adsorbed at equilibrium and at time t, respectively. k_1 and k_2 are the adsorption rate constant of pseudo-first-order and pseudo-second-order model. Linearized forms of these two models obtained by integrating Eq(2) and Eq(3) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ are expressed as Eq(4) and Eq(5).

$$\ln(q_e - q_t) = lnq_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Linear plots corresponding to pseudo-first-order and pseudo-second-order models for SA-R are shown in Figure 2(a) and 2(b), respectively. The parameters, k and q_e, of each model were calculated from the slope and the y-intercept of the corresponding linear plot and summarized in Table 1. The correlation coefficients (R^2) of pseudo-second-order model were higher than pseudo-first-order model for all conditions. The lowest value of R^2 obtained from pseudo-second-order model was 0.9989 while the highest value of R^2 obtained from pseudo-first-order model was 0.9943. In addition, $q_{e,cal}$ from pseudo-second-order model agreed reasonably well with $q_{e,exp}$ ($\Delta q_e \leq 7.7\%$) while pseudo-first-order model could not well predict the value of $q_{e,exp.}$, especially at initial concentration between 0.3×10^{-3} to 0.9×10^{-3} kg/kg-solution. Based on the correlation coefficients and Δq_e, pseudo-second-order model was selected to describe the kinetics of stigmasterol adsorption on SA-R. Considering the adsorption rate constant of pseudo-second-order model (k_2), the results show that k_2 depended on the initial concentration of stigmasterol (C_0). When C_0 was increased from 0.3×10^{-3} to 1.8×10^{-3} kg/kg-solution, k_2 decreased from 10.0313 to 0.4428 kg-adsorbent/(kg·s). This dependence of k_2 on initial concentration was previously reported in several adsorption systems (Ho and Mckay, 1999). Theoretical analysis by Azizian (2004)

clearly showed that k_2 is not an intrinsic rate constant of adsorption, but it is a complex function of adsorption rate constant, desorption rate constant and initial concentration of adsorbate.
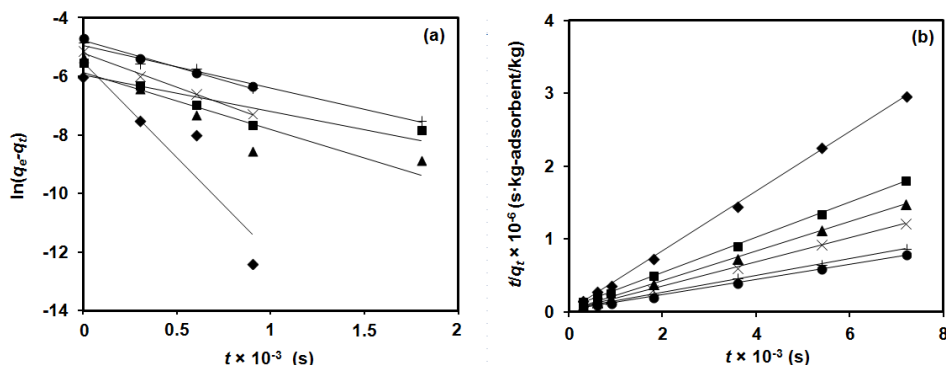

Figure 2: Linear plots of (a) pseudo-first-order and (b) pseudo-second-order kinetics models for various initial concentrations: (◆) 0.3×10^{-3}, (■) 0.6×10^{-3}, (▲) 0.9×10^{-3}, (×) 1.2×10^{-3}, (+) 1.5×10^{-3}, (●) 1.8×10^{-3} kg/kg-solution; at 303 K and 5 wt% SA-R

Table 1: Kinetic parameters of stigmasterol adsorptions on SA-R at 303 K with different initial concentrations

C_0	$q_{e,exp}$	Pseudo-first-order				Pseudo-second-order			
		k_1	$q_{e,cal}$	Δq_e (%)	R^2 (-)	k_2	$q_{e,cal}$	Δq_e (%)	R^2(-)
0.3	2.44	0.0065	3.93	61.3	0.8525	10.0313	2.45	0.4	0.9994
0.6	4.00	0.0012	2.60	35.2	0.8054	1.1144	4.14	3.5	0.9995
0.9	4.90	0.1161	2.80	42.8	0.8327	2.1669	4.93	0.6	0.9997
1.2	5.90	0.0023	5.54	6.1	0.9943	1.0602	6.06	2.7	0.9993
1.5	8.11	0.0015	7.13	12.1	0.9834	0.3139	8.73	7.6	0.9989
1.8	9.20	0.0018	8.51	7.2	0.9877	0.4428	9.57	4.0	0.9990

*Coefficient units: $C_0 \times 10^3$ (kg/kg-solution); $q_e \times 10^3$ (kg/kg-adsorbent); k_1 (s^{-1}); k_2 (kg-adsorbent/(kg·s))

3.3 Adsorption isotherm

Adsorption isotherm was investigated at 298, 303, 308 and 313 K and discussed based on the data taken after 1 h of adsorption, which were reasonably considered as the performance at the equilibrium of adsorption according to the discussion in section of adsorption capacities. Figure 3 (a) shows dependence of adsorption capacity at the equilibrium (q_e) on concentration of stigmasterol at the equilibrium (C_e) at 303 K of SA-R. In the tested range of C_e, q_e increased with C_e and saturation of adsorption was not observed. Figure 3(b) shows effect of temperature on q_e for various initial concentrations. q_e decreased when the temperature was increased. This result indicated that stigmasterol adsorption was exothermic. This dependence was significant in the case of high initial concentration and became less significant when the initial concentration was lower.

Equilibrium adsorption data were analyzed based on Langmuir, Freundlich and linear isotherm models using the corresponding linearized form of each model, listed in Table 2. Langmuir model was considered as an inappropriate model for prediction of isotherm of stigmasterol adsorption for SA-R due to the value of R^2 was extremely low. At temperature of 298 and 313 K, q_m (saturated adsorption capacity) and K_{La} (adsorption equilibrium constant in Langmuir model) were negative, which had no physical meaning for adsorption process. Since R^2 of Freundlich model were larger than R^2 of linear model, except at 298 K. Freundlich model was considered as the most suitable model to be used to predict the performance of adsorption at the equilibrium for SA-R. However, the calculated values of $1/n$ were more than 1 for temperature of 298 and 313 K, indicating increase of hydrophobic surface characteristics after monolayer adsorption. The value of K_F was significantly influenced by adsorption temperature. The highest value of K_F was obtained at 298 K. Figure 3(a) shows good resemblances of the calculated curves and the experimental data for Freundlich model. Similar plots (not shown) were obtained at the other temperatures (298, 308 and 313 K) and showed good resemblances of the calculated curves and the experimental data, as well. Nonlinear regression analysis was performed for Freundlich model and gave the $R^2 = 0.9782$ higher than linear model ($R^2 = 0.9652$). Based on regression analysis, Freundlich model was the most suitable model for prediction of effect of C_e on q_e in the tested range of $0 \leq C_e \leq 1.38 \times 10^{-3}$ kg/kg-solution and $298 \leq T \leq 313$ K.
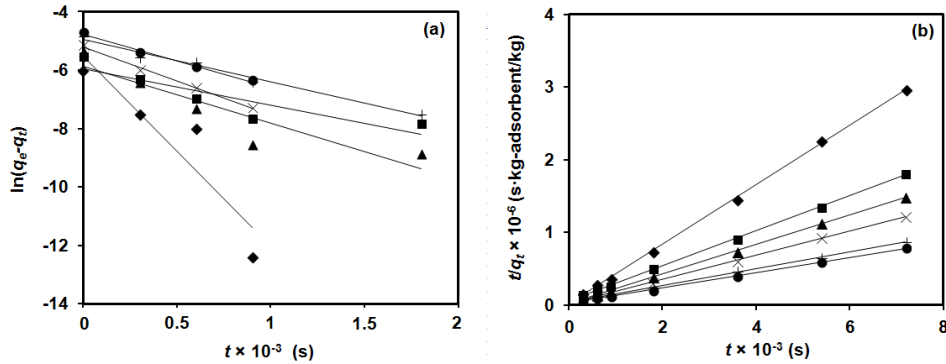
Figure 3: (a) Dependences of q_e on C_e calculated using Freundlich and linear models compared with the experimental data for adsorption of stigmasterol on SA-R (303 K, 5 wt% SA-R), (b) Effect of temperature on the adsorption capacity of SA-R at equilibrium (q_e) at various initial concentrations: ($\blacklozenge$) 0.3×10^{-3}, ($\blacksquare$) 0.6×10^{-3}, ($\blacktriangle$) 0.9×10^{-3}, ($\times$) 1.2×10^{-3}, ($+$) 1.5×10^{-3}, ($\bullet$) 1.8×10^{-3} kg/kg-solution; T = 298 to 313 K, 5 wt% SA-R

Table 2: Parameters and correlation coefficients for Langmuir, Freundlich and linear models for isotherms of stigmasterol adsorption on SA-R

Models	Langmuir: $q_e = \frac{q_m K_{La} C_e}{1+K_{La} C_e}$			Freundlich: $q_e = K_F C_e^{1/n}$			Linear: $q_e = K_{Li} C_e$	
Linearized Equation; Parameters	$\frac{C_e}{q_e} = \frac{1}{K_{La} q_m} + \frac{1}{q_m} C_e$; K_{La}, q_m			$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e)$; K_F, $1/n$			$q_e = K_{Li} C_e$; K_{Li}	
T (K)	K_{La}	q_m	R^2 (-)	K_F	$1/n$ (-)	R^2 (-)	K_{Li}	R^2 (-)
298	-197.35	-0.034	0.4696	29.785	1.180	0.9893	8.501	0.9899
303	490.36	0.021	0.6389	0.989	0.722	0.9686	6.734	0.9328
308	211.00	0.032	0.5156	1.837	0.841	0.9830	5.432	0.9797
313	-136.64	-0.024	0.4030	8.872	1.122	0.9825	3.953	0.9491

*Coefficient units: K_{La} (kg-solution/kg); q_m (kg/kg-adsorbent); K_F (kg/(kg-adsorbent(kg/kg-solution)$^{1/n}$)); K_{Li} (kg-solution/kg-adsorbent)

3.4 Adsorption thermodynamics

To obtain useful information for the design of adsorption process, thermodynamics parameters of adsorption (Gibb's free energy change: ΔG, enthalpy change: ΔH and entropy change: ΔS) were evaluated. Based on the discussion in section of adsorption isotherm, adsorption equilibrium constants at various temperatures were calculated using Freundlich model and ΔG and ΔS were calculated using Eq(6) and Eq(7), respectively.

$$\Delta G = -RT \ln K_F \tag{6}$$

$$\ln K_F = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{7}$$

From Eq(7), enthalpy change (ΔH) and entropy change (ΔS) were calculated from the slope and the y-intercept of the straight line plot between $\ln K_F$ and $1/T$. As summarized in Table 3, adsorption had negative values of ΔG, ΔH and ΔS. The negative value of ΔG indicated that the adsorption was spontaneous and feasible. The increase of ΔG with respect to temperature indicated that the adsorption was more favorable at lower temperatures. Since the calculated values of ΔG was in the range of -20,000 to 0 J/mol, stigmasterol adsorption on SA-R could be considered as physical adsorption (Yu et al., 2001). The negative value of ΔH indicated that the adsorption was in section of adsorption isotherm. The negative value of ΔS indicated associative adsorption and decreased of the randomness between the solid/liquid interfaces due to the adsorption.

3.5 Feasibility of sterol recovery using adsorption technique

In conventional sterol recovery technique, vacuum distillation must be operated at temperature around 453 to 473 K, much higher than room temperature while cold crystallization usually be operated at 253 – 288 K, much lower than room temperature, and requires extremely long crystallization time (7.92 – 2.6 $\times 10^4$ s). It should be noted that the adsorption using SA-R can be operated at the condition not far from ambient temperature and

pressure and the time required for adsorption to reach the equilibrium was extremely short compared with the crystallization time. Therefore, adsorption should be promising method in large scale operation for sterol recovery since it should reduce large amount of overall energy consumption in sterol recovery.

Table 3: Thermodynamics parameters of stigmasterol adsorption on SA-R

T (K)	ΔG (J/mol)	ΔH (J/mol)	ΔS (J/(mol·K))
298	-5,020.63		
303	-4,277.40		
308	-3,534.17	-49,339.43	-148.65
313	-2,790.94		

4. Conclusions

Analysis of kinetics, isotherm and thermodynamics of stigmasterol adsorption on commercial cation-exchange styrene-divinylbenzene resin with strong acid functional group (SA-R) revealed that SA-R was promising for separation of sterol from solution. Adsorption capacity at equilibrium of stigmasterol on SA-R increased with the increase of initial concentration of stigmasterol. The adsorption rate of stigmasterols on SA-R could be described by pseudo-second-order kinetics model. Equilibrium data was well fitted with Freundlich isotherm ($R^2 \geq 0.9686$) and better than Langmuir and linear isotherm models. The thermodynamics parameters indicated that the adsorption of stigmasterol on SA-R was exothermic and spontaneous processes.

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