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Adsorption Kinetics of Curcumin on Cotton Fabric
Kinetika adsorpcije kurkumina na bombažnem pletivu

Original Scientific Article/*Izvirni znanstveni članek*
Received/*Prispelo* 01-2018 • Accepted/*Sprejeto* 05-2018

Abstract
The adsorption kinetics study of curcumin on a cotton fabric was investigated at three different temperatures at neutral pH with 1 : 20 material liquid ratio and 1 g/L initial dye concentration. Pseudo first-order and pseudo second-order kinetics were approached to experimental data and the adsorption kinetics of curcumin on cotton fitted well with the pseudo second-order kinetic model. The activation energy was 71.96 kJ/mol, whereas enthalpy and entropy were 68.99 kJ/mol and –59.7 J/mol K, respectively. Dye adsorption declined with increasing temperature, which suggests that the process is exothermic and the negative value of entropy indicates the presence of interaction between the adsorbent and adsorbate.
Keywords: activation parameters, chemisorption, equilibrium, natural dye, turmeric

Izvleček
Na bombažnem pletivu je bila proučevana kinetika adsorpcije kurkumina pri treh različnih temperaturah v nevtralnem pH mediju s kopelnim razmerjem 1 : 20 in začetno koncentracijo barvila 1 g/L. Eksperimentalni podatki so se približali kinetikama psevdoprvega reda in psevdodrugega reda. Adsorpcijska kinetika kurkumina na bombažu ustreza kinetičnemu modelu psevdodrugega reda. Aktivacijska energija je bila 71,96 kJ/mol, entalpija in aktivacijska entropija pa sta znašali 68,99 kJ/mol oziroma –59,7 Jmol^{-1}K^{-1}. Adsorpcija barvila se je z naraščajočo temperaturo zmanjšala, kar kaže, da je proces eksotermen, negativna vrednost entropije pa kaže na prisotnost interakcij med adsorbensom in adsorbendom.
Ključne besede: kinetika, adsorpcija, bombaž, kurkumin, naravno barvilo, kurkuma

1 Introduction

Dyeing textile materials with natural dyes has a long past and had its presence already in the prehistorical ages [1]. However, since the discovery of synthetic dyes in 1856, the use of natural dyes decreased dramatically. Moreover, at the start of the twentieth century when the cost for synthetic dye manufacturing decreased substantially, natural dyes were almost ignored [2]. Nevertheless, due to its environment friendly nature, a keen interest has been gained back among the researchers to utilize natural dyes effectively especially onto natural fibres [3]. It has also been reported that in comparison with synthetic dyes, natural dyes are more biodegradable and highly compatible with environment along with their good UV-protection capability and antibacterial activity [4–6].
Turmeric, the most commonly used source of natural dyes for textiles [7], is obtained from the root of the plant *Curcuma longa*. It is rich in curcuminoids and belongs to the diaroylmethane group called diferuloylemethane [8]. The active colouring component in turmeric rhizome is curcumin, also called Natural Yellow 3 with the colour index number 75300 [9]. This dye is not only environment friendly

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DOI: 10.14502/Tekstilec2018.61.76-81

but also famous for different health benefits [10−12]. Curcumin has the molecular formula $C_{21}H_{20}O_6$ and its molecular weight is 368.38 g/mol [13].
It has been found in different studies that curcumin can be used to dye cotton with or without mordants (commonly metallic salts that possess affinity towards both fibre and dye) but using mordants can help improve the dye exhaustion and colour fastness properties of curcumin [9, 14−15].
The kinetic study of curcumin dye was approached previously by researchers on the PLA fibre. It was reported that the rate of exhaustion was greater by increasing the temperature of dyeing and a similarity was reported in the dyeing mechanism of curcumin with disperse dyeing [16]. The dyeing with curcumin on a cotton fabric was reported by scientists, where different temperatures and time durations were experimented to obtain an optimized dyeing condition. It was revealed that the exhaustion of curcumin on cotton was at its best at 75 °C for 45−60 min. [14]. However, the kinetic modelling of curcumin is also important to describe the adsorption behaviour and understand the optimum dyeing conditions more thoroughly. Though kinetic studies on cotton were conducted with other natural dyes (lac) [17−18], there is no such report available that would study the kinetics of curcumin on cotton.

2 Experimental

2.1 Materials

A single jersey scoured-bleached cotton fabric used for the process was collected from Impress-Newtex Composite Textiles Ltd, Gorai, Mirzapur, Tangail, Bangladesh. The specifications of the fabric are listed in Table 1.

Table 1: Fabric specification

Parameter	Value
Type of yarn	Combed
Yarn count [tex]	21.09
Twists [cm^{-1}]	7.87
Twist direction	Z
Loop length [mm]	2.44
Course [cm^{-1}]	20.47
Wales [cm^{-1}]	15.75
Mass per unit area [g/m^2]	140

2.2 Extraction of curcumin dye

Turmeric powder was directly collected from Square Food and Beverage Limited, Meril road, Salgaria, Pabna, 6600, Bangladesh for this current work. The extraction process was carried out in deionized water at 95 °C and neutral pH for 90 min from 1 g/L powder.

2.3 Dyeing process

The dyeing was done in a Mathis Labomat lab dyeing machine, which has the programmed temperature controlling system by IR heating and a combined air-water cooling unit. The pre-mordanting process was performed with 0.5 g/L $FeSO_4$ at 70 °C for 10 min with 1 : 20 MLR. For the dyeing of cotton, three different temperatures (i.e. 70 °C, 85 °C and 100 °C) were approached at neutral pH in 1 : 20 MLR and continued for 100 min with a 1.0 ml dye solution removed in every 2 min interval for the first 20 min, 5 min interval for 20 to 40 min and 20 min interval for 40 to 100 min for the spectroscopic measurement.

2.4 Kinetic experiments

A UV-Visible spectrophotometer (UV 1800) was used for absorbance measurements with quartz cuvette cells of 1 cm path length. The 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 liquor was calculated with the Beer-Lambert equation:

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

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

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

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

3 Results and discussion

3.1 Effect of temperature on adsorption of curcumin on cotton

The initial dye adsorption rate (h_i) of curcumin on cotton was higher in the case of higher temperature before reaching the equilibrium. Figure 1 represents the results in the first 20 min. However, at the equilibrium time, the amount of dye adsorbed by cotton declined with increasing temperature which represented an exothermic process [17]. The time needed to reach the equilibrium was shorter at higher dyeing temperatures (25 min at 70 °C, 16 min at 85 °C and 12 min at 100 °C), which can be seen in Figure 2. These results are predictably very similar to the results of our previous work of curcumin on modal, which is also a cellulose (regenerated) fibre [19].

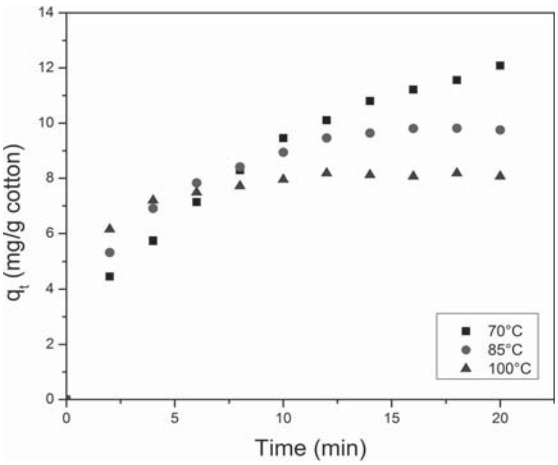

Figure 1: Effect of contact time and temperature of curcumin on cotton (0–20 min)

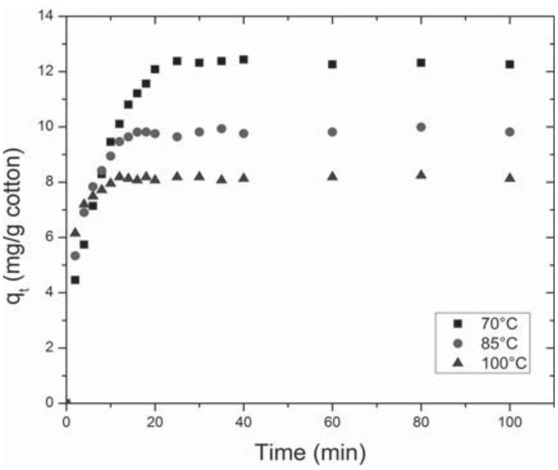

Figure 2: Effect of contact time and temperature of curcumin on cotton (0–100 min)

3.2 Kinetics of adsorption

Reactions can be treated as having a certain pseudo order under certain conditions, i.e. when the amount of one of the reactants is substantially greater than the amount of the other one, and can thus be regarded as a constant value and included in the rate constant. This is how the order of a reaction reduces and becomes a pseudo order. Despite no report on the kinetic study of curcumin on cotton exists, a report of a kinetic study of curcumin is available on a regenerated cellulose fibre, e.g. modal [19]. There are also available reports for other systems involving natural dye binding, e.g. lac dye on cotton and silk. In all cases, it was found out that a pseudo second-order kinetic law matched well with the experimental data [5, 17, 19].

In the current experiment, the pseudo first-order and second-order kinetic models were approached for the investigational data to represent the adsorption kinetics of curcumin dye on cotton. The linear form of the pseudo first-order equation, also known 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 (s^{-1}), and q_e and q_t are the amounts of dye adsorbed per gram of cotton (mg/g) at equilibrium and at a specific time, *t*. The first-order equation of Lagergren is likely to be applicable only over the preliminary stage of the adsorption and does not generally fit well for the whole range of contact times [20]. A linear plot of $ln\ (q_e - q_t)$ versus *t* indicates the applicability of the kinetic model to fit the investigational data. The rate constant, k_1, and equilibrium adsorption density, q_e, were calculated from the slope and intercept of the graph. The pseudo second-order kinetic model [20–21] based on the adsorption equilibrium can be expressed in a linear form as follows:

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

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

where k_2 (g mg^{-1} min^{-1}) is the rate constant for pseudo second-order adsorption and where h_i [22] is the initial dye adsorption rate (mg $g^{-1}min^{-1}$). If the plot of (t/q_t) versus *t* shows 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 cotton is likely to be matched with a chemisorption mechanism, which involves a chemical reaction between an absorbate and surface, and is usually categorized by higher values of enthalpy (80–240 kJ/mol) than the enthalpy of a physisorption mechanism (20–40 kJ/mol) [23].

The kinetic data obtained from curcumin adsorption in the current study was analysed using the pseudo first-order kinetic model (cf. Equation 3) as well as the pseudo second-order kinetic model (cf. Equation 4), and is shown in Figure 3 and Figure 4. The results are depicted 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 min), it follows second-order kinetics at longer times (t > 25 min).

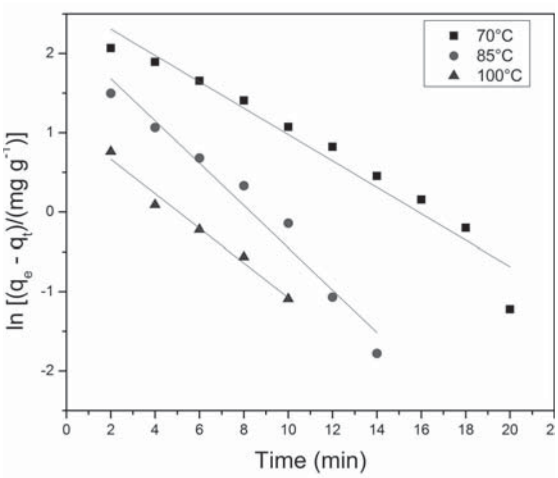

Figure 3: Plot of pseudo first-order equation at different temperatures for adsorption of curcumin on cotton

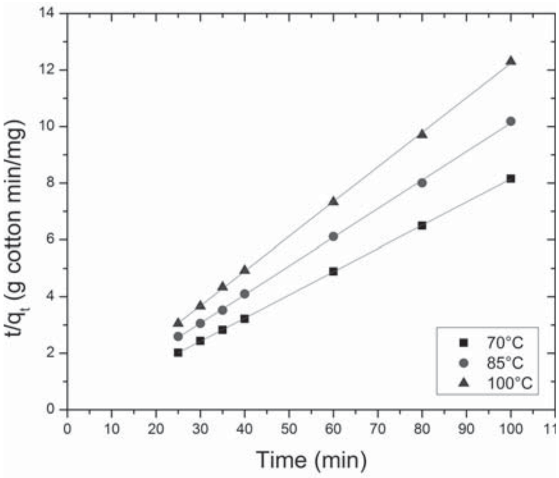

Figure 4: Plot of pseudo second-order equation at different temperatures for adsorption of curcumin on cotton

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. This indicates that the adsorption of curcumin on cotton is unlikely to be a first-order reaction. The calculated q_e values were also relatively close to the experimental q_e. Therefore, the experimental data of curcumin dyeing on cotton fitted well with pseudo second-order kinetics.

3.3 Activation parameters

From the rate constant of pseudo second-order kinetics, k_2, (cf. Table 2), the activation energy, E_a, for the adsorption of curcumin dye on cotton was determined using the Arrhenius equation [24]:

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

where A, E_a, T and R refer to the Arrhenius factor (temperature independent), the Arrhenius activation

Table 2: Comparison of pseudo first- and second-order adsorption rate constant of curcumin dyeing on cotton

Temperature [°C]	$q_{e, exp}$ [mg/g$_{cotton}$]	Pseudo first-order model		Pseudo second-order model			
		k_1 [min^{-1}]	R^2	k_2 [g$_{cotton}$ mg^{-1} min^{-1}]	$q_{e,cal}$ [mg/g$_{cotton}$]	h_i [mg g$_{cotton}$$^{-1}$ min^{-1}]	R^2
70	12.38	0.166	0.950	0.2196	12.22	32.79	1
85	9.81	0.266	0.966	0.2844	9.91	27.93	0.9996
100	8.29	0.217	0.981	1.7094	8.20	114.94	0.9998

energy (kJ/mol), absolute temperature (K) and the gas constant (8.314 J/mol K), respectively.
The Arrhenius plot of *ln k* against *1/T* for the adsorption of curcumin on cotton is shown in Figure 5 and the value of activation energy, which was calculated from the slope of the plot, is listed in Table 3.

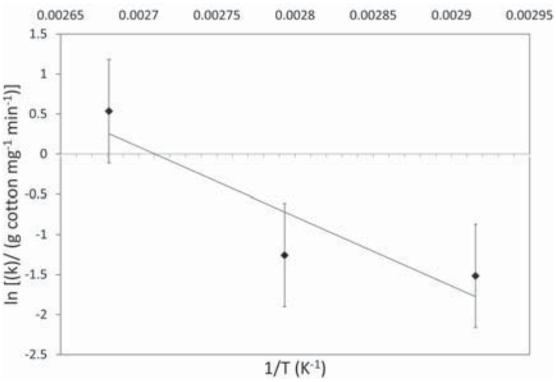

Figure 5: Arrhenius plot for adsorption of curcumin on cotton

The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation were calculated using the Eyring equation as follows:

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

where K_b and h are the Boltzman's and Planck's constant. The standard enthalpy and entropy of dyeing were calculated from the slope and intercept of the plot (cf. Figure 6) *ln* (k_2/T) versus *1/T*.
Gibbs energy of activation ($\Delta G^{\ddagger}$) was calculated with the following equation:

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

The calculated values are listed in Table 3. The negative value of the activation entropy ($\Delta S^{\ddagger}$) supported the interaction between curcumin dye and cotton.

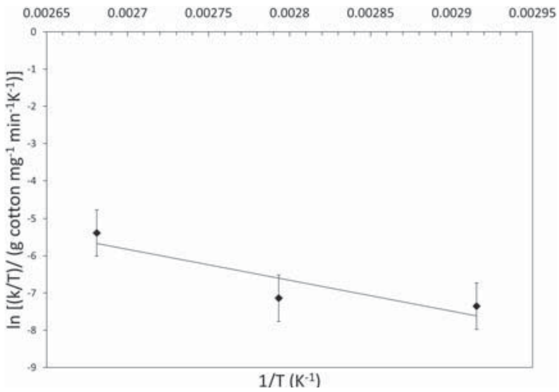

Figure 6: Eyring plot for adsorption of curcumin on cotton

4 Conclusion

The adsorption kinetics of curcumin on cotton suited with the pseudo second-order kinetic model. It was a kinetically controlled process as the initial dye adsorption rates (h_i) were higher at higher temperatures before the equilibrium time. The amount of dye adsorbed by cotton decreased with increasing temperature, which suggests that the process is exothermic. Furthermore, the positive value of free energy represents the strong affinity between the dye and substrate, and the negative value of entropy indicates the colour adsorbed more orderly on cotton with a certain interaction.

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Table 3: Activation parameters for adsorption of curcumin on cotton

Temperature [°C]	k_2 [g_{cotton} mg^{-1} min^{-1}]	*Ea* [kJ/mol]	R^2	$\Delta H^{\ddagger}$ [kJ/mol]	$\Delta S^{\ddagger}$ [J/mol K]	$\Delta G^{\ddagger}$ [kJ/mol]	R^2
70	0.2196	71.96	0.825	68.99	–59.7	89.46	0.813
85	0.2844						
100	1.7094						

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