An Adsorption Kinetic and Thermodynamic Study of Dyeing Betacyanin Extract from Dragon Fruit skin onto the Spun Silk and Acrylic Yarn.

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Background: Dragon fruit is one of the plant that can be extracted to be a natural dye. This fruit is contained a betacyanin pigment which can be dyed on to the textile fibers. The natural dye was extracted using water extraction. The betacyanin pigment was applied onto the spun silk and acrylic yarn. Two kinetic models, the pseudo first order model and pseudo-second order model were selected to follow the adsorption process. Kinetic parameters such as rate constant, equilibrium capacities and correlation coefficients for each kinetic equation were calculated and discussed. Objective: The main objective of this study is to evaluate the adsorption and kinetic parameters of dyeing betacyanin pigment extract from dragon fruit skin onto spun silk and acrylic yarn. Result: It was shown that the adsorption betacyanin pigment onto spun silk and acrylic yarn could be described by the pseudo-second order. The rate of constant was increased as temperature increased. The activation energy calculated was 55.7kJ/mol because of their properties of non-toxicity, non-pollution, soft luster and elegant color (Wu et al., 2013). Dragon fruit (Hylocereus spp) is a cactus fruit which has been recently cultivated in tropical climate regions such as Southeast Asia especially Malaysia (Clercq, 2012). The fruit is also a potential source of betalains and it is used largely for food coloring additives (Moshfeghi et al., 2013). For this study, the source of natural dye was focused with the Hylocereus polyrhizus as it is majorly cultivated in Malaysia (Ismail et al., 2012). The red colour of Hylocereus polyrhizus is attributed by betacyanins which is a class of water soluble pigment (Naderi et al., 2012). Kunnika and Prancee (2011) had reported that the peel of dragon fruit content highest amount of betacyanin amount (Kunnika and Prancee, 2011). Usually, the fruit juice

INTRODUCTION

Recently, there has been big interested in dyeing textiles with natural dyes. The demand on the application of natural dye in textile industry get increased because of their properties of non-toxicity, non-pollution, soft luster and elegant color (Wu et al., 2013). Dragon fruit (Hylocereus spp) is a cactus fruit which has been recently cultivated in tropical climate regions such as Southeast Asia especially Malaysia (Clercq, 2012). The fruit is also a potential source of betalains and it is used largely for food coloring additives (Moshfeghi et al., 2013). For this study, the source of natural dye was focused with the Hylocereus polyrhizus as it is majorly cultivated in Malaysia (Ismail et al., 2012). The red colour of Hylocereus polyrhizus is attributed by betacyanins which is a class of water soluble pigment (Naderi et al., 2012). Kunnika and Prancee (2011) had reported that the peel of dragon fruit content highest amount of betacyanin amount (Kunnika and Prancee, 2011). Usually, the fruit juice
processing manufacturer discarded the peel of dragon fruit and end up as waste. Due to that, this study was proposed to utilize the waste of dragon fruit peel into the valuable product by extract the betacyanin pigment to be as natural colorant. Generally, the betacyanin pigment has been used in food colorant and pharmaceutical (Prakash and Manikandan, 2012).

Even though the betacyanin extract has been used in food coloring additives, the potential use of betacyanin as a textile colorant has not been exploited to its full extent. Nevertheless, none study has been done on the dyeing of betacyanin onto the yarn. This study was initially proposed when one of the homemade textile industry in East Coast Malaysia claimed that the color on the fabric is not fasten and removed during the washing. They are using raw material of spun silk and the dyestuff is Remazol (Norsita et al., 2014). In the same time, the waste from the dyeing process was full of color and contained contaminants. Therefore, it is important to find out the alternative to handle this problem. Hence, it is important to study the dyeability of betacyanin pigment onto the yarn. The betacyanin pigment was tested to be dye onto spun silk and acrylic yarn in this study. The spun silk is a waste from the pure silk, low cost material which can be produced to a very exclusive fabric (Camenzind et al., 2013). While, acrylic yarn is one of the synthetic fiber, commonly used in daily application and also low cost material (Wang et al., 2013).

As a main objective in this study is to propose the betacyanin pigment as natural colorant in textile industry, it is important to understand the kinetic and thermodynamic study during the adsorption process. For example, Wu et al studied the adsorption kinetics of natural dye curcumin on PLA fibre (Wu et al., 2013). Also, Koyuncu and Red (2014) reported about the kinetic study and thermodynamic parameters of wool yarn with Rubia tinctorum L (Koyuncu and Red, 2014). So, it is significant to study the parameters of adsorption during dyeing such as rate of dye uptake, the amount of dye adsorbed onto the yarns and the thermodynamic parameters. Therefore, this research work aim is to study the adsorption kinetic and thermodynamic properties of betacyanin extract on spun silk and acrylic yarn.

In the future, the information from this study is very useful in designing the system for dyeing the natural dye with any types of fibers. The information also might helpful to understand the mechanism of adsorption behavior during the dyeing process. From this study, it is confirmed that the betacyanin pigment that had been extracted from dragon fruit peel can be used as natural dye.

**MATERIAL AND METHODS**

**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. UV-Visible spectrophotometer (UV-VIS 8500) was used for testing.

**Preparation of betacyanin dye solution:**

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) (Guesmi et al., 2012). During the extraction, the temperature was maintained at 45°C to prevent heat from damaging the plant material. The duration of extraction was fixed in 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.

**Batch kinetic experiments:**

The effect of temperature on the adsorption of betacyanin extracted onto the spun silk and acrylic yarns is investigated in the temperature range of 30 °C – 60 °C at an initial dye concentration of 1.5 g/L, MLR 1:100 without pH adjustment (Gamal et al., 2010). The weight of 1.0g of spun silk and acrylic yarns was added into each flask covered with rubber stopper and the flasks were then placed in the water bath shaker at a constant temperature with rotation of 125 rpm. After some interval time, the yarns were then rapidly withdrawn. The bath solution after dyeing was measured using UV-Vis spectrophotometry at different times. The absorbance was measured before and after dyeing (Tan et al., 2009). The dye concentration was determined at time zero and at subsequent times using a calibration curve based on absorbance at $\lambda_{max}$ 540 nm versus dye concentration in standard betacyanin solution. The dye amount adsorbed onto the yarn was calculated using the mass balance equation as before (Equation 1)

\[ q_e = \left( C_o - C_e \right) \frac{V}{W} \]

\[(1)\]
Where \( C_0 \) and \( C_t \) are the initial concentration and dye concentration (g/L) after dyeing time \( t \), respectively. \( V \) is the volume of dye solutions (mL) and \( W \) is the weight of yarns (g) used (Chairat et al., 2005).

RESULT AND DISCUSSION

The effect of temperature on the adsorption of the betacyanin extracted onto the yarns was studied to obtain information on the enthalpy change during the adsorption. The dye adsorption process was carried out a series of experiment. The experiment was carried out with different temperature of 30°C, 45°C and 60°C, and under the suitable conditions of pH 3-4, MLR = 1:100 and an SLR of 20:100 (2.42 g/L of betacyanin standard) at each case. The effect of temperature on adsorption of betacyanin extracted onto the spun silk and acrylic yarn is shown in Figure 1. As shown in the figure, the adsorption process for both yarns were increased as temperature increased. The amount of dye adsorbed increase slowly in the initial dyeing process. The adsorption capacity reached the equilibrium after 60 minutes, which the amount of dye adsorbed eventually constant as the time continued. After 120 minutes, the \( q_t \) curve flattened indicating the dyeing process reached equilibrium. The active site in the yarn surface was fully occupied and the adsorption process was less efficient. There is no more adsorption happened even the time is still running. In Figure 1, the amount of dye adsorbed in acrylic yarn at temperature of 30°C is the lowest, but it countered the highest at 60°C. This is because the dye penetrates into the fiber easier at higher temperature as the diffusion coefficient is larger (Ismail et al., 2014). The fiber is difficult to be dyed below its glass transition temperature which is 70°C to 85°C (Gashti et al., 2011). Also, Richard et al (2009) reported that the acrylic have a good fastness and dye uptake at about 80°C to 90°C (Richard et al., 2009).

![Fig. 1: Plot \( q_t \) against time (minute) for equilibrium data of betacyanin extract onto spun silk and acrylic yarn at different temperature](image)

**Kinetics of adsorption:**

It is important to understand the mechanism of adsorption nature during the dyeing process. The controlling mechanism of the adsorption nature can be determined using the pseudo first-order and pseudo second order (Hou et al., 2012). The experimental data were analyzed using the pseudo first order and pseudo second order kinetic models.

**Pseudo First Order Model:**

Pseudo first order model is a simplest kinetic analysis also known as the Lagergen equation (Tayade and Adivarekar, 2013). The Lagergen first-order model is given by the following differential equation (Equation 2):

\[
\frac{d q_t}{d t} = k_1 (q_e - q_t)
\]

(2)

Where \( q_e \) and \( q_t \) are the amounts of dye adsorbed per unit mass of yarn (g/g) at equilibrium time and time \( t \), respectively. \( k_1 \) is the rate constant was determined from plot of \( \ln (q_e - q_t) \) against \( t \). A straight line of \( \ln (q_e - q_t) \) versus \( t \) suggests the applicability of the kinetic model to be fit with the experimental data. The rate constant of pseudo first-order and equilibrium adsorption capacity, \( q_e \) were calculated from the slope.
**Pseudo second order equation:**

The pseudo second order kinetics may be expressed as Equation 3 below:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  

(3)

Where \(k_2\) is the rate constant of adsorption, \(q_e\) and \(q_t\) are the amounts of dye adsorbed per unit mass of yarn (g/g) at equilibrium time and time \(t\), respectively. The equilibrium adsorption capacity \(q_e\) and the second order rate constant \(k_2\) (mg/g.min) can be determined experimentally from the slope and intercept of plot \(t/q_t\) versus \(t\) (Errais et al., 2011). The plots of pseudo first order and pseudo second order equations at different temperature on the adsorption of betacyanin extracted onto the spun silk and acrylic yarns are presented in Figure 2 and 3, respectively. The plot of pseudo first order in figure 2 showed the straight line with the correlation of coefficient range from 0.94 to 0.99. While, the plot of straight line for pseudo second order showed the correlation of coefficient range from 0.96 to 0.99. For all cases, the correlation coefficients were higher than 0.96 indicating that the adsorption of betacyanin pigment onto the spun silk and acrylic yarn is a second order model. It also showed that the experimental data was agreed well the second order kinetic model. At the same time, Hou et al., (2011) also reported that the adsorption of sodium copper chlorophyllin on silk was followed pseudo second order (Hou et al., 2012). This suggests that the adsorption system was controlled by chemisorption which is involved valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent force or ion exchange (Sun and Tang, 2011). The rate of adsorption can be determined from the straight line of the plot. As shown in figure 1 and 2, the rate of adsorption was increased as time increased. It is suggested that the rate of adsorption getting slower as time increased. This is because the active site onto the yarn was dwindle down as the dye molecules are attached to the empty site (Salleh et al., 2011). The values of \(k_1\), \(k_2\) and equilibrium adsorption capacity \(q_e\) at three different temperatures were calculated from the plots and listed in Table 1. The effect of temperature on the adsorption of betacyanin extracted on spun silk and acrylic yarn were determined. From the experimental data, it is seen that the amount of dye adsorbed per gram of yarn for spun silk and acrylic were increased as the temperature increased. This is because of the mobility of the dye ions larger with temperature increased. Therefore, the number of molecules interacted with the active site at the yarn surface was also increased (Tayade and Adivarekar, 2013).

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**Fig. 2:** Plot \(\ln (q_e - q_t)\) against time (min) for pseudo first order spun silk and acrylic yarn at different temperature

**Fig. 3:** Plot \(t/q_t\) against time (min) for pseudo second model for spun silk and acrylic yarn at different temperature
As refer to Table 1, the pseudo first-order equation for spun silk provided the best correlation for each temperature which $R^2 > 0.96$. While, the calculated value of equilibrium adsorption density, $q_{e, \text{calc}}$ agreed very well with the experimental data using pseudo-first order equation for spun silk yarn. Similar kinetics were observed in the dyeing of *Cuminum cyminum* L on silk (Tayade and Adivarekar, 2013). In their report, the stated that the dyeing of *Cuminum cyminum* L on silk was followed the pseudo-second-order. It may contrast with the result as their experimental was conducted in higher temperature. According to Muhammad et al (2015), the rate constant increased with temperature suggested that the adsorption kinetic is temperature-dependent (Muhammad et al., 2015). As shown in Table 1, the rate constants were contrast with the report from Muhammad (2015). The rate constant for spun silk and acrylic yarn showed that the adsorption process between betacyanin extract with spun silk and acrylic yarn were not depending on the temperature. The rate constants are randomly distributed upon the temperature. The rate constant for acrylic is the slowest compared to spun silk yarn at every temperature conditions. These results suggested that the acrylic yarn is less tendency to absorb the betacyanin extract.

### Table 1: Comparison of the pseudo first and second-order adsorption rate constants and calculated and experimental $q_e$ values at different temperatures.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Yarn</th>
<th>$q_{0, \text{exp}}$ (mg/g)</th>
<th>Pseudo first-order model</th>
<th>Pseudo second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_1$ (min$^{-1}$)</td>
<td>$q_{e, \text{cal}}$ (mg/g)</td>
<td>$r^2$</td>
</tr>
<tr>
<td>30°C</td>
<td>SS</td>
<td>0.605</td>
<td>0.0672</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>0.47</td>
<td>0.0638</td>
<td>0.49</td>
</tr>
<tr>
<td>45°C</td>
<td>SS</td>
<td>1.46</td>
<td>0.0284</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>1.98</td>
<td>0.0249</td>
<td>2.04</td>
</tr>
<tr>
<td>60°C</td>
<td>SS</td>
<td>1.93</td>
<td>0.0328</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>2.37</td>
<td>0.0283</td>
<td>2.27</td>
</tr>
</tbody>
</table>

### Activation parameters for the adsorption of betacyanin extracted onto the yarns:

The activation energy of the adsorption can be defined the dependence of the diffusion coefficient on the dyeing temperature and also represents the energy barrier that the dye molecule should overcome to diffuse into the fiber molecules (Ferrero and Periolatto, 2012). The activation energy of the adsorption of betacyanin extracted onto the yarn can be calculated by using the Arrhenius equation stated in Equation 2:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Where $E_a$, $R$ and $A$ refer to the Arrhenius activation energy, gas constant and the Arrhenius factor, respectively. The slope of the plot of $\ln k$ versus $1/T$ was used to evaluate $E_a$.

The enthalpy ($\Delta H^\#$), entropy ($\Delta S^\#$) and free energy ($\Delta G^\#$) of activation were also calculated using Eyring equation as follows:

$$\ln \left( \frac{k_i}{h_i} \right) = \ln \left( \frac{k_i}{h_i} \right) + \frac{\Delta S^\#}{R} - \frac{\Delta H^\#}{RT}$$

Where $k_i$ and $h_i$ refer to Boltzmann’s constant and Plank’s constant, respectively. The enthalpy ($\Delta H^\#$) and entropy ($\Delta S^\#$) of activation were calculated from the slope and intercept of a plot of $\ln (k/T)$ versus $1/T$.

The free Gibbs energy of activation ($\Delta G^\#$) can be written in terms of enthalpy and entropy of activation:

$$\Delta G^\# = \Delta H^\# - T \Delta S^\#$$

The straight line of Arrhenius equation was illustrated in figure 4. From the figure 4, it is shows that the straight line of spun silk is higher that acrylic yarn. It is suggested that the spun silk has a minimum energy barrier or activation energy higher than acrylic yarn. The calculated activation energy ($E_a$) and the enthalpy of activation ($\Delta H^\#$) for dyeing process of betacyanin extracted onto the silk and acrylic yarn is shown in Table 2. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical adsorption. The physical adsorption or physisorption process usually has a low activation energy ranges between 5 kJ/mol and 40 kJ/mol, while chemical adsorption or chemisorption process encounters a high activation energy at ranges of 40 kJ/mol to 800 kJ/mol (Ismail et al., 2014). From the plot of $\ln (k/T)$ against $1/T$ in Figure 5, the values of enthalpy ($\Delta H^\#$) and entropy ($\Delta S^\#$) for the activation were 132.1 kJ/mol and -31.91 J/mol.K for spun silk, meanwhile values for acrylic yarn are 87.82 kJ/mol and 101.34 J/mol.K. The values of entropy is negative indicate that the dyeing process reflects more aggregation and the interaction between plant extracted and the spun silk (Arora et al., 2012). It is because the adsorbed dyes become more restrained within fiber molecules than dyeing solution as the values of entropy represent the entropy difference of the dye molecules within the fiber.
Fig. 4: Arrhenius plot for the adsorption of spun silk and acrylic yarn dyeing with betacyanin extracted.

Table 2: The calculated values of activation energy parameters for the adsorption of betacyanin extracted onto spun silk and acrylic yarn

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (J/mol)</th>
<th>Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS</td>
<td>AC</td>
<td>SS</td>
<td>AC</td>
</tr>
<tr>
<td>30</td>
<td>78.15</td>
<td>101.45</td>
<td>132.1</td>
<td>87.82</td>
</tr>
<tr>
<td>45</td>
<td>77.67</td>
<td>99.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>77.19</td>
<td>98.42</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5: Plot of ln (K/T) against 1/T for the adsorption of dyeing process (SS = spun silk, AC = acrylic yarn)

As it is assumed an isolated system, the energy cannot be gained or lost based on the fundamental thermodynamic concepts. The entropy change is the only driving force that involved in that system. To study the spontaneity of the dyeing process, the thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and the free energy change (ΔG°) were calculated. It also can support the exothermic behavior of the adsorption of betacyanin extracted onto the spun silk and acrylic yarn after it reached equilibrium.

The thermodynamic parameters for the adsorption process can be evaluated using the following equations (Chairat, 2009).

\[ K_c = \frac{C_{ads}}{C_a} \]  

\[ \Delta G^° = -RT\ln K_c \]
In the above equations, $K_c$ is the equilibrium constant and $C_{ad,e}$ and $C_e$ are the dye concentration adsorbed at equilibrium (g/l) and the concentration of the dye left in the dye bath at equilibrium (g/l) respectively. $T$ is the solution temperature (K) and $R$ is the gas constant. Enthalpy ($\Delta H^o$) and the entropy ($\Delta S^o$) of the adsorption are calculated from the slope and intercept of Van’t Hoff plots of $\ln K_c$ versus $1/T$.

![Plot of $\ln K_c$ against $1/T$ for the adsorption of betacyanin extracted onto the spun silk and acrylic yarn](image)

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

(7)

The calculated thermodynamic parameters are listed in Table 3. The negative values of $\Delta G^o$ for adsorption of betacyanin extracted onto the spun silk and acrylic yarn indicate that the adsorption process is spontaneous (Chairat, 2009). The values of enthalpy change ($\Delta H^o$) for adsorption betacyanin extracted onto the spun silk and acrylic yarn is -71.9 kJ/mol and -9.38kJ/mol, respectively. It can conclude that the process of adsorption is exothermic, so raising the temperature leads to lower affinity and less adsorbed amount of dye at equilibrium (Kongkachuichay et al., 2010). In addition, the change of entropy found in negative indicates that the randomness decrease at the solid-solution interface during the adsorption of betacyanin extracted onto the both yarns. The adsorption becomes constrained within the yarns than in dyeing solution.

**Table 3:** Thermodynamic parameters for the adsorption of betacyanin extracted onto the spun silk and acrylic yarn

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta S^o$ (J/mol.K)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SS</td>
<td>AC</td>
<td>SS</td>
<td>AC</td>
</tr>
<tr>
<td>30</td>
<td>-7.84</td>
<td>-9.04</td>
<td>-71.9</td>
<td>-211.9</td>
</tr>
<tr>
<td>45</td>
<td>-4.11</td>
<td>-2.77</td>
<td>-9.38</td>
<td>-281.9</td>
</tr>
<tr>
<td>60</td>
<td>-1.52</td>
<td>-0.72</td>
<td>-0.72</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Conclusion:**

The adsorption kinetics of betacyanin extract on spun silk and acrylic yarn were investigated in this study. From the experiment data, equilibrium of the adsorption process was found to follow the pseudo-second-order kinetic model with the activation for spun silk and acrylic yarn are 55.7 kJ/mol and 44.5kJ/mol, respectively. This indicated that the adsorption of betacyanin pigment onto spun silk and acrylic yarn are likely to be controlled by the chemisorption process. In the last part, the thermodynamic parameters for the adsorption process were determined. The negative values of $\Delta G^o$ indicated the adsorption process for both yarn is spontaneous. The negative values of $\Delta H^o$ indicated the energy was released during the adsorption process. The negative values of $\Delta S^o$ showed that the randomness of dye to be adsorbed onto the yarn is decreased due to the less movement and the possibility to be dyed is minor as the temperature increased.

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REFERENCES


