Equilibrium and Kinetic Modeling of the Adsorption of Stevioside on Amberlite XAD-7 Beads

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Abstract

The behaviour of the stevioside adsorption process from the stevia extract solutions onto XAD-7 beads was studied in a batch system. The equilibrium isotherms and the kinetics of adsorption with respect to the initial stevioside concentration (370, 667, 1185, and 1956 μg/ml), solution temperature (25°C, 55°C, and 75°C) and weight of resin used (0.1 g, 0.3 g, and 0.5 g) were investigated at pH 9. Langmuir and Freundlich adsorption models were tested to describe the experimental isotherms and isotherm constants. The equilibrium data was found to fit well to the Langmuir model in the saturation concentration range from 0 to 820 μg/ml. The maximum monolayer adsorption capacities obtained from the Langmuir model were 398, 385 and 270 mg/g for 0.1 g XAD-7 beads used, respectively at temperature 25°C, 55°C, and 75°C and pH 9. The pseudo first-order and second-order kinetics models were used to describe the kinetic data and the rate constants were also evaluated. The experimental data fitted well to the second-order kinetic model. The initial stevioside concentration and the weight of resins used both significantly affect the adsorption capacity but the temperature and the solution pH were found to be relatively minor factors. Adsorption capacity increases with the increase of initial stevioside concentration, and solution pH as well as the decrease of the solution temperature, and resin weight used. The activation energy is 20 kJ/mol for the adsorption of stevioside on 0.1 g XAD-7 beads used at pH 9 with an initial stevioside concentration of 370 μg/ml.

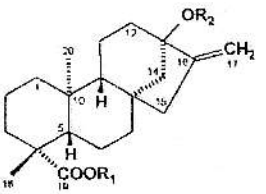
Keywords:

Adsorption capacity, adsorption rate, stevioside, stevia extract solution, Amberlite XAD-7

Introduction

The sweet tasting compounds present in the leaves of *Stevia rebaudiana* comprises mainly of dulcoside A, rebaudioside A, B and steviolbioside, rebaudioside D and E, rebaudioside C or dulcoside B and stevioside. They occur in high concentration levels in *Stevia rebaudiana* leaves. The four most significant compounds are stevioside (5-10 % w/w), rebaudioside A (2-4 % w/w), rebaudioside C (1-2 % w/w) and dulcoside A (0.4-0.7 % w/w) [1].

Stevioside has been rated as having about 300 times the relative sweetness intensity of 0.4 % (w/v) sucrose solution. However, the compound exhibits some bitterness and undesirable aftertaste [2]. The structures of these stevia sweeteners [3] are shown in Figure 1 and Figure 2. In each case, the aglycone is steviol. These stevia sweeteners are similar in structure in that a steviol aglycone is connected at C-4 and C-13 to mono-, di- or trisaccharides consisting of glucose and/or rhamnose residues [4].



	R_1	R_2
1 Stevioside	Glc	Glc-Glc (2→1)
2 Rebaudioside A	Glc	Glc-Glc (2→1) | Glc (3→1)
3 Rebaudioside C (= Dulcoside B)	Glc	Glc-Rha (2→1) | Glc (3→1)
4 Rebaudioside D	Glc-Glc (2→1)	Glc-Glc (2→1) | Glc (3→1)
5 Rebaudioside E	Glc-Glc (2→1)	Glc-Glc (2→1)
6 Dulcoside A	Glc	Glc-Rha (2→1)

Glc = β-D-glucopyranosyl; rha = α-L-rhamnopyranosyl

Figure 1 - Structures of sweet tasting ent-kaurene diterpenes isolated from Stevia rebaudiana

ISBN:983-2643-15-5

In order to recover stevioside sweetener from *Stevia rebaudiana*, the dried leaves are extracted with deionised water or with an organic solvent such as alcohol. The extracts are then subjected to several refining steps to purify and enrich the stevioside compounds affecting the sweetness intensity. There have been numerous methods [5-11] for recovery and separation of stevioside from *Stevia rebaudiana* plant. However, the use of adsorption process by utilizing the Amberlite XAD-7 as an adsorbent [11] showed a promising result.

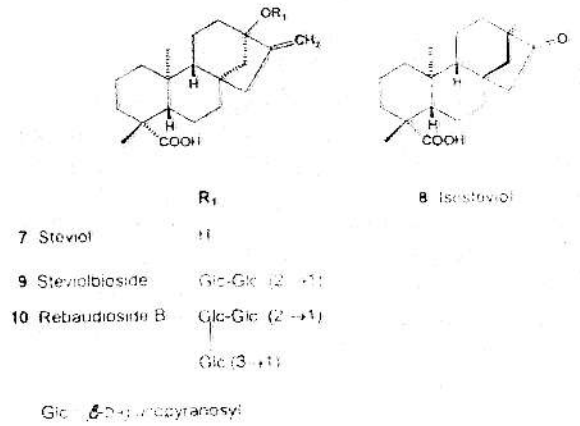


Figure 2 - Chemical Structures of Derivatives of the Stevia rebaudiana sweet ent-kaurene diterpenoid Constituents

Synthetic neutral resins namely Amberlite XAD-7 is a polymeric adsorbent and is slightly polar. It is a non-ionic aliphatic acrylic polymer, which derives its adsorptive properties from its macroreticular structure (containing both a continuous polymer phase and a continuous pore phase). It also contains high surface area. This macroreticular structure also given Amberlite XAD-7 an excellent physical and thermal stability. Due to its aliphatic nature, Amberlite XAD-7 polymeric adsorbent can adsorb non-polar compounds from aqueous systems, and can also adsorb polar compounds from non-polar solvents [12]. Apart from increasing stevioside recovery to over 90 % (w/w), this process also regenerates and reuses the resin used, therefore saving operating costs.

This paper reported the study on the behaviour of the adsorption process using XAD-7 as an adsorbent in the stevioside process recovery. The uptake capacity of stevioside onto XAD-7 adsorbent can be affected by various factors such as initial stevioside concentrations, solution pH, solution temperature and weight of adsorbent used. All of these factors will be described in this paper. The equilibrium and kinetics of adsorption of stevia extract solution onto the XAD-7 were studied at pH 9. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption rates were measured and determined in correlation with initial stevioside concentrations, solution temperature and weight of adsorbent used.

Approach and Methods

Materials

Samples of *Stevia rebaudiana* leaves were purchased from Nasuha Enterprise Sdn. Bhd. Pagoh, Johor. The extraction of stevioside from the leaves was carried out in the extraction vessel. The crude stevia extracts were then subjected to tangential flow microfiltration (0.45μm) and ultrafiltration (100kD and 30kD MWCO) membrane separation system (Milipore, USA) to reduce the impurities and unwanted compounds. The stevia extracts solution produced was stored in the freezer at 5°C. The pH of the sample was adjusted using the solution of 1 N NaOH and 1 N HCl.

Amberlite XAD-7 (Fluka Chemie AG, Switzerland) in bulk quantity was supplied as a water-wet product imbibed with sodium chloride and sodium carbonate salts to retard bacterial growth. Before use, the resin was washed with deionised water to remove the salts and then been over dried at 50°C. Stevioside assay was carried out by anthrone reaction and was analysed using spectrophotometer at A_{620} nm (Genesys10 UV/Vis, USA).

Batch Equilibrium Study

In the experiments of batch equilibrium adsorption isotherm, the stevia extract solution at pH 9 was diluted four times with the dilution factor of 0.6 to give four different initial concentrations that are 370, 667, 1185, and 1956 μg/ml, respectively. For each concentration, an amount of 20 ml of the stevia extract solution was prepared in a 50 ml centrifuge tube containing 0.1 g XAD-7. The centrifuge tube was then placed in the incubator shaker. The stevia extracts solution was shaken well at 300 rpm in the incubator shaker and the temperature was set at 25 ± 1 °C. 1 ml of sample was taken out for analysis at 0, 10, 20, 60, 80, 120, and 180 minutes. After reaching equilibrium state at 3 hours, the samples were analysed for stevioside concentration using spectrophotometer. The experiment was repeated for different temperature (55°C and 75°C) and weight of resins used (0.3 g and 0.5 g). The amount of adsorption at equilibrium, q_e (mg/g) was obtained from Equation (1).

$$q_e = \frac{(C_o - C_e)V_o}{X_o} \qquad (1)$$

where C_o and C_e are the initial and equilibrium adsorbate concentrations (μg/ml), respectively. The V_o is the initial volume of the solution and X_o is the initial weight of the adsorbent used.

ISBN:983-2643-15-5

Batch Kinetic Study

In the experiments of batch kinetic study, an amount of 0.1 g XAD-7 and 20 ml of stevia extracts were prepared in a 50 ml of centrifuge tube and then was placed in the incubator shaker. The experiment was conducted at different pH value by adjusting the pH of the stevia extracts solution to pH 7, 8, 9, and 10 using NaOH and HCL solution, respectively. The stevia extracts solution with the desired pH was shaken well at 300 rpm in the incubator shaker and the temperature was set at 25 ± 1 °C. 1 ml of sample was taken out for analysis at 0, 10, 20, 60, 80, 120, and 180 minutes. After reaching equilibrium state at 3 hours, the samples were analysed for stevioside concentration using spectrophotometer. The experiment was repeated for different temperature (55°C and 75°C) and weight of resins used (0.3 g and 0.5 g).

Results

Equilibrium Adsorption

Figure 3 shows the equilibrium adsorption isotherm for stevioside adsorption on 0.1 g beads at pH 9 and three different temperatures. From Figure 3, it is seen that the adsorption capacity is much higher at 25°C with 240 mg/g stevioside uptake for 0.1 g XAD-7 used. Favourable isotherms were determined based on the shape of the isotherms, which are convex upward.

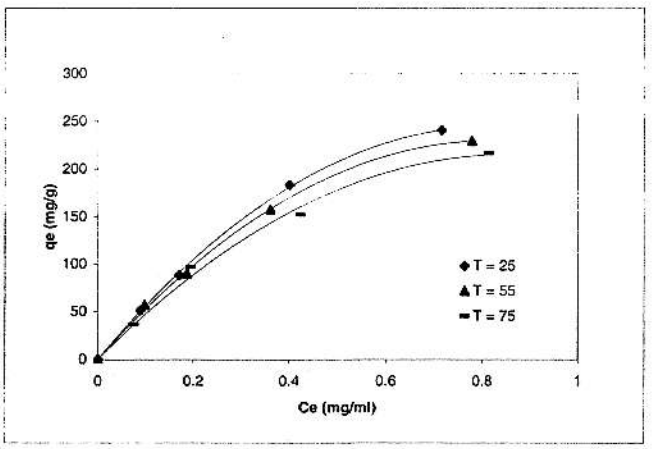


Figure 3 - Equilibrium Adsorption of Stevioside on 0.1 g XAD-7 Beads at Different Temperature.

In order to study the behaviour of the stevioside adsorption at equilibrium, two common equilibrium adsorption models have been performed namely Langmuir and Freundlich model. The Langmuir [13] isotherm has found successful application in many real sorption processes and is expressed as:

$$q_e = Q.b.C_e / 1 + (b.C_e) \qquad (2)$$

where Q (mg/g) is the maximum amount of the stevioside per unit weight of XAD-7 to form a complete monolayer coverage on the surface bound. Ce (µg/ml) is the concentration of stevioside at equilibrium. b is the Langmuir constant related to the affinity of binding sites. Q represents a practical limiting adsorption capacity when the surface is fully covered with stevioside molecules and assists in the comparison of adsorption performance. The derivatives of Langmuir equation is:

$$1/q_e = 1/(b.Q.C_e) + 1/Q \qquad (3)$$

Equation above can be used to linearise data that conforms to the Langmuir model. In the graphical evaluation of Langmuir isotherm constant according to Equation (3), the slope is equal to $1/(b.Q.C_e)$ and the intercept is equal to $1/Q$.

The Freundlich isotherm [14] is used to describe a special case for heterogeneous surface energies where the term b of the Langmuir equation varies as a function of q_e, which is strictly due to variation in heat of adsorption. The equation is rewritten as:

$$q_e = K_f.C_e^{1/n} \qquad (4)$$

where K_f and n are Freundlich constants. The constants are temperature dependent and are used as indicators of adsorption capacity and adsorption intensity. This equilibrium equation is non-linear and data are usually fitted to the logarithmic form of equation:

$$\log q_e = \log K_f + 1/n \log C_e \qquad (5)$$

which should give a straight line plotting log q_e versus log C_e. The slope and intercept of a straight line are equal to $1/n$ and log K_f, respectively. A larger value for $1/n$ indicates a larger change in adsorption effectiveness over different equilibrium concentrations. Also, when $1/n$ is >1.0, the change in adsorbed concentration is greater than the change in the solute concentration [15]. The plot of Langmuir and Freundlich isotherms were given at Figure 4 and Figure 5. The values for the Langmuir and Freundlich isotherm constants were given in Table 1.

Kinetics of Adsorption

Effect of pH and temperature

Figure 6 shows the effect of pH on adsorption of stevioside onto 0.3 g XAD-7 at 25°C with initial concentration of 1956 µg/ml. It can be seen that pH 9 gave the highest number of adsorption capacity among the other pH values. The effect of temperature on the stevioside adsorption is shown in Figure 7. Three different temperatures were evaluated at pH 9 and

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0.1 g XAD-7 is used. The results indicated that the temperature 25°C provides the maximum adsorption value.

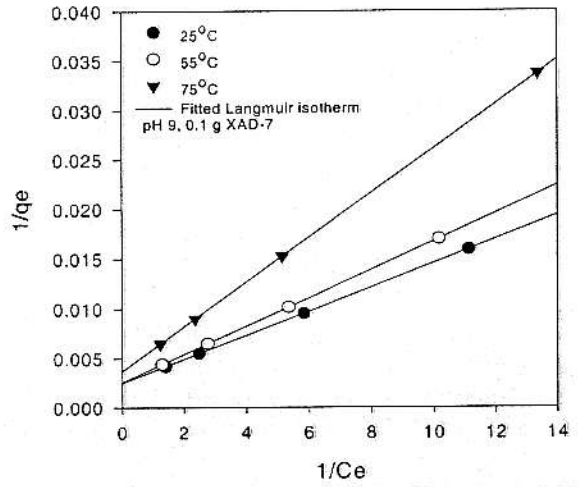

Figure 4 - Langmuir Plot on 0.1 g XAD-7 Beads at Different Temperature.

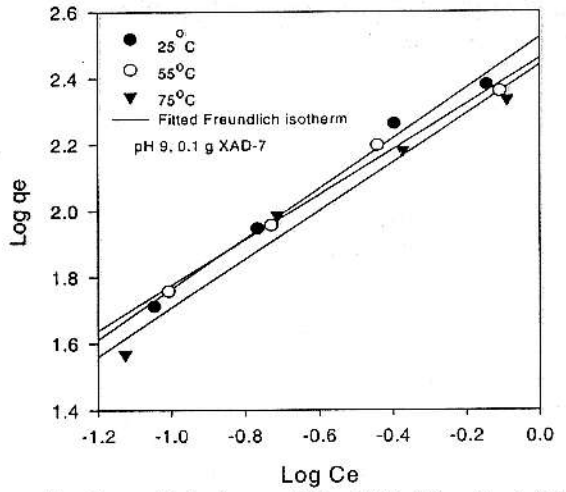

Figure 5 - Freundlich plot on 0.1 g XAD-7 beads at different temperature.

Table 1 Langmuir and Freundlich Isotherm Constants at Different Temperature and Weight of XAD-7 Beads.

Temp. (°C)	Weight (g)	Langmuir		R^2	Freundlich		R^2
		Q	b		Kf	n	
25	0.1	398	2.1	0.996	333	1.3	0.989
55	0.1	385	1.8	0.995	306	1.5	0.938
75	0.1	270	1.7	0.993	275	1.4	0.974
25	0.3	131	5.4	0.979	184	1.6	0.992
55	0.3	130	5.2	0.992	184	1.5	0.960
75	0.3	115	5.1	0.992	186	1.3	0.958
25	0.5	131	7.1	0.991	183	1.4	0.982
55	0.5	122	6.9	0.998	154	1.5	0.981
75	0.5	71	6.5	0.995	123	1.6	0.994

Effect of Initial Concentration and Weight of XAD-7 Used

The effect of initial concentration of the stevia extract solution on 0.3 g XAD-7 with pH 9 and temperature of 55°C is shown in Figure 8. The plot shows that most of the stevioside is adsorbed to achieve adsorption equilibrium in about 120 minutes. Figure 9 shows the effect of the weight of XAD-7 used in the stevioside adsorption at 25°C and pH 9.

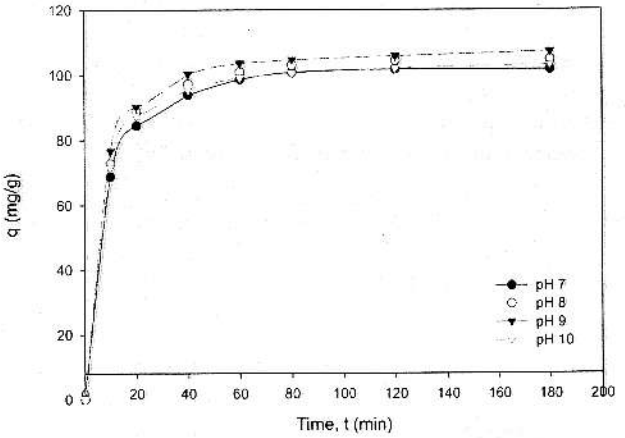

Figure 6 - Adsorption Kinetics of Stevioside on 0.3 g XAD-7 Beads at Different pH.

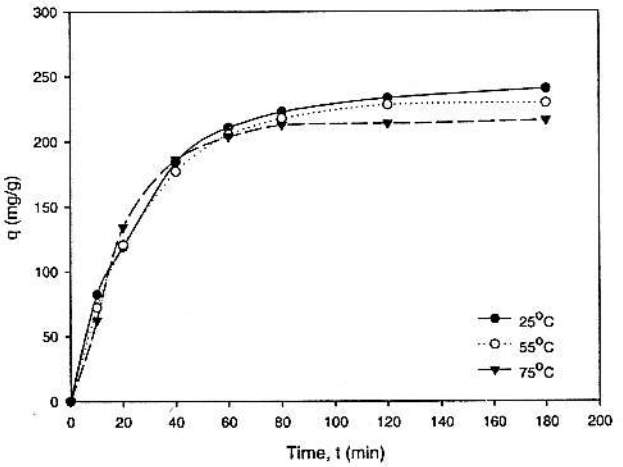

Figure 7 - Adsorption Kinetics of Stevioside on 0.1 g XAD-7 Beads at Different Temperature.

Rate Constant Study

Adsorption of stevioside onto XAD-7 beads may involve a chemisorption, which could control the reaction rate. This kinetic analysis is based on reaction kinetic mostly pseudo first-order or multiple pseudo first-order mechanism. In order to investigate the mechanism of adsorption, the rate constants of chemisorption for the stevioside were determined using the equation of a pseudo first-order system

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by Lagergren [16], and a pseudo second-order mechanism, respectively. The equations are used to test the experimental data of initial concentration, temperature, and the weight of XAD-7 used at pH 9.

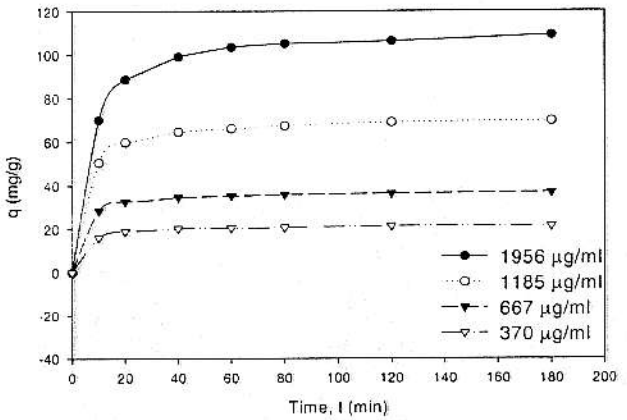

Figure 8 - Adsorption Kinetics of Stevioside on 0.3g XAD-7 Beads at Different Initial Concentration.

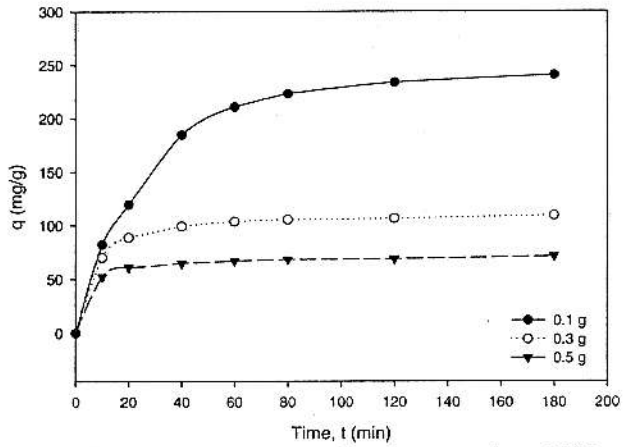

Figure 9 - Adsorption Kinetics of Stevioside at 25°C on Different Weight of XAD-7 Beads Used.

For the rate constant for first-order chemisorption:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \qquad (6)$$

Integrating this equation for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ and $q_t = q_t$, gives:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303}t \qquad (7)$$

where q_1 and q_t are the amounts of stevioside adsorbed on XAD-7 at equilibrium and a time t, respectively (mg/g), and k_1 is the equilibrium rate constant of first-order adsorption (per min). A straight line of log (q_1-q_t) versus t suggests the applicability of this kinetic model to fit the experimental data. The intercept of this plot should be equal to log (q_1). Otherwise, the reaction is not likely to be a first-order, even though the plot has high correlation coefficient with the experimental data.

For the rate constant of the pseudo second-order chemisorption process:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \qquad (8)$$

Integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_2 - q_1)} = \frac{1}{q_2} + k_2 t \qquad (9)$$

where q_2 is the amount of stevioside adsorbed on XAD-7 at equilibrium (mg/g) and k_2 is the equilibrium rate constant of pseudo second-order chemisorption (g/mg *per* min). Again, q_2 should be equal to the experimentally obtained equilibrium capacity. The second-order kinetic model can be rearranged to obtain a linear form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_2} + \frac{t}{q_2} \qquad (10)$$

If second-order adsorption kinetics is applicable, the plot of t/q versus t should show a linear relationship. Table 2 shows a comparison of results for different initial stevioside concentration between first-order and second-order kinetic model obtained from the experimental data at 25°C on 0.5 g XAD-7 beads used. The plot for the second-order kinetic model of this experimental data is shown in Figure 10.

Thermodynamics

Almost all reactions are accelerated by rise in temperature. Variation of rate constant with temperature is expressed by the Arrhenius equation as:

$$k = A\exp^{-(E_a/RT)} \qquad (11)$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (12)$$

The rate constant, k at different temperature can be applied to estimate the activation energy of the adsorption of

ISBN:983-2643-15-5

stevioside on XAD-7 beads [16]. Assuming that the correlation among the rate constant k_2, temperature, T and activation energy, E_a follow Arrhenius equation, which bring on to the following expression:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + const. \qquad (13)$$

where R is the gas constant (8.314 *J/mol.K*). The slope of plot of ln k versus *1/T* is used to evaluate the E_a (kJ/*mol*). Figure 11 shows the plot of ln k_2 versus *1/T* on 0.1 g XAD-7 beads at different initial concentration. The results of *Ea* obtained from this plot are given in Table 3.

Table 2 - Comparison of First-order and Second-order Adsorption Rate Constant.

First-order kinetics model				
Initial Conc. (µg/ml)	qe_{exp} (mg/g)	k_1 (per min)	q_1 (mg/g)	R^2
1156	70.9062	0.0248	25.8782	0.7787
1185	40.0000	0.03635	9.1338	0.763
667	23.1385	0.03675	5.6171	0.8101
370	13.4923	0.02546	2.9406	0.6383
Second-order kinetics model				
Init. Conc. (µg/ml)	qe_{exp} (mg/g)	k_2 (g/mg per min)	q_2 (mg/g)	R^2
1156	70.9062	0.003188	72.0814	0.9997
1185	40.0000	0.01593	40.3368	.9998
667	23.1385	0.02724	23.3276	0.9999
370	13.4923	0.0357	13.5747	0.9998

*qe_{exp} is qe obtained from the experiment; q_1 and q_2 are calculated from the Equation (7) and Equation (10).

Another thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the adsorption of stevioside onto XAD-7 beads are determined by following equation [17]. The adsorption of free energy, ΔG can be related to the Langmuir constant, b by the following equation [18]:

$$\Delta G = -RT \ln K_{ad} \qquad (14)$$

where K_{ad} is the adsorption equilibrium constant obtained from the value of b in the Langmuir isotherm. The relation between the K_{ad} and the thermodynamic parameters of ΔH and ΔS can be described by Van't Hoff's equation:

$$\ln K_{ad} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (15)$$

The value of ΔH and ΔS were calculated from the slope and intercept of the Vant's Hoff plot, respectively. The Van't Hoff plot for 0.1 g XAD-7 beads is shown in Figure 12 with ΔH is –4.1301 kJ/mol and ΔS is –0.007689 kJ/mol.K. A negative value of ΔH indicates the exothermic nature of the adsorption of stevioside onto the XAD-7 surface. The values of ΔG obtained from this plot are tabulated in Table 4. The negative value of ΔG shows the spontaneous adsorption of stevioside onto the XAD-7 beads.

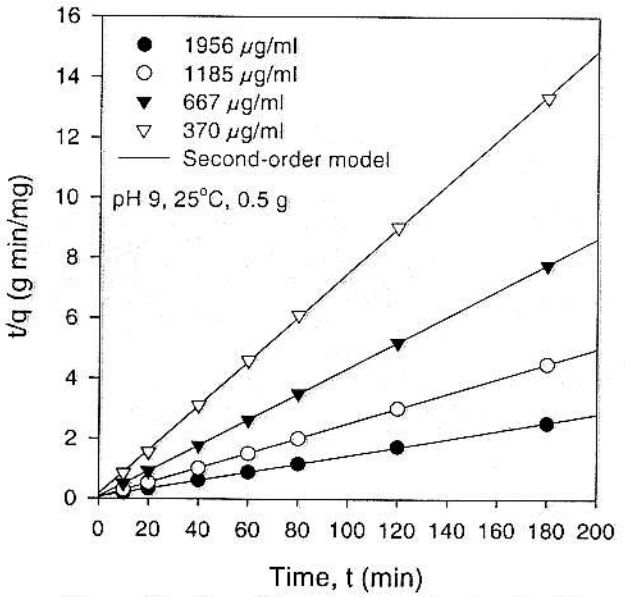

Figure 10 - Plot of Pseudo Second-order Model at Different Initial Concentration.

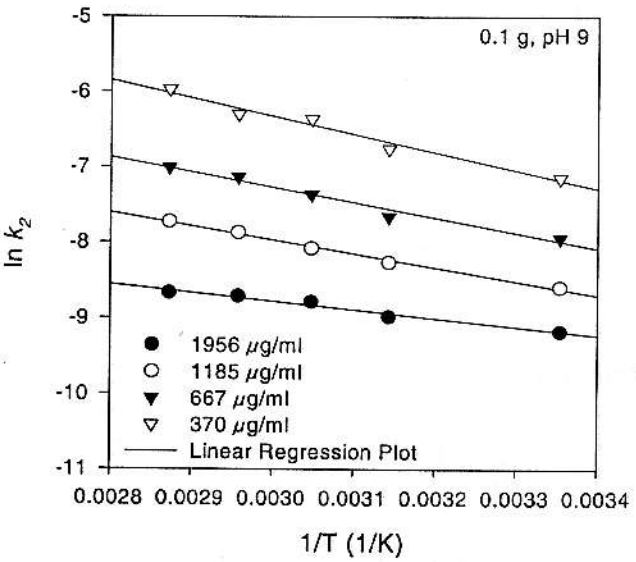

Figure 11 - The Plot of ln k_2 vs. 1/T at Different Initial Concentration

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Table 3 - Activation Energy, E_a for Adsorption of Stevioside on 0.1 g XAD-7 Used at Different Initial Concentration.

Init. Conc. (µg/ml)	Ea (kJ/mol)
1156	9.2597
1185	15.0657
667	16.6866
370	19.9035

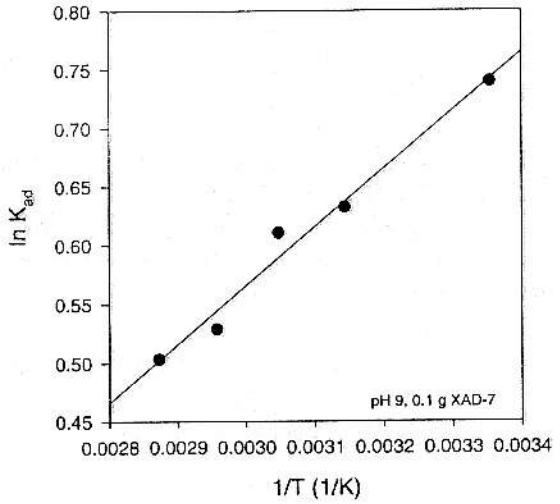

Figure 12 - The Van't Hoff Plot for 0.1 g XAD-7 Used

Table 4 - Gibbs Free Energy for Adsorption of Stevioside on 0.1 g XAD-7 Beads.

Temp. (°C)	Kad	ΔG (kJ/mol)
25	2.0944	-1.83251
45	1.8814	-1.67175
55	1.8414	-1.66566
65	1.6972	-1.48716
75	1.6546	-1.45756

Discussions

In this study, it was found that the equilibrium data was fitted very well to the Langmuir model in the saturation concentration range from 0 to 820 µg/ml with the overall correlation coefficients, R^2 is greater than 0.9. The maximum monolayer adsorption capacities obtained from the Langmuir model were 398, 385 and 270 mg/g for 0.1 g XAD-7 beads used, respectively at temperature 25°C, 55°C, and 75°C and pH 9. The Langmuir constant Q, increase with decreasing temperature and weight of adsorbent used. At the same time, some of the equilibrium data fits quite well to the Freundlich model. However, the low correlation coefficients, R^2 show poor agreement of Freundlich isotherm with the experimental data.

In the study on the kinetics of adsorption, the effect of the solution pH shows a minor influence in this kinetics study. However, from the previous study, it was found that low amounts of stevioside was adsorbed onto XAD-7 beads in acidic condition because of low possibility of formation of the covalent bond between stevioside and XAD-7. This is due to the higher number of H^+ ions compared to OH^- ions in the solution which resulted in an increased in the solubility of the stevioside that has a hydroxyl group. An addition of OH^- from NaOH in the base condition will decrease the polarity of the stevioside and reduce the stevioside solubility in the solution. From Figure 6, it shows that an increase in the pH of the solutions leads to an increase in the adsorption capacity of stevioside on the XAD-7 until the pH 9. However, pH 10 does not lead to a better result because the stevioside molecules become slightly unstable. It has been noticed that stevioside molecules decomposes at alkaline pH levels of greater than 10 [2]. The effect of the temperature also shows a minor influence in the stevioside adsorption. Refer to Figure 7, there is a different trends on the adsorption rate and adsorption capacity at different temperature obtained under and above the equilibrium time. Under the equilibrium time, an increase in the temperature leads to an increase in stevioside adsorption rate and adsorption capacity, which indicates a kinetically controlling process. After the equilibrium time, the decrease of adsorption capacity with increasing the temperature indicates that the adsorption of stevioside onto XAD-7 beads is an exothermic process and the released energy leads to the greater mobility of molecules and desorption of those previously adsorbed [19]. From Figure 8, it was found that an increase in the initial stevia extract solution concentration leads to an increase in the adsorption capacity of the stevioside. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial stevioside concentration. The amount of adsorbent used has given a significant affect on the adsorption capacity. An increase in the amount of adsorbent used has decreases the adsorption capacity and the adsorption rate since the effective surface area is higher for the same volume and concentration of stevioside.

From the computed results for the first-order kinetic model in Table 2, they show a low number of correlation coefficients, R^2. At the same time, unreasonable values of q_1 were obtained, which are too low compared with the experimental q_e values. This suggests that the adsorption of stevioside onto XAD-7 is not a first-order reaction. However, the results for the second-order adsorption rate constant have gave a better correlation coefficient, R^2 and also shows a q_2 that almost equal to the experimental data, q_e. These indicate that the adsorption of stevioside onto XAD-7 belongs to the second-order kinetic model. The

ISBN:983-2643-15-5

activation energy obtained from this study seems to be small with the maximum value of 20 kJ/mol.

Conclusions

This study on the adsorption of stevioside onto a polymeric adsorbent namely Amberlite XAD-7 investigates the effect of solution pH, solution temperature, initial concentration of stevia extract solution, and weight of XAD-7 beads used. An increase in the pH of the solutions also has increased the adsorption capacity of stevioside on XAD-7 with the highest adsorption capacity was obtain at pH 9. Both the initial stevioside concentration and weight of adsorbent used significantly affect the adsorption capacity. However, minor changes were obtained on the adsorption capacity in the study of the effect of the temperature and the solution pH. Adsorption capacity increases with the increase of initial stevioside concentration, and solution pH as well as the decrease of the solution temperature. and resin weight used. The Langmuir equation fits well with the equilibrium isotherm in the saturation concentration range from 0 to 820 μg/ml. However, the fit of the isotherm data to the Freundlich equation gives a low correlation coefficient. The pseudo second-order kinetic model fits well with the dynamic behaviour for the adsorption of stevioside onto XAD-7 beads under several different stevioside concentration, temperatures, and weight of XAD-7 used in whole ranges studied. However, the pseudo first-order fits the experimental data poorly for the entire range under study. This suggests that the rate-limiting step may be the chemisorption but not the mass transport. This study also showed that the adsorption of stevioside onto XAD-7 was an exothermic process.

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ISBN:983-2643-15-5