Langmuir and Freundlich Isotherm Model for Adsorption of Betacyanin Pigment onto Spun Silk and Acrylic Yarns

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ABSTRACT

A study on the equilibrium adsorption of the betacyanin pigment extracted from the dragon fruit peel onto spun silk and acrylic yarn was conducted. The equilibrium adsorption data were tested into Langmuir and Freundlich isotherms at different temperatures. By linearizing the equilibrium isotherm, the best isotherm model equation was determined using coefficient of determination (R^2 value). It was found that the equilibrium data was fitted well by the Freundlich isotherm model for acrylic yarn at temperature of 30°C with R^2 of 0.97.

Keywords: isotherm, betacyanin, spun silk, acrylic, adsorption

1.0 Introduction

The interest in natural dye textile colorants has increased significantly in the last few years due to the worldwide tendency for the substitution of synthetic dye in several areas especially in the textile industry. This is because synthetic dyes have several drawbacks such as being environmentally unfriendly, toxic and causing allergic reactions leading to health problems, including cancer, and damage to the immune system [1]. Natural dyes are one of the products that have commercial value because their non-carcinogenic and biodegradable nature is safe for both the environment and the consumers [2]. On the basis of their origins, natural dyes are broadly classified into three categories, namely, plant, mineral and animal origins [3]. Plants are the major source of natural dyes. They are extracted from henna leaves [4], *hibiscus mutabilis* [5], *curcuma longa* (turmeric)([6], *gardenia jasmoides ellis* (gardenia) [7] and *carthamus tinctorius L* (safflower) [8]. One of the newest sources which have gained attention and replaced the synthetic dyes is the red-violet color from dragon fruit peel. Dragon fruit, also known as pitaya / pitahaya, or in scientific name *Hylocereus polyrhizus*, is one of the tropical fruits belonging to the Cactaceae, the cactus family. Dragon fruit gets its name from its 'scales' or bracts on the surface giving it a 'dragon-like' appearance [9]. Dragon fruit has translucent dark-red flesh considered as a rich source of nutrients and minerals such as vitamin B1, vitamin B2, vitamin B3 and vitamin C, protein, fat, carbohydrate, flavonoid and also highly valued antioxidant properties [2]. Meanwhile, the peels mostly discarded and normally end up as waste. The peels is vibrant red violet in color, which may arguably be suggested as a natural alternative to the synthetic dye. Thus, natural colorant from plant sources are receiving growing interest from both food manufacturers and consumers in order to replace synthetic colorants. Moreover, natural colorant such as the one from the dragon fruit peel can also be potentially used in cosmetics and pharmaceutical products. Nevertheless, such uses in the textile industry is still limited. Hence, this paper presents the study of the adsorption mechanism of betacyanin extracted from the dragon fruit peel onto the spun silk and acrylic yarns.

2.0 Methodology

2.1 Materials

Two yarns were used in this study, namely, spun silk and acrylic yarn which purchased from the Pusat Tenun, Kuantan, Pahang. The dragon fruits were bought from a farm near Universiti Malaysia Pahang where the experiments took place.

2.2 Betacyanin extract

The peels of dragon fruits were cut into small particles of approximately 1mm each. Next, the dragon fruit peel cuts were blended to extract the juice so that betacyanin pigment could be obtained. The 10g of macerated dragon fruit peels were mixed with 50 mL of acidified water which ratio of 99:1(water:HCl) [10]. During the extraction, the temperature was maintained at 45^{o}C in order to prevent heat from damaging the plant material. The duration of extraction was fixed to 30 minutes. Then, the solution was separated from the plant tissue by using a Buchner funnel with filter paper and connected with a vacuum pump. In the end, the pigment extracted was centrifuged at the speed of 9000 rpm for 15 minutes. The final solution was kept in a dark brown bottle and stored in the freezer for further analysis.

2.3 The adsorption experiment

For the adsorption experiment, the first batch equilibrium was performed. The experiments were carried out by shaking the yarns (1.0 g) with different concentrations of dye solution (100 mL) in a conical flask at different temperatures of 30 °C, 45 °C and 60 °C in a thermostated shaker bath operating at 125 rpm. The amount of dye in the solution was monitored by UV-visible spectroscopy [12]. Then, the dye uptake by yarns was determined by subtraction of dye solution before and after dyeing [13]. The initial and equilibrium dye concentrations 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 equation:

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

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) [14].

3.0 Results and Discussion

3.1 Langmuir adsorption isotherm

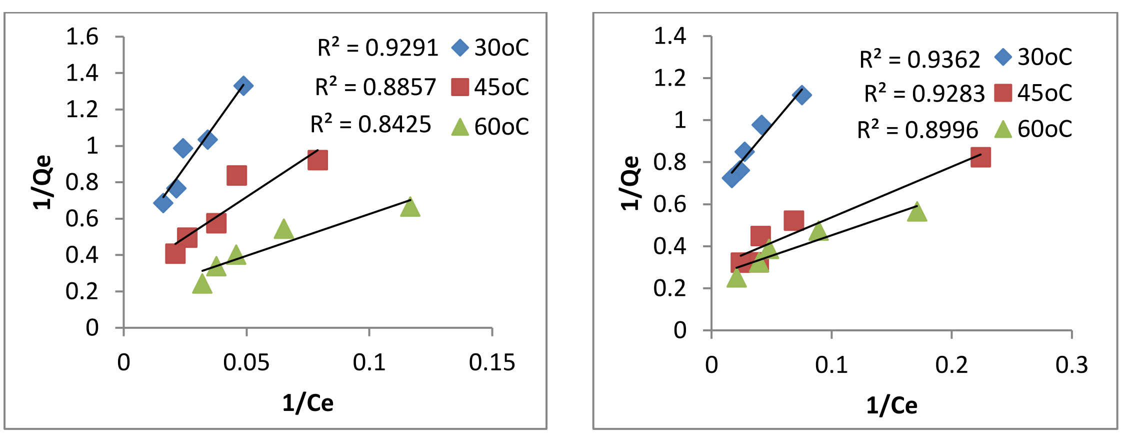
The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes. A basic assumption of the Langmuir theory is that the sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no other adsorption can be taking place at that site. Theoretically, a saturation value is reached when no further sorption can be taking place. In describing the adsorption process, Langmuir equation is the most widely used for two parameter equations which have the linear form of:

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

For lower concentration, the following form of the Langmuir equation has been 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 the 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 while 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 [15]. 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 a plot of 1/*cue* versus $1/C_{e.}$ The calculated Q and b are reported in Table 1. Figure 1 shows the results of the Langmuir isotherms for spun silk and acrylic yarn at different temperatures.



(a) (b)

Figure 1: Plots of $1/Q_e$ against $1/C_e$ of adsorption isotherms of (a) spun silk and (b) acrylic yarn at different temperatures.

Generally, for Langmuir adsorption parameters indicating the small values of *b* (Langmuir constant) means that the absorbent is effective in low solution concentration. As shown in the following Table 1, the highest determination of the coefficient of the adsorption data, R^2 was 0.93, which fitted the experimental data for spun silk at temperatures of 30°C, followed by 45°C and 65°C with R^2 values of 0.88 and 0.84, respectively. The experimental data for acrylic yarn showed that the highest coefficient of determination, R^2 was at 30°C with 0.94, followed by 45°C with R^2 value of 0.93 and 60°C with R^2 value of 0.89. Hence, it can be concluded from the findings in this study that the spun silk yarn had lower coefficient of determination compared to the acrylic yarn.

Meanwhile, the values of *Qo* for spun silk were found to be 2.42 g/g, 3.64 g/g and 6.02g/g for dyeing temperatures of 30°C, 45°C and 60°C, respectively while the values of Q_o for acrylic yarn were 1.574g/g, 3.37g/g and 3.89g/g for dyeing temperatures 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 [14]. In this study, results showed that as the temperature increased, the amount of betacyanin extracted onto the spun silk and acrylic yarn also increased.

Table 1: Langmuir isotherm constant of adsorption of extracted betacyanin onto spun silk and acrylic yarn for different temperatures

Temperature (°C)	Spun silk yarn			Acrylic yarn		
	Q (g/g of silk)	*b* (mL/g)	R^2	*Q* (g/g of silk)	*b* (mL/g)	R^2
30	2.42	0.0218	0.9291	1.574	0.094	0.9362
45	3.64	0.0308	0.8425	3.37	0.123	0.9283
60	6.02	0.0361	0.8857	3.89	0.1314	0.8996

3.2 Freundlich adsorption isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogenous system. The Freundlich equation is expressed as:

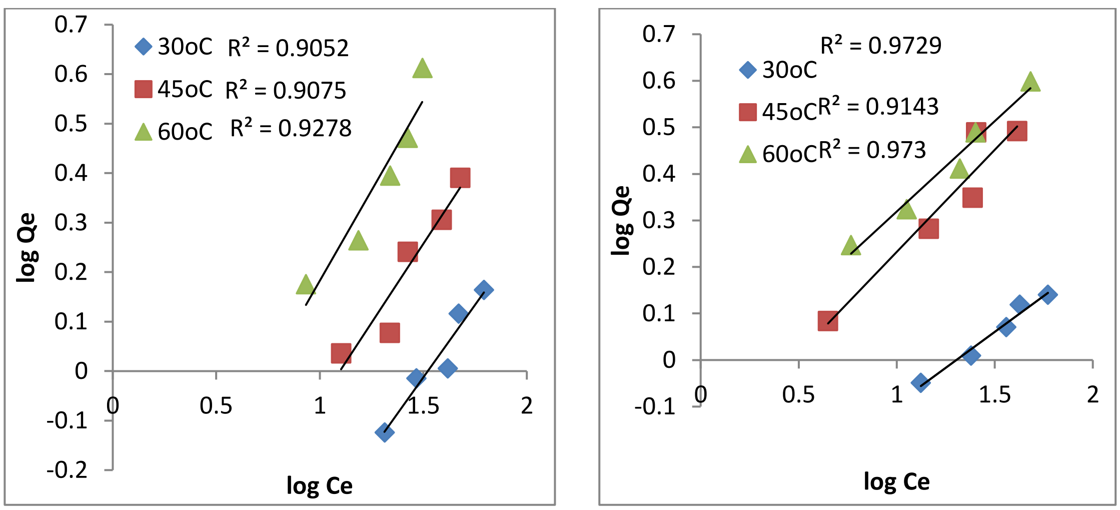
$$q_e = K_F C_e^{1/n} \qquad (5)$$

where K_F and n are Freundlich constant with K_F (mg/g(L/mg)$^{1/n}$) is the adsorption capacity of the sorbent and *n* giving an indication of the adsorption process favorability.

To determine the constant K_F and *n*, the linear form of the equation may be used to produce a graph of *log* (q_e) against *log* (C_e) expressed as:

$$log\, q_e = log\, K_F + \left(\frac{1}{n}\right) log\, C_e \qquad (6)$$

The 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 extracted betacyanin onto the spun silk and acrylic yarn are illustrated in Figure 3. The calculated values of K_f and *n* are presented in Table 2. The constant K_f is an approximate indicator of adsorption capacity, while 1/*n* is a function of the strength of adsorption in the adsorption process [16]. 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. Similar trend was observed for acrylic yarn as the calculated K_f was 0.39, 0.62 and 0.85 at different temperatures of 30°C, 45°C and 60°C, respectively. It was observed in the present study that as the temperature increased, the value of K_f also increased. It had been reported in the literature that if the value of K_f increased as the temperature increased, the adsorption process was favorably exothermic [12].



(a) (b)

Figure 2: Plots of log *Qe* against log *Ce* of Freundlich isotherm model for (a) spun silk and (b) acrylic yarn at different temperatures

The magnitude of the exponent 1/*n*, gives an indication about the favorability of adsorption such that in the favorable adsorption process. The value of 1/*n* should be in the range of 0 to 1 [17]. Meanwhile, if *n* =1, then the partition between two phases would be independent of the concentration. If 1/*n* < 1, this indicates normal adsorption [18]. As presented in Table 4, the values of 1/*n* for betacyanin adsorption onto the spun silk and acrylic yarn were below 1, indicating that the adsorption was normal and favorable. The values of K_f and *n* are parameters characteristic of the sorbent-sorbate system which must be determined by data fitting, whereas the linear regression would generally be used to determine the parameters of kinetic and isotherm models.

Table 2: Freundlich isotherm constant of adsorption of extracted betacyanin onto spun silk and acrylic yarn at different temperatures

Temperature (°C)	Spun silk				Acrylic yarn			
	K_f (mg/g)	$1/n$	n (mL/mg)	R^2	K_f (mg/g)	$1/n$	n (mL/mg)	R^2
30	0.1042	0.58	1.7059	0.91	0.3958	0.31	3.2394	0.9729
45	0.1999	0.64	1.5671	0.91	0.6215	0.44	2.2789	0.8912
60	0.2834	0.73	1.3696	0.93	0.8523	0.39	2.5740	0.9056

4.0 Conclusion

This paper presents the findings of the study on the equilibrium adsorption of extracted betacyanin onto the spun silk and acrylic yarn using equilibrium isotherms based on two models, namely, Langmuir and Freundlich isotherm model. The value of R^2 The adsorption capacity (K_f) from the Freundlich isotherm model of acrylic yarn was found to be higher than that of spun silk. The values of constant K_F and n in the Freundlich isotherm model showed the adsorption process was favorably exothermic and normal.

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