Abu Naser Md. Ahsanul Haque[1], Manwar Hussain[2], Shamima Akter Smriti[1], Fahmida Siddiqa[1], Nawshin Farzana[1]
[1]Daffodil International University, Department of Textile Engineering, 102 Shukrabad, Mirpur Road, Dhanmondi, Dhaka-1207, Bangladesh
[2]Hanyang University Erica campus, Department of Chemical Engineering, 55 Hanyangdaehakro, Sangnok-gu Ansan-si, Gyeonggi-do 426-791, South Korea

Kinetic Study of Curcumin on Modal Fabric
Študij kinetike kurkumina na modalni tkanini

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Abstract
A kinetic study of curcumin on modal fabric was carried out using an initial dye concentration of 1 g/L at three different temperatures, 70 °C, 85 °C and 100 °C, at pH 7 and an material to liquor ratio of 1:20. Pseudo first-order and pseudo second-order kinetics were applied, and it was found that the adsorption kinetics of curcumin on modal fabric matched the pseudo second-order kinetic model. The activation energy was found to be equal to 71.14 kJ/mol, while the enthalpy and entropy of activation were 68.16 kJ/mol and –66.02 J/molK respectively.
Keywords: curcumin, kinetics, modal, adsorption

Izvleček
Na tkanini iz modalnih vlaken je bila proučevana kinetika kurkumina z začetno koncentracijo barvila 1 gL^{-1} pri treh različnih temperaturah, 70 °C, 85 °C in 100 °C, pH 7 in kopelnem razmerju 1 : 20. Proučevana sta bila modela kinetike psevdoprvega reda in psevdodrugega reda in ugotovljeno je bilo, da kinetika kurkumina na tkanini iz modalnih vlaken ustreza kinetičnemu modelu psevdodrugega reda. Aktivacijska energija je bila 71,14 kJmol^{-1}, entalpija in aktivacijska entropija pa 68,16 kJ/mol in –66,02 Jmol^{-1}K^{-1}.
Ključne besede: kurkumin, kinetika, modalna vlakna, adsorpcija

1 Introduction

Modal is a bio-based regenerated cellulose fibre that is a type of viscose fibre, although it differs from the latter. It has a smoother cross section and a higher molecular weight than viscose [1]. Although modal has a similar texture to cotton and silk, it is cooler and its absorbency is greater because it has a higher contact angle than viscose [2]. The performance of modal is quite similar to cotton. However, it is softer and smoother than mercerised cotton. In addition, it is resistant to mineral deposits from hard water and can be dyed very easily. It can also made colour fast after dyeing, if it is immersed in warm water [3−4].
Global environmental awareness has resulted in recent renewed interest in natural dyes [5]. This is because natural dyes are more biodegradable, offer good UV-protection and antibacterial activity, and are highly compatible with the environment compared with different synthetic dyes [6−8].
Dyeing on modal fabrics with natural dyes has been reported by very few researchers. For example, the colour strength and fastness properties of modal were investigated after dyeing modal, cotton and modal-cotton blend (50:50) with kumkuma, indigo and barberry, and some synthetic dyes by Radhika and Moses (2014) [9]. In a different study, they assessed the antibacterial, anti-odour and UV protection behaviours of the same fabrics after dyeing with the same dyes [10]. Those fabrics were also tested for absorbency and wicking, and dyeability with natural dyes [11]. Moreover, a study was reported on modal fibre based on absorption

Corresponding author/*Korespondenčni avtor:*
Abu Naser Md. Ahsanul Haque
Telephone: +8801715580985
E-mail: anmahaque@gmail.com

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characteristics performed using a water drop test, the measurement of colour strength and the observation of SEM [12]. However, there is no report available that has studied the kinetics of any natural dye on modal fabric.
Turmeric, the most popular natural dye for textiles [13], comes from the root of *Curcuma longa*. It is rich in curcuminoids and belongs to the diaroylmethane group named diferuloylemethane [14]. It is not only environment friendly, but is also famous for different health benefits [15–17]. Over the years, it has been selected for antibacterial dyeing on different natural and manmade fibres by several researchers [18–20].
Curcumin is the active colouring component in turmeric rhizome, which is also called Natural Yellow 3, with a colour index (CI) number of 75300 [21]. Its molecular formula is $C_{21}H_{20}O_6$ and its molecular weight is 368.38 g/mol [22]. The chemical structure of curcumin is shown in Figure 1.

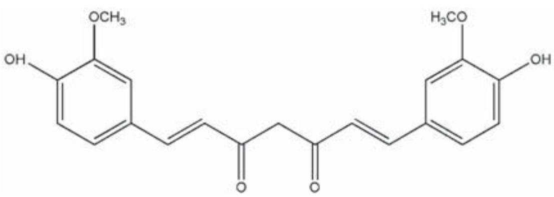

Figure 1: Chemical structure of curcumin (keto form) [14]

2 Experimental

2.1 Material

The single jersey pre-treated modal fabric used for the experiment was collected from Impress-Newtex Composite Textiles Ltd, Gorai, Mirzapur, Tangail, Bangladesh. The specifications of the fabric are listed in Table 1.

Table 1: Specifications of fabric

Parameter	Value
Yarn count [tex]	22.71
Courses [cm^{-1}]	18.90
Wales [cm^{-1}]	13.39
Loop length [mm]	2.50
Mass per unit area [g/m^2]	144

2.2 Extraction of curcumin

Turmeric powder was bought from Square Food and Beverage Ltd, Meril Road, Salgaria, Pabna, 6600, Bangladesh. The dye was obtained by extracting the powder (1 g/L) from deionised water at 95 °C and pH 7 for 90 minutes. The solution had a yellowish colour.

2.3 Dyeing process

The dyeing of modal fabric using curcumin was performed in a Mathis Labomat lab dyeing machine that uses a programmed temperature controlling system by IR heating and a combined air-water cooling unit. The pre-mordanting process was carried out with 0.5 g/L $FeSO_4$ at 70 °C for 10 minutes with a 1:20 material liquid ratio (MLR). For the dyeing of modal, three different temperatures (70 °C, 85 °C and 100 °C) were applied at pH 7 with an MLR of 1:20. The dyeing processes were continued for 100 minutes. A 1.0 mL dye solution was removed at two-minute intervals for the first 20 minutes, at five-minute intervals from 20 to 40 minutes and at 20-minute intervals from 40 to 100 minutes for the spectroscopic measurement of absorbance.

2.4 Kinetic experiments

A UV-visible spectrophotometer (UV 1800) was used for absorbance measurements with quartz cuvette cells of 1 cm path length. Dye concentrations were determined at time zero and at subsequent times from the absorbance values at λ_{max} 419 nm. The concentration of dye in the liquid was calculated using the Beer-Lambert equation:

$$A = \varepsilon \, l \, c \qquad (1),$$

where, A is the absorbance, c is the concentration of the dye solution (mg/L), l is the path length of light (cm) and ε is the dye extinction coefficient (L mg^{-1} cm^{-1}).
The dye extinction coefficient for curcumin (0.01031 L mg^{-1} cm^{-1}) was obtained by calculating the slope of a calibration curve (c versus A) where concentration values were known. The amount of dye (mg/g) absorbed on modal at a given time q_t was calculated using the following mass-balance relationship formula:

$$q_t = \frac{(C_0 - C_t)V}{W} \qquad (2),$$

where, C_0 is the initial dye concentration (mg/L) and C_t is dye concentration (mg/L) after time t. V is the volume of solution (mL) and W represents the weight of modal fabric in grams.

3 Results and discussion

3.1 Effect of temperature on adsorption of curcumin on modal

It was observed that the initial dye adsorption rate (h_i) of curcumin on modal fabric was higher at higher temperatures before reaching the equilibrium point. The time required to reach the equilibrium point was also lesser at higher dyeing temperatures (35 minutes for 70 °C, 25 minutes for 85 °C and 16 minutes for 100 °C), which can be seen in Figure 3. Although the time required to reach equilibrium is greater for lower dyeing temperatures, a greater amount of dye was absorbed on the substrate compared to the higher temperature dyeing. These are all indications of a kinetically controlled exothermic process. The amount of dye absorbed in modal (mg/g modal) in first 25 minutes is shown in Figure 2.

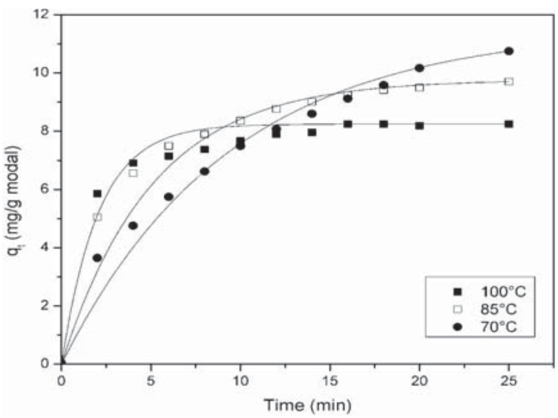

Figure 2: Effect of contact time and temperature of curcumin on modal (0–25 minutes) at an initial dye concentration of 1 g/L, an MLR of 1:20 and pH 7.0

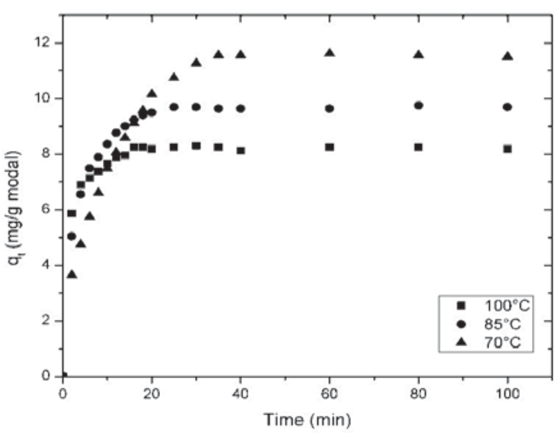

Figure 3: Effect of contact time and temperature of curcumin on modal (0–100 minutes) at an initial dye concentration of 1 g/L, an MLR of 1:20 and pH 7.0

3.2 Kinetics of adsorption

Under certain conditions, reactions can be treated as having a certain pseudo order. For example, in cases when the concentration of one of the reactants is considerably higher than that of the other, it can be regarded as a constant and included in the rate constant. For this reason, the order of the reaction reduces and becomes a so-called pseudo order. Although there are no reports on kinetic studies of curcumin on modal, there are reports for other systems involving natural dye binding, e.g. lac dye on silk and cotton, where in both cases a pseudo second-order kinetic law matched well the experimental data [7, 23]. In our experiments presented here, pseudo first-order and second-order kinetic models were applied to treat the kinetics of adsorption of curcumin on modal. The linear form of the pseudo first-order equation, which is also recognised as the Lagergren equation, is as follows:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (3),$$

where, k_1 is the rate constant of pseudo first-order adsorption (min^{-1}), and q_e and q_t are the amounts of dye adsorbed per gram of modal (mg/g) at equilibrium and at a specific time t.

The first-order equation of Lagergren is likely to be applicable for only the primary stage of adsorption, and generally does not fit well for the entire range of contact times [24]. A linear plot of $ln(q_e–q_t)$ versus t indicates the applicability of the kinetic model to the experimental data. The rate constant k_1 (min^{-1}) and equilibrium adsorption density q_e were calculated from the slope and intercept of the graph.

The pseudo second-order kinetic model, based on adsorption equilibrium, can be expressed in linear form as follows [24–25]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4),$$

$$h_i = k_2 q_e^2 \quad (5),$$

where, k_2 is the rate constant (g/mg min) for pseudo second-order adsorption and where h_i is the initial dye adsorption rate in mg/g min [26]. If the plot of (t/q_t) versus t showed a linear relationship, pseudo second-order kinetics is applicable. The slope and intercept of (t/q_t) versus t were considered to calculate the pseudo second-order rate constant k_2 and q_e.

The overall range of adsorption of curcumin on modal is likely to be in line with a chemisorption mechanism, which involves a chemical reaction between an absorbate and surface, and is usually characterised by higher values of enthalpy than that of a physisorption mechanism (20–40 kJ/mol).

Kinetic data obtained from curcumin adsorption in the current study, was analysed using the pseudo first-order kinetic model (Equation 3), and the pseudo second-order kinetic model (Equation 4) and shown in Figures 4 and 5. The results are represented in Table 2. The data show that, although the kinetics of adsorption is a first-order process in the initial stage (at times $t < 20$ minutes), it follows second-order kinetics at longer times ($t > 25$ minutes). The correlation coefficients obtained from the pseudo second-order kinetic model were very close to 1 (more than 0.999) and also higher than that of the pseudo first-order kinetic model. These facts indicate that the adsorption of curcumin on modal is unlikely to be a first-order reaction. The calculated q_e values were also very close with the experimental q_e. Thus, the experimental data of curcumin dyeing on modal matched well with pseudo second-order kinetics.

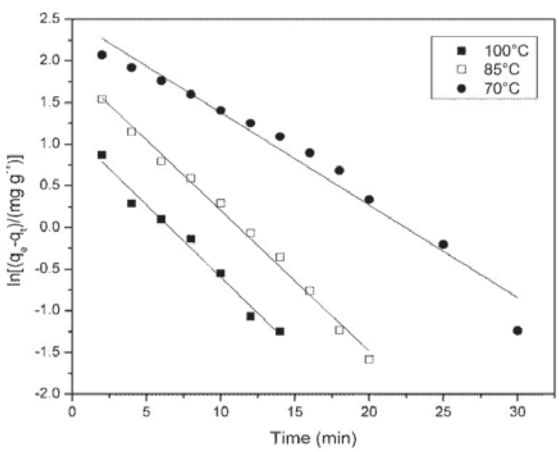

Figure 4: Plot of the pseudo first-order equation at different temperatures for the adsorption of curcumin on modal

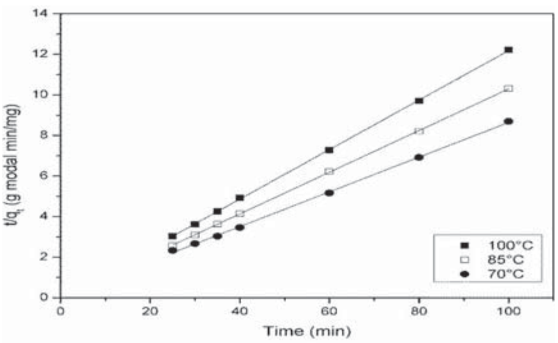

Figure 5: Plot of the pseudo second-order equation at different temperatures for the adsorption of curcumin on modal

3.3 Activation parameters

From the rate constant of pseudo second-order kinetics k_2 (Table 2), the activation energy (E_a) for the adsorption of curcumin on modal was determined using the Arrhenius equation [27]:

$$lnk = lnA - \frac{E_a}{RT} \quad (6),$$

where, A, E_a, T, and R refer to the Arrhenius factor (temperature independent), the Arrhenius activation energy (kJ/mol), absolute temperature (K) and the gas constant (8.314 J/mol K) respectively.

The Arrhenius plot of *lnk* against *1/T* for the adsorption of curcumin on modal is shown in Figure 6, while the value of activation energy which was calculated from the slope of the plot is listed in Table 3. The enthalpy ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) were calculated using the Eyring equation, as follows:

$$ln\left(\frac{k}{T}\right) = ln\left(\frac{K_b}{h}\right) + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \quad (7),$$

where, K_b and h are the Boltzman's constant and Planck's constant respectively. The enthalpy and entropy of activation of dyeing were calculated from the slope and intercept of the plot (Figure 7) $ln(k_2/T)$ versus $1/T$.

Table 2: Comparison of pseudo first- and second-order adsorption rate constant of curcumin dyeing on modal at an initial dye concentration of 1 g/L, an MLR of 1:20 and pH 7.0

Temperature [°C]	$q_{e, exp}$	Pseudo first-order model		Pseudo second-order model			
	[mg/g modal]	k_1 [min^{-1}]	R^2	k_2 [g modal/mg min]	$q_{e, cal}$ [mg/g modal]	h_i [mg/g modal min]	R^2
70	11.56	0.088	0.862	0.0892	11.68	12.18	0.999
85	9.70	0.169	0.993	0.4288	9.74	40.65	0.999
100	8.24	0.173	0.982	0.6539	8.19	43.86	0.999

Table 3: Activation parameters for the adsorption of curcumin on modal at an initial dye concentration of 1 g/L, an MLR of 1:20 and pH 7.0

Temperature [°C]	k_2 [g modal/ mg min]	*Ea* [kJ/mol]	R^2	$\Delta H^{\neq}$ [kJ/mol]	$\Delta S^{\neq}$ [J/mol K]	$\Delta G^{\neq}$ [kJ/mol]	R^2
70	0.0892	71.14	0.914	68.16	–66.02	90.81	0.907
85	0.4288					91.80	
100	0.6539					92.79	

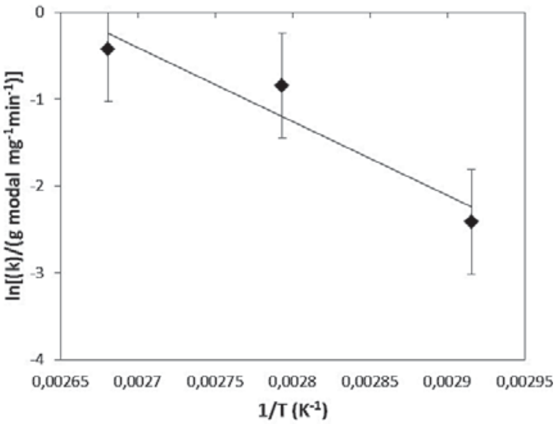

Figure 6: Arrhenius plot for the adsorption of curcumin on modal

Free energy ($\Delta G^{\neq}$) was calculated using the following equation:

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (8).$$

The calculated values are listed in Table 3. The negative value of the activation entropy ($\Delta S^{\neq}$) is evidence of the complexation of curcumin with modal fabric, which decreases the number of particles in the system.

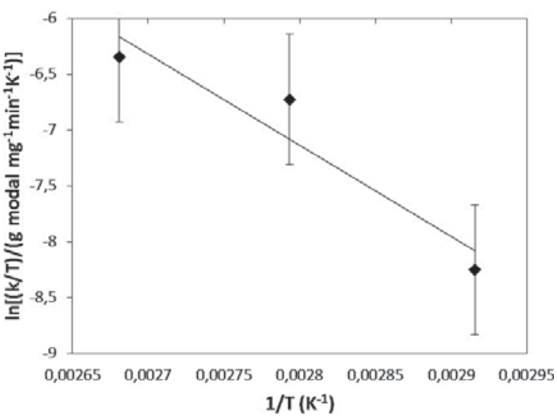

Figure 7: Eyring plot for the adsorption of curcumin on modal

4 Conclusion

The adsorption kinetics of curcumin on modal fabric in this research matched the pseudo second-order kinetic model. It was found to be a kinetically controlled process, as the initial dye adsorption rates (h_i) were higher at higher temperatures before equilibrium was reached. The process was observed to be exothermic, as a greater amount of dye was absorbed on modal at lower temperatures, while the activation energy for the adsorption process was found to be 71.14 kJ/mol.

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