Chemical Engineering Journal 254 (2014) 579–585

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption kinetics, isotherm and thermodynamics studies of flavones from *Vaccinium Bracteatum Thunb* leaves on NKA-2 resin

Yiyong Chen [a,*], Dejin Zhang [a,b]

[a] School of Biology and Food Engineering, Changshu Institute of Technology, Changshu 215500, China
[b] School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221008, China

HIGHLIGHTS

- NKA-2 resin had a good adsorption and desorption performances for the adsorption of flavones from VBTL.
- The Freundlich isotherm model and the pseudo first-order model were suitable to characterize the process of adsorption.
- The process of adsorption was spontaneous and exothermic.
- The adsorption process was controlled by physical mechanism rather than chemical mechanism.

ARTICLE INFO

Article history:
Received 4 May 2014
Received in revised form 26 May 2014
Accepted 27 May 2014
Available online 5 June 2014

Keywords:
Flavone
Adsorption
Kinetics
Isotherm
Thermodynamics
Vaccinium bracteatum thunb leaves

ABSTRACT

In this paper, the adsorption and desorption characteristics of flavones from *Vaccinium Bracteatum Thunb* leaves (VBTL) were investigated using NKA-2 resin to separate flavones from VBTL. Based on static experiments with NKA-2 resin, adsorption kinetics, isotherms and thermodynamics of flavones from VBTL on NKA-2 resin were investigated. Results showed that NKA-2 resin had a good adsorption and desorption performances for the adsorption of flavones from VBTL, the adsorption capacity of NKA-2 resin was 9.55 mg/g, the ratios of adsorption and desorption were 57.88% and 76.54%, respectively. It was found that the Freundlich isotherm model and the pseudo first-order model were suitable to characterize the process of adsorption. The values of thermodynamic parameters including the changes of Gibbs free energy (ΔG^*), entropy (ΔS^*) and enthalpy (ΔH^*) demonstrated the process of adsorption was spontaneous and exothermic. The adsorption process was controlled by physical mechanism rather than chemical mechanism.

1. Introduction

Vaccinium bracteatum Thunb (named as Wu Fan Shu in China), a traditional Chinese herbal medicine, is widely grown throughout China, which belongs to the same genus as blueberry [1]. Some physiological functions of flavones from *Vaccinium Bracteatum Thunb* leaves (VBTL) such as affecting blood glucose and plasma lipid levels [2], antioxidant activity [3] have been investigated. In view of the pharmacological properties, flavones has a great potential to be used as clinical therapeutic agents, food additives or nutraceutical products [4]. Consequently, separation and purification of flavones is necessary to increase the added value of VBTL.

Recently, macroporous resin as adsorbent was widely used for separating [5–9], which is based on Van der Wals force or hydrogen bond interaction. Column chromatography packed with macroporous resin has unique adsorption properties and advantages including ideal pore structure and various surface functional groups available, low operation expense, less solvent consumption and easy regeneration [6]. Therefore, macroporous resin was chosen as adsorbent in our work.

The preliminary separation and purification of flavones from VBTL have been carried out by column chromatography packed with macroporous resin [10]. However, up to now, kinetics, isotherm and thermodynamics on the adsorption of flavones from VBTL have not been investigated. Adsorption kinetics can describe the adsorption process of flavones from VBTL quantitatively as time elapses. It is crucial for designing the adsorption facilities and understanding the adsorption types and mechanisms [11]. In addition, adsorption isotherms are important for the description of how molecules or ions of adsorbate interact with adsorbent surface sites and critical in optimizing the use of adsorbent [12]. For adsorption thermodynamics, the thermodynamic parameters including free energy change, enthalpy change and entropy change

---

* Corresponding author. Tel.: +86 51252251560.
E-mail address: greenpop6688@126.com (Y. Chen).

http://dx.doi.org/10.1016/j.cej.2014.05.120
1385-8947/

can provide in-depth information on inherent energetic changes that are associated with adsorption [13]. In fact, the thermodynamic parameters are the actual indicators for the practical application of a process [14].

In view of the importance of adsorption equilibrium and mechanism in industry process, in this research, the adsorption kinetics, isotherm and thermodynamics of flavones from VBTL were systematically investigated by using NKA-2 resin. Pseudo first-order, Weber and Morris intra-particle diffusion and pseudo second-order models [15] were employed to describe the adsorption behaviors of kinetics. Based on experimental equilibrium data at different temperatures, isotherm models including Langmuir [16] and Freundlich [17] models were used to simulate the adsorption process of flavones from VBTL on NKA-2 resin. Basic thermodynamic parameters including adsorption enthalpy change (ΔH^*), adsorption free energy change (ΔG^*) and adsorption entropy change (ΔS^*) were assessed. Furthermore, by calculating thermodynamic parameters, thermodynamic function relationships and adsorption isotherm equations were obtained. Our research can lay the foundation for a theoretical basis of flavones adsorption from VBTL on adsorption resin for industry application.

2. Materials and methods

2.1. Materials and chemicals

Fresh VBTL were purchased from LiYang City, Jiangsu province of China, and were air-dried till to the moisture content below 8%. The VBTL were ground to pass 80 meshes and stored in sealed plastic bags. Quercetin (purity > 98%) was obtained from Guizhou Dida Biological Technology Co., Ltd. All the chemicals used were analytical grade.

2.2. Pretreatment of NKA-2 resin

The physical properties of NKA-2 resin were summarized in Table 1. NKA-2 resin was pre-treated with 1 mol/L HCl and 1 mol/L NaOH solutions successively to remove the monomers and porogenic agents trapped inside the pores during the synthesis process, and then dried at 60 °C under vacuum. Prior to adsorption experiments, pre-weighed amounts of resin was soaked in 95% ethanol for 24 h and the adsorbent was subsequently washed with distilled water.

2.3. Preparation of crude flavones extracts from VBTL

The dry VBTL (50 g) were extracted by deionized water (2 L) at 60 °C for 2 h. After filtration, the crude extracts were concentrated at 60 °C under reduced pres-sure by rotary vaporization. Crude flavones extracts from VBTL were obtained.

2.4. Determination of flavones content

Quercetin was employed as a standard compound to determine the content of flavones by spectrophotometry in this study. The calibration curve was plotted using the absorbance at 434 nm as the abscissa and the corresponding concentration of flavones (mg/L) as the ordinate. The linear regression equation was $C = 15.46A - 0.063$ ($R^2 = 0.99975$), its linear range was between 0 and 14 mg/L.

Table 1
Physical properties of NKA-2 resin.

Name	Polarity	Surface area (m^2/g)	Average pore diameter (Å)	Particle diameter (mm)
NKA-2	Polar	160–200	145–155	0.3–1.25

2.5. Adsorption and desorption properties of NKA-2 resin

In order to acquire the adsorption and desorption properties of NKA-2 resin, static adsorption and desorption tests were performed in this study. In adsorption experiment, 1 g resin (dry weight basis) with 30 mL of crude extracts solution (initial concentration of flavones was 0.55 mg/mL) was added into flask. The flask was shaken (120 rpm) in oscillator at 25 °C for 12 h, then the concentration of flavones in the liquid phase was determined by spectrophotometry. The capacity of adsorption (Q_e-mg/g) and the ratio of adsorption (E) were quantified as the following equations:

$$Q_e = \frac{(C_0 - C_e)V_i}{W} \tag{1}$$

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e (mg/mL) are the initial and equilibrium concentrations of flavones in the solution, respectively. V_i (mL) is the volume of initial sample solution. W (g) is the weight of the tested dry resin.

Desorption study was performed as follows: after reaching adsorption equilibrium, the NKA-2 resin was washed by deionized water and then desorbed with 30 mL of 50% (v/v) ethanol solution. The solution was shaken (120 rpm) in oscillator at 25 °C for 12 h, then the concentration of flavones in the eluent sample was analyzed by spectrophotometry. The following equation was used to quantify the ratio of desorption (D):

$$D\,(\%) = \frac{C_d V_d}{(C_0 - C_e)V_i} \times 100 \tag{3}$$

where C_d is the concentration of the solute in the desorption solution (mg/mL) and V_d is the volume of the eluent (mL).

2.6. Static adsorption curve of flavones and adsorption kinetics

The static adsorption curve of flavones on NKA-2 resin was studied by adding pre-weighed amounts of resin (equal to 1 g dry resin) into 30 mL crude flavones extracts from VBTL solution(concentration of flavones was 0.51 mg/mL), then it was shaken (120 rpm) in oscillator at 25 °C until reaching adsorption equilibrium. The concentration of flavones in the solution was determined every certain time by spectrophotometry.

2.7. Adsorption isotherms and thermodynamics

An amount of 1 g NKA-2 resin was added to a 100 mL flask with 30 mL crude flavones extracts from VBTL solutions at different concentrations of flavones. The flasks were shaken (120 rpm) in oscillator at 25 °C, 35 °C and 45 °C for 8 h, respectively. The equilibrium concentrations at different temperatures were determined by spectrophotometry.

3. Results and discussion

3.1. Adsorption and desorption properties of NKA-2 resin

The adsorption and desorption performances associate with chemical features to the solute and the properties of the adsorbents [8]. On one hand, resins with similar polarity to solute exhibited better adsorption ability. On the other hand, physical features of resin played an important role in processes of adsorption and desorption [5]. It was found that the adsorption capacity of NKA-2 resin was 9.55 mg/g, the ratios of adsorption and desorption were 57.88% and 76.54%, respectively. The results indicated NKA-2 resin possessed a strong affinity for the flavones from VBTL, and the process of adsorption was reversible. Consequently, NKA-2 resin can be used as adsorbent in the adsorption process of separating flavones from VBTL. In addition, taking the polarity of NKA-2 resin into consideration, the results suggested that the flavones from VBTL was probable polar compound based on the theory of similarity and intermiscibility.

3.2. Static adsorption curve of flavones on NKA-2 resin

Static adsorption curve was studied to acquire the most suitable adsorption time. The result was presented in Fig. 1. The result indicated that the adsorption reached equilibrium when time was 3 h. Therefore, the best adsorption time was 3 h.

3.3. Adsorption kinetics

Adsorption kinetics can describe the adsorption rate of the adsorbate on an adsorbent at specific initial concentration and temperature, and the time required for the adsorption from the beginning to the equilibrium can be known from the kinetics [18]. The reaction rate of the adsorbate uptake, which is required for selecting the optimum operating conditions for the full-scale batch process, can be elucidated with adsorption kinetics studies. For a solid–liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intra-particle diffusion or both [19]. Various kinetics models have been suggested for adsorption, such as the pseudo-first order, the pseudo-second order and the Weber and Morris intra-particle diffusion kinetics models, etc.

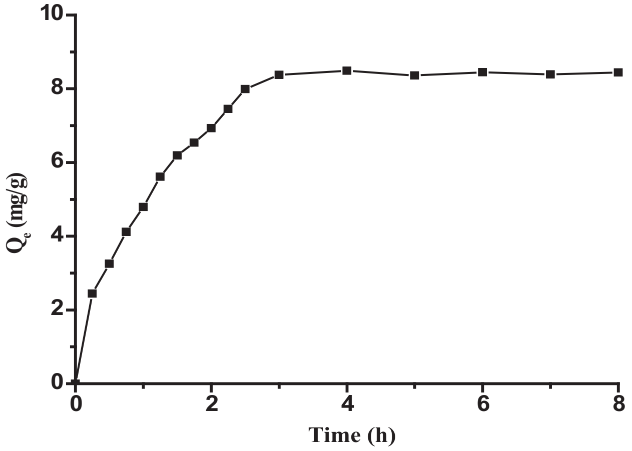

Fig. 1. Static adsorption curve of flavones on NKA-2 resin.

3.3.1. Pseudo first-order model

The pseudo first-order can assess many different adsorption situations, including (i) systems close to equilibrium; (ii) systems with time-independent solute concentration or linear equilibrium adsorption isotherm; and (iii) special cases of more complex systems [20]. The equation is:

$$\frac{d_{Q_t}}{d_t} = k_1(Q_e - Q_t) \tag{4}$$

Eq. (4) can be integrated as follow:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{5}$$

where Q_e (mg/g) and Q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively. k_1 is the rate constant for pseudo first-order equation.

Polt of $\ln(Q_e - Q_t)$ versus t allows calculation of the rate constant k_1 and Q_e. The result was shown in Fig. 2A and Table 2. A straight linearity in Fig. 2A and the correlation coefficient ($R^2 = 0.99519$) implied that the adsorption system followed the pseudo first-order model.

3.3.2. Pseudo second-order model

The pseudo second-order equation assumed that the sorption rate was proportional to the number of active sites occupied onto the sorbent [21]. The pseudo second-order equation is expressed as:

$$\frac{d_{Q_t}}{d_t} = k_2(Q_e - Q_t)^2 \tag{6}$$

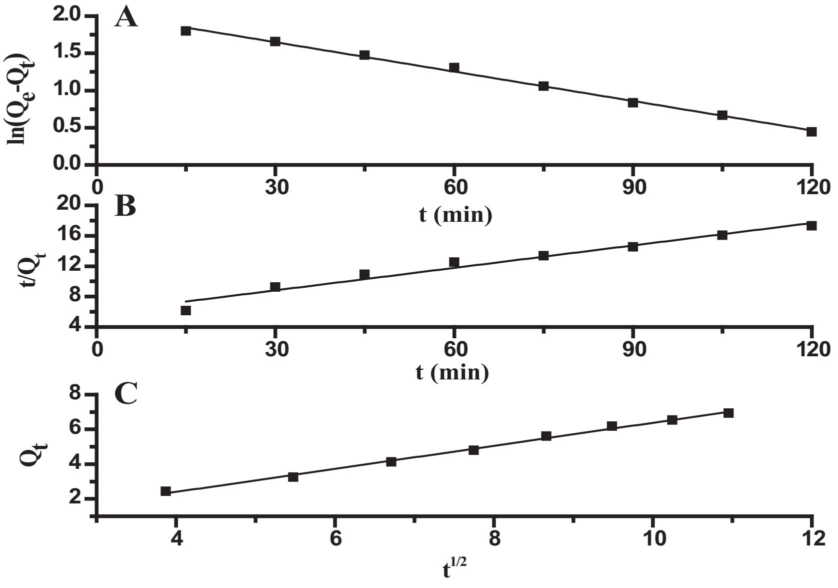

Fig. 2. Modeling of kinetics data using (A) pseudo first-order kinetics, (B) pseudo second-order kinetics, and (C) Weber and Morris intra-particle diffusion model.

Table 2
Kinetics parameters for flavones adsorption onto the NKA-2 resin.

Kinetics model	Equation	R^2	Parameters
Pseudo first-order model	$\ln(Q_e\text{-}Q_t) = -0.01318t + 2.04492$	0.99519	$k_1 = 0.01318$ $Q_e = 7.73$ mg/g
Pseudo second-order model	$t/Q_t = 0.09841t + 5.87068$	0.96584	$k_2 = 0.00165$ $Q_e = 10.16$ mg/g
Weber and Morris intra-particle diffusion model	$Q_t = 0.663t^{1/2} - 0.25002$	0.99422	$k_3 = 0.663$ $I = -0.25002$

Eq. (6) can be rearranged to the linearized form with t/Q_t and t as independent variable as:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \tag{7}$$

where Q_e (mg/g) and Q_t (mg/g) are the adsorption capacities at equilibrium and time t respectively, k_2 is the rate constant for pseudo second-order equation.

By plotting t/Q_t against t, k_2 can be calculated. The result was shown in Fig. 2B, A straight linearity in Fig. 2B implied the pseudo second-order model was suitable for describing the adsorption kinetics of flavones onto NKA-2 resin. However, as shown in Table 2, the correlation coefficient of the pseudo second-order model was lower than the pseudo first-order model, which may indicate the pseudo first-order model is more suitable to predict the kinetics in this study.

3.3.3. Weber and Morris intra-particle diffusion model

Adsorption kinetics was controlled by adsorption mechanism and rate-limiting step of the process [22].The process of adsorption of flavones onto NKA-2 resin can occur through three consecutive steps: (1) mass transfer of adsorbate from boundary film to the surface of resin (film diffusion); (2) mass transport of adsorbate molecules within the pores of resin (intra-particle diffusion); (3) adsorption of the adsorbate molecules on the interior surface of resin. The third step is a fast and non-limiting step in the adsorption process. So the adsorption rate can be limited by the first and/or the second steps [23]. The intra-particle diffusion model can be shown as follow:

$$Q_t = k_3 t^{1/2} + I \tag{8}$$

where Q_t (mg/g) is the adsorption capacity at time t, k_3 is the intra-particle diffusion rate constant, I is a constant that gives idea about the thickness of the boundary layer, the larger the value of I, the greater the boundary layer effect is [24].

If the plot gives a straight line and pass through the origin, the adsorption process is controlled only by the intra-particle diffusion. If the plot shows multi-linear characteristic or does not pass through the origin, the adsorption process is controlled by two or more diffusion mechanism [25]. The result was presented in Fig. 2C. The result showed that the straight lines did not pass origin, which suggested that both film diffusion and intra-particle diffusion were significant.

3.4. Adsorption isotherms and thermodynamics

3.4.1. Adsorption isotherm

The adsorption capacity of adsorbate on the adsorbent can be described by the following function:

$$Q_e = f[T, C_e, E] \tag{9}$$

where Q_e is the adsorption capacity of adsorbate, C_e is the equilibrium concentration of adsorbate, E is adsorption energy.

For a given solid–liquid system, E is a constant when T is a certain value, therefore, C_e is the only factor associated with Q_e, the relationship between Q_e and C_e is adsorption isotherm. Adsorption isotherms characterize the adsorbate distribution between adsorbed on adsorbent and in solution when adsorption equilibrium is reached at a constant temperature [26]. At present, the most common models are Langmuir and Freundlich isotherms. Consequently, Langmuir and Freundlich models were employed to describe the adsorption behaviors.

$$\text{Langmuir equation}: \quad Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{10}$$

$$\text{Freundlich equation}: \quad Q_e = K_F C_e^{1/n} \tag{11}$$

where Q_e is the capacity of adsorption (mg/g), C_e is the equilibrium concentration (mg/mL), $Q_{\max}$ is the calculated maximum adsorption capacity, K_L is the Langmuir constant, K_F and $1/n$ are the Freundlich constants.

The Langmuir equation is applicable to homogenous adsorption where adsorption process has equal activation energy, based on the following basic assumptions [27]:

(i) molecules are adsorbed at a fixed number of well-defined localized sites;
(ii) each site can hold one adsorbate molecule;
(iii) all sites are energetically equivalent;
(iv) there is no interaction between molecules adsorbed on neighbouring sites.

The fitted result of Langmuir isotherm was presented in Fig. 3 and Table 3. The correlation coefficient (R^2) of Langmuir equation was high, which suggested that the Langmuir isotherm model was suitable. In addition, the essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless

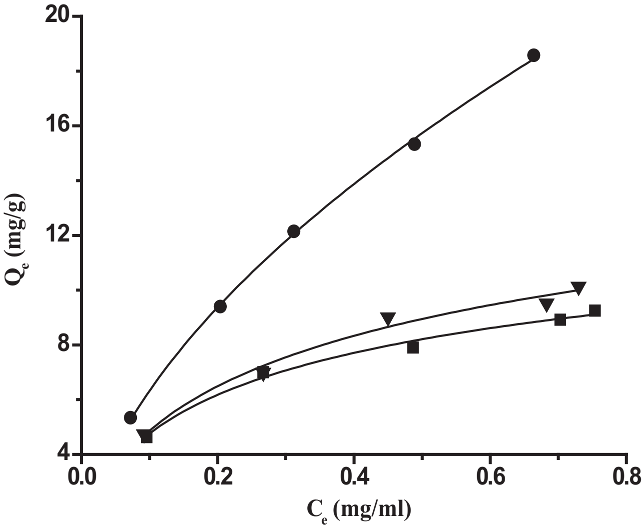

Fig. 3. Langmuir isotherm of flavones on NKA-2 resin at 25 °C (●), 35 °C (▼),45 °C (■).

Table 3
Adsorption isotherm equation and parameters of flavones on NKA-2 resin.

Temperature		25 °C	35 °C	45 °C
Langmuir equation	Linear equation	$C_e/Q_e = 0.03168C_e + 0.01549$	$C_e/Q_e = 0.08283C_e + 0.00435$	$C_e/Q_e = 0.09332C_e + 0.0131$
	$Q_{\max}$	31.57	12.07	10.72
	K_L	2.045	19.04	7.12
	R^2	0.99848	0.96982	0.98204
	R_L	0.28–0.66	0.04–0.17	0.10–0.36
Freundlich equation	Linear equation	$\ln Q_e = 0.55879 \ln C_e + 3.14037$	$\ln Q_e = 0.36326 \ln C_e + 2.43133$	$\ln Q_e = 0.32392 \ln C_e + 2.31698$
	K_F	23.11	11.37	10.14
	$1/n$	0.55879	0.36326	0.32392
	R^2	0.99941	0.98308	0.98132

constant separation factor or equilibrium parameter R_L [28], which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{12}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of flavones.

The values of R_L indicate whether the isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($R_L < 1$), or irreversible ($R_L = 0$) [29]. The values of R_L at different temperatures were presented in Table 3. The results suggested that the isotherm was favorable.

Compared with the Langmuir isotherm model, the Freundlich isotherm model describes adsorption process on heterogeneous surfaces and is suitable to describe adsorption in a narrow range of solute concentration [22]. The Freundlich equation (Eq. (11)) can be rearranged to the linearized form with $\ln Q_e$ and $\ln C_e$ as independent variable as:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{13}$$

K_F is a Freundlich affinity parameter for a hetero-disperse system and n is related to the magnitude to the sorption driving force and to energy distribution of the sorption sites [30]. The value of $1/n$, one of Freundlich constants, indicates the type of isotherm. When $0 < 1/n < 1$, the adsorption is favorable; when $1/n = 1$, the adsorption is irreversible; and when $1/n > 1$, the adsorption is unfavorable [25]. As shown in Table 3, the value of $1/n$ indicated that the adsorption of flavones by NKA-2 resin was favorable. On the other hand, the linear plot of $\ln Q_e$ and $\ln C_e$ shown in Fig. 4 also suggested the applicability of Freundlich adsorption isotherm as the correlation coefficient was high. Compared with Langmuir isotherm model, the average correlation coefficient of Freundlich isotherm model was higher, consequently, Freundlich isotherm model may be more suitable to the process of adsorption in this study, which indicated that the present adsorption system was a surface energy heterogeneity.

3.4.2. Adsorption thermodynamics

Proper assessment of thermodynamics can provide in-depth information regarding the inherent energy and structural changes of adsorbent after adsorption and also provide the mechanism involved in adsorption process [31]. The adsorption of flavones in the solid–liquid interface is the process of migration from liquid phase, chemical potential in the liquid phase and solid–liquid interface are equal when the process of adsorption reaches equilibrium.

Chemical potential in the liquid phase:

$$\mu_l = \mu_l^* + RT \ln(x_l f_l) \tag{14}$$

Chemical potential in the solid–liquid interface:

$$\mu_{s-l} = \mu_{s-l}^* + RT \ln(x_{s-l} f_{s-l}) \tag{15}$$

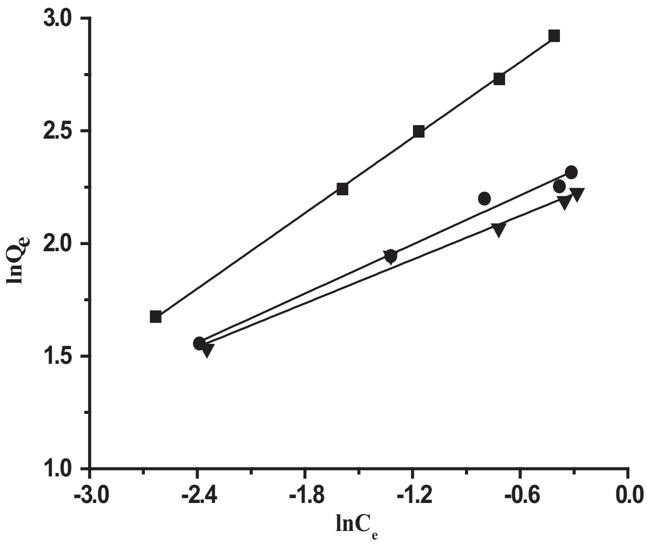

Fig. 4. Freundlich isotherm of flavones on NKA-2 resin at 25 °C (■),35 °C (●), 45 °C (▼).

where μ_l and $\mu_{s\text{-}l}$ are chemical potentials in the liquid phase and solid–liquid interface, μ_{s-l}^* and μ_l^* are standard chemical potentials, x_l and $x_{s\text{-}l}$ are mole fractions of flavones in the liquid and solid–liquid interface, R is the gas constant and T is the temperature (K). When the process of adsorption reaches equilibrium, adsorption Gibbs free energy $\Delta G = 0$, therefore:

$$\Delta G = \mu_{s-l} - \mu_l = \Delta G^* + RT \ln\left(\frac{x_{s-l} f_{s-l}}{x_l f_l}\right) = 0 \tag{16}$$

For dilute solution, $f_{s\text{-}l} = 1$, $f_l = 1$. x_l and $x_{s\text{-}l}$ can be replaced by their activity coefficient $a^{s\text{-}l}$ and a^l, consequently:

$$\Delta G^* = -RT \ln\left(\frac{a^{s-l}}{a^l}\right) \tag{17}$$

where ΔG^* is the change of standard Gibbs free energy. As the equilibrium constant $K = a^{s-l} a^l$, Eq. (17) can be rearranged to the form:

$$\Delta G^* = -RT \ln K \tag{18}$$

Langmuir constant $K_L = \frac{K}{a^l}$, we assume that $a^l = 1$, ΔG^* can be calculated as:

$$\Delta G^* = -RT \ln K_L \tag{19}$$

Enthalpy change can be calculated by Clausius–Clapeyron equation [31]:

$$\frac{d(\ln C_e)}{dT} = -\frac{\Delta H^*}{RT^2} \tag{20}$$

where ΔH^* is the enthalpy change at specific Q_e and C_e at temperature T. Eq. (20) can be linearized as follows:

$$\ln C_e = \frac{\Delta H^*}{RT} + C \tag{21}$$

Entropy change can be calculated as follows:

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \tag{22}$$

As Freundlich isotherm model was more suitable to describe the adsorption behaviors on NKA-2 resin, $\ln C_e$ at different temperatures can be calculated by linear equation of Freundlich isotherm model when Q_e (mg/g) were 6, 8, 10, 12, respectively. Therefore, Fig. 5 was obtained, the correlation coefficients were 0.86162, 0.80064, 0.80274 and 0.80984, respectively, which suggested that Eq. (21) was suitable to be applied for the enthalpy change calculation, the calculated result were presented in Table 4. The negative value of ΔH^* implied the exothermic nature of the adsorption process [32]. In general, exothermic heat is required by an adsorption process (unless adsorption is very weak) to compensate for loses in entropy [33]. In fact, there are many papers in the literature concerning adsorption heats with negative values [8,34]. The result was compatible with the experiment of adsorption isotherms, which suggested that Q_e decreased when T increased. In addition, it was logical that the absolute value of ΔH^* increased with the increase of Q_e. The differences of ΔH^* between Q_e (6, 8, 10, 12 mg/g) were 14.13, 10.91 and 8.95 J/mol, respectively. The reason of reduction of heat may be that the process of adsorption will occur on the most active sites at the beginning of adsorption. Subsequently, with increasing in adsorption capacity, adsorption occurred on the sites of adsorbent with less activity. In addition, the absolute value of ΔH^* for each sample was lower than 40 KJ/mol, which indicated that the adsorption process was controlled by physical mechanism rather than chemical mechanism [22]. This result shows that the interaction between resin and flavones is mainly electrostatic (Coulombic interactions) [35].

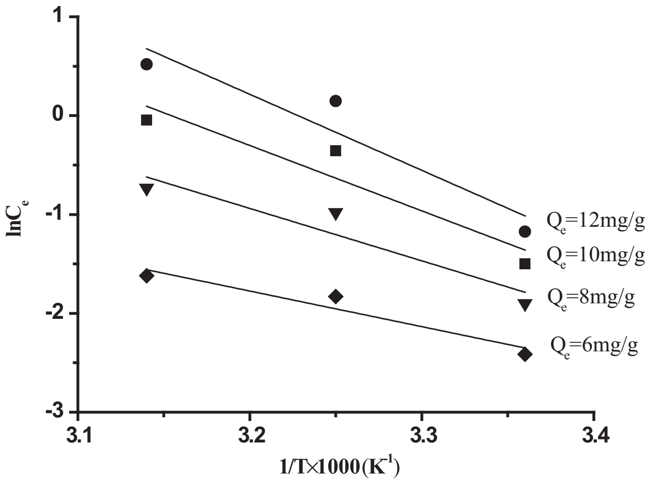

Fig. 5. Fitting curve of $\ln C_e$ and $1/T \times 1000$ for determining enthalpy change of adsorption.

Table 4
Thermodynamic parameters of flavones adsorption on NKA-2.

Q_e (mg/g)	ΔH^* (J/mol)	ΔH^* (J/mol)			ΔH^* (J/mol/K)		
		25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
6	−29.93	−1772.45	−7545.25	−5189.64	5.85	24.40	16.23
8	−44.06				5.80	24.35	16.18
10	−54.97				5.76	24.32	16.15
12	−63.92				5.73	24.29	16.12

ΔG^* and ΔS^* can be calculated by Eqs. (19) and (22). The result was presented in Table 4. The negative value of ΔG^* confirmed the feasibility of the present adsorption process and the spontaneous nature of the adsorption [34]. The positive value of ΔS^* at different temperatures reflected the good affinity of flavones from VBTL toward NKA-2 resin and the increased randomness at the solid/solution interface during the adsorption of flavones onto NKA-2 resin [36].

4. Conclusions

The current study has demonstrated that NKA-2 resin had a good adsorption and desorption performances for the adsorption of flavones from VBTL. The adsorption capacity of NKA-2 resin was 9.55 mg/g, the ratios of adsorption and desorption were 57.88% and 76.54%, respectively. The Freundlich isotherm model and the pseudo first-order model were found to be suitable to characterize the process of adsorption of flavones from VBTL. In the investigation of adsorption thermodynamics, the $\Delta G^* < 0$ and $\Delta S^* > 0$ indicated that the process of adsorption was spontaneous. The negative ΔH^* implied that the process of adsorption was exothermic. In addition, the adsorption process was controlled by physical mechanism rather than chemical mechanism.

References

[1] L. Wang, Y. Zhang, M. Xu, Y. Wang, S. Cheng, A. Liebrecht, H. Qian, H. Zhang, X. Qi, Anti-diabetic activity of *Vaccinium bracteatum Thunb* leaves' polysaccharide in STZ-induced diabetic mice, Int. J. Biol. Macromol. 61 (2013) 317–321.
[2] L. Wang, X.T. Zhang, H.Y. Zhang, H.Y. Yao, H. Zhang, Effect of *Vaccinium bracteatum Thunb* leaves extract on blood glucose and plasma lipid levels in streptozotocin-induced diabetic mice, J. Ethnopharmacol. 130 (2010) 465–469.
[3] L. Wang, H.N. Xu, H.Y. Yao, H. Zhang, Phenolic composition and radical scavenging capacity of *Vaccinium Bracteatum Thunb* leaves, Int. J. Food. Prop. 14 (2011) 721–725.
[4] W. Liu, S. Zhang, Y.G. Zu, Y.J. Fu, W. Ma, D.Y. Zhang, Y. Kong, X.J. Li, Preliminary enrichment and separation of genistein and apigenin from extracts of pigeon pea roots by macroporous resins, Bioresour. Technol. 101 (2010) 4667–4675.
[5] Z. Zhao, L. Dong, Y. Wu, F. Lin, Preliminary separation and purification of rutin and quercetin from *Euonymus alatus* (Thunb) Siebold extracts by macroporous resins, Food Bioprod. Process. 89 (2011) 266–272.
[6] G. Jia, X. Lu, Enrichment and purification of madecassoside and asiaticoside from *Centella asiatica* extracts with macroporous resins, J. Chromatogr. A 1193 (2008) 136–141.
[7] Q. Xiong, Q. Zhang, D. Zhang, Y. Shi, C. Jiang, X. Shi, Preliminary separation and purification of resveratrol from extract of peanut (*Arachis hypogaea*) sprouts by macroporous adsorption resins, Food Chem. 145 (2014) 1–7.
[8] Y. Liu, J. Liu, X. Chen, Y. Liu, D. Di, Preparative separation and purification of lycopene from tomato skins extracts by macroporous adsorption resins, Food Chem. 123 (2010) 1027–1034.
[9] Y. Fu, Y. Zu, S. Li, R. Sun, T. Efferth, W. Liu, S. Jiang, H. Luo, Y. Wang, Separation of 7-xylosyl-10-deacetyl paclitaxel and 10-deacetylbaccatin III from the remainder extracts free of paclitaxel using macroporous resins, J. Chromatogr. A 1177 (2008) 77–86.
[10] L. Wang, H.Y. Yao, Purification of black pigment from *Vaccinium bracteatum Thunb* leaves by resin, Nat. Prod. Res. Dev. 18 (2006) 20–24.
[11] L. Ding, H. Deng, C. Wu, X. Han, Affecting factors, equilibrium, kinetics and thermodynamics of bromide removal from aqueous solutions by MIEX resin, Chem. Eng. J. 181–182 (2012) 360–370.
[12] M. Özacar, İ.A. Şengil, H. Türkmenler, Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin, Chem. Eng. J. 143 (2008) 32–42.
[13] F. Liu, L. Li, P. Ling, X. Jing, C. Li, A. Li, X. You, Interaction mechanism of aqueous heavy metals onto a newly synthesized IDA-chelating resin: isotherms, thermodynamics and kinetics, Chem. Eng. J. 173 (2011) 106–114.
[14] W. Qian, X. Lin, X. Zhou, X. Chen, J. Xiong, J. Bai, H. Ying, Studies of equilibrium, kinetics simulation and thermodynamics of cAMP adsorption onto an anion-exchange resin, Chem. Eng. J. 165 (2010) 907–915.
[15] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by Sphagnum moss peat, Can. J. Chem. Eng. 76 (1998) 822–827.
[16] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1402.
[17] H. Frendlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 1100–1107.

[18] X. Wang, X. Yuan, S. Han, H. Zha, X. Sun, J. Huang, Y.N. Liu, Aniline modified hypercrosslinked polystyrene resins and their adsorption equilibriums, kinetics and dynamics towards salicylic acid from aqueous solutions, Chem. Eng. J. 233 (2013) 124–131.

[19] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, Adv. Colloid Interface 143 (2008) 48–67.

[20] M.L. Soto, A. Moure, H. Domínguez, J.C. Parajó, Recovery, concentration and purification of phenolic compounds by adsorption: a review, J. Food Eng. 105 (2011) 1–27.

[21] C.W. Wong, J.P. Barford, G. Chen, G. McKay, Kinetics and equilibrium studies for the removal of cadmium ions by ion exchange resin, J. Environ. Chem. Eng. 2 (2013) 698–707.

[22] Z.P. Gao, Z.F. Yu, T.L. Yue, S.Y. Quek, Adsorption isotherm, thermodynamics and kinetics studies of polyphenols separation from kiwifruit juice using adsorbent resin, J. Food Eng. 116 (2013) 195–201.

[23] Y.S. Ho, G. Mckay, Competitive sorption of copper and nickel ions from aqueous solution using peat, Adsorption 5 (1999) 409–417.

[24] Y. Shi, X. Kong, C. Zhang, Y. Chen, Y. Hua, Adsorption of soy isoflavones by activated carbon: kinetics, thermodynamics and influence of soy oligosaccharides, Chem. Eng. J. 215–216 (2013) 113–121.

[25] S. Vasiliu, I. Bunia, S. Racovita, V. Neagu, Adsorption of cefotaxime sodium salt on polymer coated ion exchange resin microparticles: kinetics, equilibrium and thermodynamic studies, Carbohyd. Polym. 85 (2011) 376–387.

[26] H. Zhang, A. Li, J. Sun, P. Li, Adsorption of amphoteric aromatic compounds by hyper-cross-linked resins with amino groups and sulfonic groups, Chem. Eng. J. 217 (2013) 354–362.

[27] M.A. Abdullah, L. Chiang, M. Nadeem, Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents, Chem. Eng. J. 146 (2009) 370–376.

[28] T.W. Webi, R.K. Chakravort, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J. 20 (1974) 228–238.

[29] U.Y.C. Sharma, A.S.K. Sinha, S.N. Upadhyay, Characterization and adsorption studies of *Cocos nucifera* L. Activated carbon for the removal of methylene blue from aqueous solutions, J. Chem. Eng. Data 55 (2010) 2662–2667.

[30] W.J. Weber, P.M. Mcginley, L.E. Katz, Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport, Water Res. 25 (1991) 499–528.

[31] T.S. Anirudhan, P.G. Radhakrishnan, Kinetics, thermodynamics and surface heterogeneity assessment of uranium(VI) adsorption onto cation exchange resin derived from a lignocellulosic residue, Appl. Surf. Sci. 255 (2009) 4983–4991.

[32] Y.M. Chen, X.H. Jin, D. Gao, H.F. Xia, J.H. Chen, Thermodynamics and kinetics of lysozyme adsorption onto two kinds of weak cation exchangers, Biotechnol. Bioproc. E. 18 (2013) 950–955.

[33] H. Koyuncu, A.R. Kul, N. Yildiz, A. Calimli, H. Ceylan, Equilibrium and kinetic studies for the sorption of 3-methoxybenzaldehyde on activated kaolinites, J. Hazard. Mater. 141 (2007) 128–139.

[34] R.I. Yousef, B. El-Eswed, A.H. Al-Muhtaseb, Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: kinetics, mechanism, and thermodynamics studies, Chem. Eng. J. 171 (2011) 1143–1149.

[35] X. Wang, R. Deng, X. Jin, J. Huang, Gallic acid modified hyper-cross-linked resin and its adsorption equilibria and kinetics toward salicylic acid from aqueous solution, Chem. Eng. J. 191 (2012) 195–201.

[36] C. Duran, D. Ozdes, A. Gundogdu, H.B. Senturk, Kinetics and isotherm analysis of basic dyes adsorption onto almond shell (*Prunus dulcis*) as a low cost adsorbent, J. Chem. Eng. Data 5 (2001) 2136–2147.