Regression Analysis for the Adsorption Isotherms of Natural Dyes onto Bamboo Yarn

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Abstract - *The adsorption of three natural dyes which extracted from Turmeric, Red Dragon Fruit Peel (RDFP) and Blue Butterfly Pea Flower (BBPF) onto bamboo yarn was studied. The results revealed that the potential of selected natural dyes on replacing the existing synthetic dyes in industry and the synthetic fibre with the natural fibre (bamboo yarn). Equilibrium isotherms were analyzed using the Langmuir, Freundlich, and Temkin isotherms. In order to determine the best-fit isotherm for each adsorption of natural dye on bamboo yarn, four error analysis methods were used to evaluate the data: the squares of the errors (SSE), residual root mean square error (RMSE), chi- square test, χ^2 and coefficient of determination, R^2 statistic test for determination of a non-linear model. Results indicated that the good fit of Temkin models for Turmeric dye, Freundlich model for RDFP dye and Langmuir model for BBPF dye with the higher value of coefficient of determination, R^2 but lower value of squares of the errors (SSE), residual root mean square error (RMSE) and chi- square test, χ^2.*

Key Words*: *Adsorption, Isotherm model, Error analysis, natural dyes, Bamboo yarn

1.INTRODUCTION

Natural dyes can offer not only rich and varied source of dyestuff, but also the possibility of an income through sustainable harvest and sale of these plants. The natural dyes present in plants and animals are pigmentry molecules, which impart colour to the materials [1]. An international awareness about environment, ecology and pollution control creates an upsurge in the use of natural dyes in the middle of 20th cen- tury. During the last few decades, increasing attention has been paid by the researchers all over the globe towards various aspects of natural dye applications [2]. Natural dyes are obtained mainly from plants, producing different colors like yellow, red, blue, brown, black and a combination of these colors [3]. Bamboo fiber has been historically referred to as an ultimate green material where it is a renewable and sustainable raw material, and used as a natural source of textile materials due to owing excellent performance such as softness, smoothness, luster, comfortableness, breath ability, hygroscopicity and so on. Natural fibers have been broadly used in apparel industry due to their great properties [4] where it has been reported to have many health benefits and functionalities, such as antibacterial activity, anti-oxygenation, anti-carcinogenicity and UV protection performance [5]. There are more researches reported on the characteristics and properties of the bamboo in order to improve the characteristic of the bamboo fibres [6];[7];[8];[9];[10] but little literature on the use of bamboo yarn as a new fiber in textile industry which applied using natural dyes on it. These properties can bring fabric added value when Blue Butterfly Pea Flower, Red Dragon Fruit Peel and Turmeric extract are used as dyes. As a part of the approach to understand the dyeing mechanism and improving the dyeing performance of natural dyes on variety of natural dyes and natural textile materials, fundamental physical studies are important. Recently several investigations on dyeing properties of natural dyed textile materials have been undertaken using the evaluations of thermodynamic and kinetic parameters [2]. Adsorption and kinetic aspects of *Terminalia chebula* extract on woolen yarn [2], Dragon Fruit Peel onto the spun silk yarn [11], *Cuminum cyminum L.* on silk [1] , *Rubia tinctorum L* on wool yarn [12], etc., have been investigated to understand the dyeing mechanism of natural dyes on textile materials. In this study, Chi-square test was used, and isotherm parameters were determined using the method of least squares. Two two-parameter equations, the Freundlich and Langmuir isotherms, and Temkin isotherm, were utilized due to their ability to model equilibrium adsorption data. Results of the linear and non-linear correlation analyses of these three isotherms were compared using the adsorption of three natural dyes extracted from Blue Butterfly Pea Flower, Red Dragon Fruit Peel and Turmeric.

2. MATERIALS AND METHOD

2.1 Blue butterfly pea flower (BBPF)

The BBPF are obtained from the backyard at Taman Mahkota Aman, Kuantan Pahang. The raw material was kept dried in the oven at laboratory and then was grinded.

2.2 Red dragon fruit peel (RDFP)

The RDFP are collected from commercial orchard located at Gambang, Pahang, Malaysia. The raw material was peeled to get its waste, which was then blended and stored at -20^{o}C not more than 2 days (48 hours) so that blend material is kept fresh and to avoid the colour from fading because of oxidation process.

2.3 Turmeric

The turmeric was obtained from a mall in Taman Tas, Kuantan Pahang. The raw material was peeled and then blended into small pieces. The blended turmeric was stored at -20°C not more than 2 days (48 hours) in order to make blend material is kept fresh and to avoid the colour from fading because of oxidation process.

2.4 Bamboo Yarn

Bamboo yarns were obtained by Pusat Tenun Pekan, Pahang which was made by 100% from bamboo fibres.

2.5 Preparation of samples

Natural dye was prepared by using water extraction. The natural dyes were blended or grinded into small pieces, about 1mm, to increase the surface area. Then, the natural dye was extracted by applying ratio 0.12 g/mL corresponding to the ratio of 1.2 g of raw material to 10 mL of water. The mixture was then centrifuged at 4 °C, 10000rpm for 15 minutes [13]. The mixture was filtered to collect the supernatant dye. The mixture was centrifuged for the second time at 4 °C , 12000rpm for 10 minutes to ensure that there is no more sediment or precipitate present in the dye solution. Finally, filtration of the supernatant was done by using filter paper [14] and pH was adjusted by HCl and NaOH if needed. The resulting extract was used for the further experiment.

2.6 Adsorption procedure

For the adsorption studies, the batch equilibrium was performed first. The experiments were carried out by soaking bamboo yarn (0.2 g) with different concentrations of dye solution (20 mL) in several conical flasks for about 90 minutes for BBPF and turmeric dye, 100 minutes for RDFP dye. The amount of dye in the solution was monitored by UV-Visible spectroscopy. Then, the dye uptake by bamboo yarn was determined by subtraction of dye solution before and after dyeing [11]. The solution was analyzed for the remaining dye concentration using a spectrophotometer at λ_{max} of 525nm, 538nm and 419nm for BBPF, RDFP and Turmeric dye respectively. The amount of dye adsorbed at equilibrium q_e (mg/g) was calculated by the following Equation 1:

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

The adsorption capacity q_e (mg of dye per g of adsorbent) was calculated using the following equation. Where C_0 is the initial dye concentration (mg/L) in the solution, C_e is the Unbound dye concentration (mg/L) at equilibrium. V is the initial volume (L) of the dye solution and m is the dry adsorbent dosage (g) and W is the weight of bamboo yarn (g) [15].

2.7 Equilibrium isotherms

Equilibrium isotherm equations are used to describe the experimental adsorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the adsorption mechanisms and the surface properties and affinities of the sorbent. The three most common isotherms for describing solid–liquid adsorption systems are the Langmuir, the Freundlich, and the Temkin isotherms.

The Langmuir isotherm

The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

The constants q_m and K_L are characteristics of the Langmuir equation and can be determined from a linearized form of Equation (3), represented by

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \qquad (3)$$

which will have a straight line with a slope of $1/(K_L q_m)$. and an intercept of $1/q_m$ when $1/q_e$ is plotted against $1/C_e$, where Ce is the equilibrium concentration (mg/ L), qe the amount of dye adsorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), and K_L is the adsorption equilibrium constant (mL/mg) where of slope $1/(K_L q_m)$ and an intercept of $1/q_m$.

The Freundlich isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal adsorption that involves heterogeneous adsorption and is expressed by the following equation:

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

The equation may be linearized by taking the logarithm of both sides

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (5)$$

which will have a straight line with a slope of 1/n and an intercept of $\log(K_F)$ when $\log(q_e)$ is plotted against $\log(C_e)$, where K_F and 1/n are empirical constants dependent on several environmental factors.

The Temkin isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate

Interactions. The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{b_T}\ln K_T C_e \qquad (6)$$

which can be represented in the following linear form

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (7)$$

where K_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is a constant related to heat of adsorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K). As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity adsorbed q_e against ln C_e and the constants were determined from the slope and intercept.

2.8 Error Analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data [16]. In this study, linear coefficients of determination and a non-linear the squares of the errors (SSE), Residual root mean square error (RMSE), Chi- square test, χ2 and coefficient of determination, R^2 were used.

The sum of the squares of the errors (SSE)

The sum of the squares of the error (SSE) values was evaluated using the Equation 8:

$$\sum_{i=1}^{n} \left(q_e - q_{e,m}\right)^2 \qquad (8)$$

Residual root mean square error (RSME)

The residual root mean square error (RMSE) values were evaluated using Equation 9:

$$\sqrt{\sum_{i=1}^{n} \left(q_e - q_{e,m}\right)^2} \qquad (9)$$

Chi-square (χ^2) tests

Chi-squares (χ^2) values were evaluated using the Equation 10:

$$\chi^2 = \sum \frac{\left(q_e - q_{e,m}\right)^2}{q_{e,m}} \qquad (10)$$

Where $q_{e,m}$ is the equilibrium capacity obtained by calculating from the model (mg/g), and q_e is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be a small number; if they are different, χ^2 will be a large number. Therefore, it is necessary to also analyze the data set using the Chi-square test to confirm the best- fit isotherm for the adsorption system.

3. RESULTS AND DISCUSSION

3.1 The Langmuir isotherm

Typically, the adsorption data were analyzed according to the linear form of the Langmuir isotherm (Equation 3). Plots of the specific adsorption, $1/q_e$ against the equilibrium concentration, $1/C_e$ for BBPF, RDFP and Turmeric dye are shown in Figure 1. The linear isotherm constants of q_m, K_L and the coefficient of determination, R^2 are presented in Table 1. These isotherms were found to be linear over the entire natural dyes studied with extremely high R^2 values only for RDFP and BBPF. The R^2 values suggest that the Langmuir isotherm provides a good model of the adsorption system. The adsorption constant, K_L and the saturated monolayer sorption capacity, q_m for RDFP dye were higher than those BBPF and Turmeric. In Table 2, a comparison of values of the Langmuir monolayer saturation capacity, q_m is made for the adsorption of three natural dyes onto bamboo yarn.

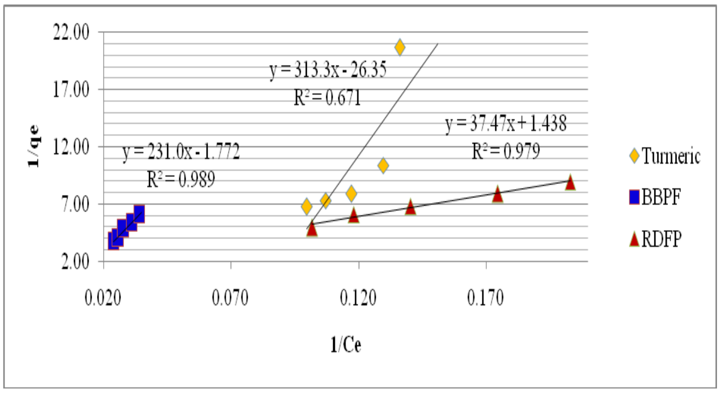

Figure 1: Langmuir isotherms (Equation 3) of natural dyes adsorbed onto bamboo yarn

3.2 The Freundlich isotherm

The linear Freundlich isotherm plots for the adsorption of the three selected natural dyes on bamboo yarn are presented in Figure 2. Examination of the plot suggests that the linear Freundlich isotherm is also a good model for the adsorption of natural dyes. Table 1 shows the linear Freundlich adsorption isotherm constants of K_F, 1/n, and the coefficients of determination, R^2. The magnitude of the exponent 1/n gives an indication about the favorability of the adsorption process . As listed in Table 1, the values of 1/n for Turmeric and RDFP dye adsorbed on bamboo yarn were below 1, which shows that the adsorption is normal and favorable to be done while 1/n>1 for BBPF dye which indicated the adsorption is unfavourable. Based on the R^2 values, the linear form of the Freundlich isotherm appears to produce a reasonable model for adsorption in only two out of three systems, with the BBPF and RDFP isotherms seemingly better fits of the experimental data than Turmeric.

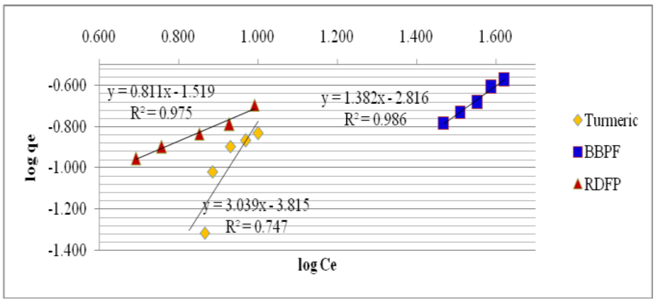

Figure 2: Freundlich isotherms (Equation 5) of natural dyes adsorbed onto bamboo yarn

3.3 The Temkin isotherm

The Temkin plots for bamboo yarn were illustrated in Figure 3, while the isotherm constant of K_T and B are listed in Table 1. As listed in Table 1, the correlation coefficient of determination, R^2 for adsorption of three natural dyes on bamboo yarn produced a reasonable model. The positive value of B for all adsorption of natural dyes on bamboo yarn indicates the adsorption reaction is exothermic.

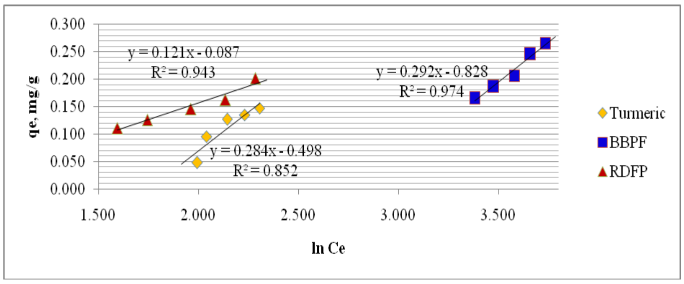

Figure 3 Temkin isotherms (Equation 7) of natural dyes adsorbed onto bamboo yarn

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

Natural Dye	Langmuir Equation (3)			Freundlich Equation (5)			Temkin Equation (7)		
	q_m	K_L	R^2	n	K_F	R^2	K_T	B	R^2
Turmeric	0.0380	0.0841	0.6710	0.3291	0.0002	0.7470	0.1732	0.2840	**0.8520**
BBPF	0.5643	0.0077	**0.9890**	0.7236	0.0015	0.9860	0.0587	0.2920	0.9740
RDFP	0.6954	0.0384	**0.9790**	1.2331	0.0303	0.9750	0.4872	0.1210	0.9430

3.4 Non-linear analysis

The sum of the squares of the errors (SSE), Residual root mean square error (RMSE), Chi- square test, χ2 and coefficient of determination, R^2 were obtained and are shown in Table 2. By comparing the values of the error functions,, the Temkin isotherm was the best-fitting isotherm for adsorption of Turmeric dye on bamboo yarn, followed by the Freundlich model for adsorption of RDFP dye on bamboo yarn and Langmuir isotherm for adsorption of BBPF on bamboo yarn. The models show a high degree of correlation with low squares of the errors (SSE), Residual root mean square error (RMSE) and Chi- square test, χ2 values. This is clearly shown in Table 2, confirming the good fit of Temkin models for Turmeric dye, Freundlich model for RDFP dye and Langmuir model for BBPF dye with the higher value of coefficient of determination, R^2. Thus, the non-linear sum of the squares of the errors (SSE), Residual root mean square error (RMSE), Chi- square test, χ2 analysis proved that this method of could avoid the errors.

Table 2 Comparison of non-linear regression of the Squares of the errors (SSE), Residual root mean square error (RMSE), Chi- square test, χ2 and coefficient of determination, R^2

Natural Dye	Langmuir Equation (2)				Freundlich Equation (4)				Temkin Equation (6)			
	SSE	RMSE	χ^2	R^2	SSE	RMSE	χ^2	R^2	SSE	RMSE	χ^2	R^2
Turmeric	645.11300	25.39900	52.05900	0.50355	0.00170	0.04129	0.01784	0.96139	**0.00093**	**0.03057**	**0.01107**	**0.97932**
BBPF	0.00021	0.01458	0.00118	0.99738	**0.00017**	**0.01287**	**0.00093**	**0.99796**	0.00029	0.01707	0.00174	0.99638
RDFP	**0.00009**	**0.00967**	**0.00042**	**0.99944**	0.00010	0.01005	0.00046	0.99940	0.00018	0.01357	0.00088	0.99890

4. CONCLUSIONS

This paper was presented the studies on equilibrium adsorption of three natural dyes extracted from Turmeric, RDFP and BBPF onto bamboo yarn. The study was carried out by by using three isotherm models, namely Langmuir, Freundlich and Temkin isotherm. The isotherm models were further analyzed using error analysis. Studies of the adsorption isotherms revealed that Turmeric adsorption on bamboo yarn was followed the Temkin models followed by the Freundlich model for adsorption of RDFP dye on bamboo yarn and Langmuir isotherm for adsorption of BBPF on bamboo yarn. To conclude, the selected natural dyes of extracted from Turmeric, RDFP and BBPF proved that this natural dyes could be used as a dye for dyeing on bamboo yarn and it has the potential to replace the existing synthetic dye.

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