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Regression Analysis for the Adsorption Isotherms of Betacyanin Extracts from the Dragon Fruit Peel onto the Spun Silk Yarn.

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Abstract- The betacyanin pigment extracted from the dragon fruit peel has a potential to be a natural dye as an alternative to replace the synthetic dyes. To investigate the dyeability of spun silk with betacyanin pigment, the adsorption isotherm models were performed. The equilibrium adsorption data were analyzed using the Langmuir, Freundlich, and Temkin isotherm models. In order to determine the best-fit isotherm for each system, three error analysis methods were used to evaluate the data, namely the sum of the squares of the errors, residual root mean square error and chi-square test. On the basis of low three error analysis and high correlation of determination, it was found that the Langmuir isotherm model fitted well with the experimental data. Therefore, it can be concluded that the adsorption process of betacyanin pigment onto the spun silk followed the Langmuir isotherm model. Moreover, the adsorption features of the experimental system might be caused by the monolayer adsorption.

Index terms ¬adsorption, betacyanin, dragon fruit, error analysis, natural dye

Natural dye has been used in textile industry since the ancient time. It is one of the products that have commercial value as it is safe to nature and biodegradable [1]. One of the newest sources that gets the attention to replace the synthetic dyes is a red-violet color from dragon fruit peel. Dragon Fruit or *Hylocereus polyrhizus*, is one of the tropical fruits that belongs to the Cactaceae, the cactus family. Dragon fruit is also known as pitaya/pitahaya. This fruit gets its name from its skin, which has 'scales' or bracts on the surface, that gives it a 'dragon-like' appearance [2]. In the dragon fruit juice processing industry, the peels are normally discarded and regarded as waste.. The peels contain vibrant red-violet colour, which is promising to be an alternative to the synthetic dyes. Natural colorant from plant sources has received growing interest from both food manufacturers and consumers to replace synthetic colorant, but the usage in the textile industry is still limited. In order to understand the behavior of the dye and the fiber during textile dyeing, it is important to study the mechanism of the dyeing process [3]. The mechanism of the dyeing process can be determined by designing the system using adsorption model [4]. Several isotherm models can describe the solid-liquid adsorption systems such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and others. According to Ho et al (2004), the linearized regression of isotherm model can be worst or the best because it only depends on the correlation coefficient of determination, R^2 [5]. Therefore, several researchers have determined the adsorption isotherm parameters by using non-linear regression and subsequently performed the error analysis between the experimental data and predicted isotherm data. With that purpose, this paper presents the adsorption mechanism of betacyanin extracted dyed on the spun silk using three isotherm models namely Langmuir, Freundlich and Temkin isotherm. In addition, error analysis was carried out to test the adequacy and accuracy of the equilibrium experimental data.

II. MATERIALS AND METHODS

A. *Preparation of sample/materials*

The peels of the dragon fruit were cut into small units at about 1mm in size. The processed dragon peels were blended to get the juice before continuing to the pigment extraction. During the extraction, the temperature was maintained at 45^{o}C and the duration was fixed for 30 minutes. After extraction, the solution was passed through an ordinary screen with 1mm mesh size equipped with a layer of cheesecloth [6]. Then, the residue solution was separated from the plant tissue by using a Buchner funnel with filter paper and connected to the vacuum pump. In the end, the pigment extracted was centrifuged at 15000 rpm for 10 minutes at 10°C [7]. The last solution was kept in the dark brown storage bottle and put in the freezer for further usage.

B. *Adsorption experiment*

For the adsorption studies, the batch equilibrium was performed first. The experiments were carried out by shaking silk yarn (1.0g) with different concentrations of dye solution (100mL) in several conical flasks. The conical flasks were placed in a thermostated shaker bath operated at 125rpm and were shaken at a temperature of 30 °C, 45 °C and 60 °C for about 45minutes. The amount of dye in the solution was monitored by UV-Visible spectroscopy [8]. Then, the dye uptake by silk yarn was determined by subtraction of dye solution before and after dyeing [9]. The initial and equilibrium dye concentration were determined using a calibration curve based on absorbance at λ_{max} 538nm versus dye concentration in standard curve dye solutions. The amount of dye adsorbed at equilibrium q_e (mg/g) was calculated by the following mass balance based on Equation 1:

$$q_e = \frac{V(C_i - C_e)}{M} \tag{1}$$

where V is the volume of solution used in the adsorption experiment, C_i and C_e are the initial and equilibrium dye concentration (g/L), respectively, and M is the mass of yarn (g) [10]

III. RESULTS AND DISCUSSION

IV. Adsorption Isotherm models

Langmuir adsorption isotherm

For describing the adsorption process, Langmuir equation is the most widely used for two parameter equation which has the linear form (Equation 2):

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right) C_e \qquad (2)$$

For lower concentration, the following form of the Langmuir equation (Equation 3) is found to be more satisfactory:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e} \qquad (3)$$

In the above equation, *Q* represents the maximum amount of dye adsorbed per unit weight of the fiber to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e,; q_e is the amount of dye adsorbed per unit weight of fiber at equilibrium and *b* is the Langmuir constant related to the affinity of the binding sites [11]. The value of *Q* represents a practical limiting adsorption capacity when the surface is fully covered with the dye molecules and assists in the comparison of adsorption performance. The values of *Q* and *b* are calculated from the intercepts and slopes of the straight lines of the plot of $1/q_e$ versus $1/C_e$. The calculated *Q* and *b* are listed in Table 1. Figure 1 showed the plot of the Langmuir equation for adsorption process of spun silk and betacyanin pigment. Generally, small values of *b* (Langmuir constant) for Langmuir adsorption parameters means that the absorbent is effective at low solution concentration. As shown in the table 1, the highest correlation coefficient for the adsorption data is 0.93, which fits the experimental data of spun silk at temperature 30^{o}C, followed with 60°C and 45°C with R^2 of 0.88 and 0.84, respectively. The values of Q_o for spun silk was found to be 2.42 g/g, 3.64 g/g and 6.02g/g for dyeing temperature of 30°C, 45°C and 60°C respectively. The value of Q_o signifies the amount of dye required to form a complete monolayer equilibrium [10]. It shows that the amount of betacyanin pigment adsorbed onto the spun silk increased as the temperature increased.

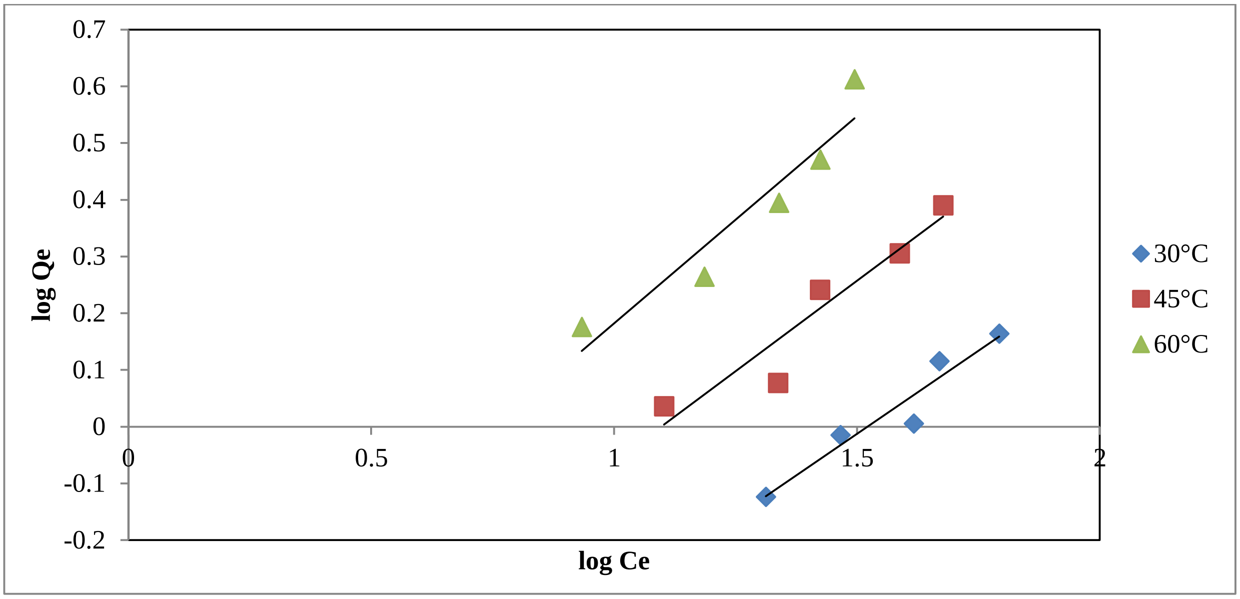

Figure 1 Plot 1/*Qe* against 1/*Ce* for Langmuir isotherm model of betacyanin adsorbed onto the spun silk yarn.

Freundlich adsorption isotherm

To determine the constant K_F and n, the linear form of the equation was used to produce a graph of ln (q_e) against ln (C_e) expressed as Equation 4:

$$ln\, q_e = ln\, K_F + \left(\frac{1}{n}\right) \ln C_e \qquad (4)$$

Values of K_F and n were calculated from the intercept and slope of the plot $ln\, q_e$ versus $ln\, C_e$. The plots of adsorption process for betacyanin adsorbed onto the spun silk were illustrated in Figure 2. Calculated values of K_f and n are presented in Table 1. The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the adsorption strength in the adsorption process [12]. The value of K_f calculated from the intercept of the plot for spun silk were 0.104, 0.1999 and 0.283 for 30°C, 45°C and 60°C respectively. The value increased as temperature increased. Chairat et al (2005) reported that if the value of *Kf* increased as temperature increased, the adsorption process is favorable to be exothermic [8]. The magnitude of the exponent 1/n gives an indication about the favorability of the adsorption process. The value of 1/n should be in the range of 0 to 1 [13]. On the other hand, if n =1 then the partition between the two phases are independent of the concentration. If the value of 1/n < 1, it indicates a normal adsorption [4]. As listed in Table 1, the values of 1/n for betacyanin adsorbed on the spun silk were below 1, which shows that the adsorption is normal and favorable to be done.

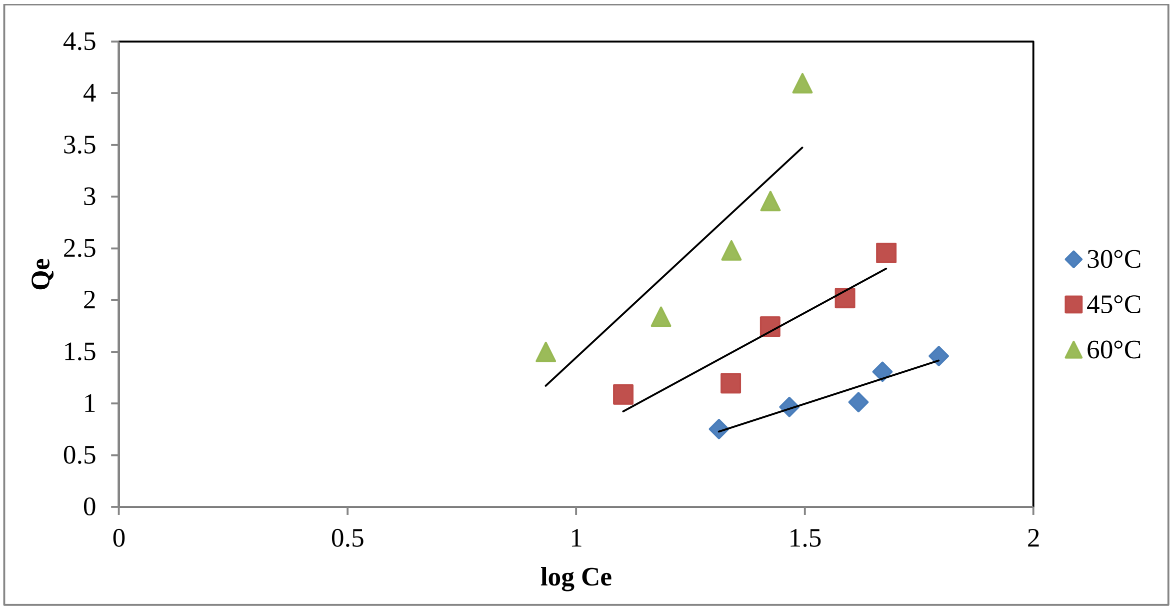

Figure 2 Plot log *Qe* against log *Ce* of Freundlich isotherm model for adsorption of betacyanin extracted onto the spun silk yarn.

Temkin isotherm

The equation for Temkin isotherm model is shown in Equation 5:

$$q_e = \left(\frac{RT}{b}\right)\ln(AC_e) \tag{5}$$

And can be linearized as Equation 6:

$$q_e = B\ln A + B\ln C_e \tag{6}$$

where B = RT/b, b is the Temkin constant related to the heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R is the gas constant (8.314J/ mol.K) and T is the absolute temperature (K). The Temkin plots for spun silk were illustrated in Figure 3, while the constant A and B are listed in Table 1. As shown in Figure 3, the correlation coefficient of determination for adsorption experimental data were 0.91, 0.91 and 0.93 for 30°C, 45°C and 60°C respectively. The constant '*b*' related to the variation of the adsorption energy concluded from the Temkin isotherm is listed in Table 1. The positive value of *b* indicates the adsorption reaction is exothermic [4]

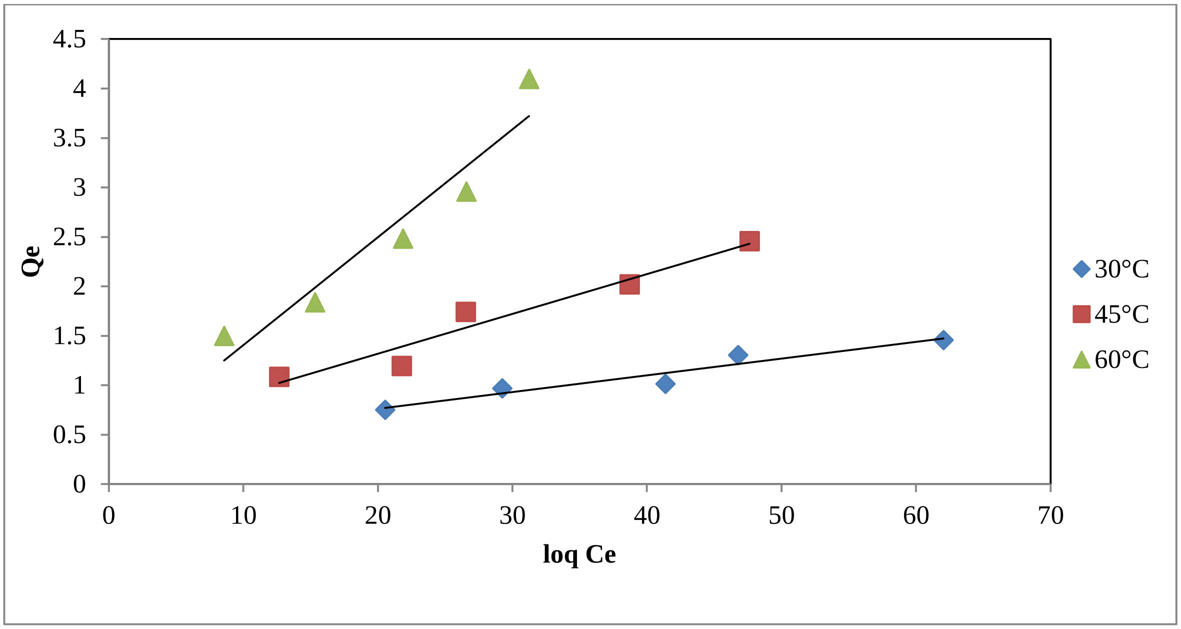

Figure 3 Plot *Qe* against log *Ce* for Temkin isotherm model of adsorption betacyanin extracted onto the spun silk yarn.

Table 1 Comparison of linear regression coefficients of determination, R^2 and isotherm parameters

Temp	**Langmuir**			**Freundlich**				**Temkin**		
(°)	*Q*	*b*	R^2	K_f	*1/n*	*n*	R^2	A_t	*B*	R^2
30°C	2.42	0.02	0.93	0.11	0.58	1.71	0.91	0.45	1.44	0.90
45°C	3.64	0.03	0.85	0.19	0.64	1.57	0.91	0.49	2.41	0.91
60°C	6.02	0.04	0.89	0.28	0.73	1.39	0.93	0.52	4.1	0.93

A. Error Analysis

The best isotherm model can be determined using the analysis of the correlation coefficient (R^2). Ho et al (2005) claimed that the optimization of isotherm studies requires an error analysis in order to be able to evaluate the fit of the isotherm to the equilibrium experimental data [14]. Therefore, three different error functions were employed, namely the sum of the squares of the errors (SSE), Residual root mean square error (RMSE) and Chi-squares (χ^2).

The sum of the squares of the errors (SSE)

The sum of the squares of the error (SSE) values was evaluated using the Equation 7:

$$\sum_{i=1}^{n}\left(q_{e.calc} - q_{e,meas}\right)_i^2 \tag{7}$$

Residual root mean square error

The residual root mean square error (RMSE) values were evaluated using Equation 8:

$$\sqrt{\frac{1}{\mathrm{n-p}}\sum_{\mathrm{i=1}}^{\mathrm{m}}(\mathrm{q_{e,calc}} - \mathrm{q_{e,mean}})_1^2} \tag{8}$$

Chi-square (χ^2) tests

Chi-squares (χ^2) values were evaluated using the Equation 9:

$$\sum_{i=1}^{m}\frac{(\mathrm{q_{e,calc}} - \mathrm{q_{e,meas}})_1^2}{q_{e,meas}} \tag{9}$$

Values of error analysis were listed in Table 2. Analysis of Table 2 shows that the Langmuir and Freundlich models have a smaller error in every temperature conditions and the Temkin model did not show high accuracy even the R^2 is quite high. Ugurlu (2009) claimed that the best fit of the model can be selected based on smaller values of error analysis and higher value of correlation coefficient, R^2 [15]. Based on Table 2, it was found that the Langmuir isotherm at temperature 30°C is possiblythe best fit to the experimental equilibrium data according to that condition. The theory of Langmuir isotherm assumed that the monolayer coverage of adsorbate is identical and equivalent to the homogeneous adsorbent surface. Therefore, no further adsorption occur when the adsorbent reached its saturation point and the dye has occupied the site in the equilibrium[16]. The results revealed that the adsorption of betacyanin onto the spun silk followed the Langmuir theory. Kangkachuichay et al (2010) reported that the Langmuir isotherm model gives a better adjustment for natural indigo adsorption onto silk yarn [9]. On the contrary, the Temkin isotherm denoted very different outcome at every temperature condition. This shows that the Temkin isotherm is not suitable to be fit for the adsorption of spun silk with betacyanin extract.

Table 2 Three different error analysis values of the isotherms selected for spun silk yarn adsorption process

Temperature	Isotherms	Error Analysis			
		R^2	SSE	RMSE	Chi square
30°C	Langmuir	0.93	0.03	0.17	0.03
	Freundlich	0.91	0.39	0.62	0.33
	Temkin	0.91	44.42	6.67	40.81
45°C	Langmuir	0.84	0.17	0.17	0.11
	Freundlich	0.91	0.12	0.35	0.07
	Temkin	0.91	102.19	10.10	61.59
60°C	Langmuir	0.89	16.39	4.04	5.39
	Freundlich	0.93	0.52	0.72	0.16
	Temkin	0.93	31.93	5.65	17.58

V. CONCLUSION

This paper presented the studies of equilibrium adsorption of betacyanin onto the spun silk characterized by using three isotherm models, namely Langmuir, Freundlich and Temkin isotherm. The isotherm models were further analyzed using error analysis. Based on the equilibrium experimental data and by comparing three types of error analysis, it has been found that Langmuir isotherm at 30°C is the best fitting isotherm according to the higher values of coefficient of determination.. It can be concluded that the dyeing mechanism of betacyanin extract was influenced by the temperature in order to build up the monolayer equilibrium on the surface of spun silk yarn. The adsorption was also favorable in lower concentrations. The results have shown that the betacyanin pigment extracted from the dragon fruit peel can be dyed onto spun silk and it has the potential to replace the red color synthetic dye.

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