Indian Journal of Fibre & Textile Research
Vol. 39, September 2014, pp. 310-313

A new kinetic model for cotton reactive dyeing at different temperatures

Mohamed Hamdaoui[1,2,a] & Ahlem Lanouar[2]
[1]L.E.S.T.E Laboratory, [2]Textile Department, National School of Engineers, University of Monastir, Tunisia

Received 15 July 2013; accepted 2 September 2013

Reactive dyeing kinetic on cotton at different temperatures has been studied. The dyeing experiments are carried out using liquor-to-materials ratio of 40:1 in a sealed stainless steel dyebath housed on the Ahiba Nuance Speed. A new kinetic model is proposed that describes the dye exhaustion at different durations. This mathematical equation is used to interpret the experimental data in terms of kinetic parameters of the dye molecules. The results show that the theoretical predictions are in reasonable agreement with experimental data with higher average regression coefficients. It is also observed that the exhaustion process of reactive dye in cotton fabrics could be divided into two steps, viz rapid and slow processes.

Keywords: Adsorption kinetics, Cotton fabric, Parallel exponential kinetics model, Reactive dye

1 Introduction

Cotton fabrics are known since last 7000 years[1]. Today, cotton textiles represent more than half of the global textile market[2], and the demand is expected to continue[3,4]. This dominance is mainly due to its natural comfort and simple process of its dyeing and finishing compared to synthetic fibre. This is because of the excellent ability of cotton to absorbs water (solvent of dye)[5,6].

Today, the available synthetic dye classes for dyeing cellulosic fibres are the direct and reactive dyes (water soluble anionic dyes), and the vat and sulfur dyes categorized as nonionic as they were water-insoluble in their original form. All of these dye classes have some advantages along with some limitations[7]. In industry and especially for the apparel textiles, the predominant dye-fibre combination used is of cotton fibre and reactive dyes[8]. Reactive dyeing of cotton fabrics is fundamentally a process of transferring the dye molecule onto the cellulosic fibre through the aqueous medium (dye exhaustion) followed by dye penetration into the fiber (dye diffusion). When the cotton fibres are immersed in the dye bath, the rearrangement of charge groups at the interface between the fibre and the aqueous environment leads to the appearance of negative charges on the fibres surface[9]. A reactive dye is usually sulphonated to provide aqueous solubility and poses a negative charge in the dye bath. That's why, it is necessary to use a large quantity of inorganic electrolyte in the dye bath to overcome the barrier of electrostatic repellency for the dyes to diffuse through the fibre – water interface. The presence of the electrolyte assists the dye molecules to leave the dyebath and to enter into the fibre polymer system[10].

In the case of the exhaust dyeing, the cotton fabrics start absorbing the reactive dye as soon as it is immersed into the dye liquor. As a result, the concentration of the reactive dye in the dyebath decreases gradually. This shift of dyes towards the fibre is generally referred to as exhaustion. The degree of dyebath exhaustion as a function of time describes the rate and extent of the dyeing process. To realize the exact reproducibility of the required colour and to find an answer to the industrial question, it is quite important to study and analyze the evolution of the dye exhaustion with time and the adsorption kinetic of dye molecules.

The aim of the present work is to propose a simple mathematical model to predict the complete profile of the dyeing exhaustion. The developed model allows us to determine the adsorption kinetic of molecules of dyes and the equilibrium exhaustion rate of the dyebath.

2 Materials and Methods

Experiments were carried out on cotton woven fabrics. The weave structure was plain, the warp count was 30 yarns/cm and the filling count was 35 yarns/cm. The weight ratio of the fabric was 230 g/m². To remove the warp sizes applied to yarns

---

[a] Corresponding author.
E-mail : hamdaouimohamed@yahoo.fr

prior to weaving, a desizing treatment was realized. Also, to remove the waxes and oils attached to greige fabric that interfere with proper dyeing, a scouring treatment was given.

The fabric was bleached at 90°C for 30 min in a solution containing 4 mL/L of hydrogen peroxide (35%), 2 g/L of sodium carbonate and 2 g/L of stabilizer. The dyeing procedures were carried out according to the manufacturer's instructions. It was performed according to the procedure outlined in Fig. 1, with the corresponding amounts of salt and alkali (Table 1). The dyeing processes were carried out in a laboratory apparatus (AHIBA Nuance, DataColor), with a liquor-to-fibre ratio of 40:1.

The commercial dye used in this study was the Levafix Brillant Blue E-FFN gran 150%. The UV-visible absorption spectrum in water of this dye was recorded using Biochrom Spectrophotometry. Its absorption spectrum showed that the maximum absorption wavelength was 594 nm.

2.1 Determination of Dye Concentration

In this study, an UV-visible absorption Biochrom Spectrophotometry was used to determine the concentration of dye through absorbance measurements using quartz cells of path length 1 cm at the characteristic maximum wavelength. The main principle in the quantitative UV-visible technique is the linear relation between absorbance at the maximum wavelength and concentration, as given by the Beer-Lambert law.

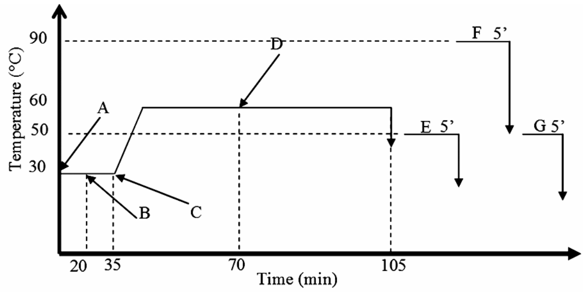

Fig. 1—Dyeing procedure (A-G are process steps as shown in Table 1)

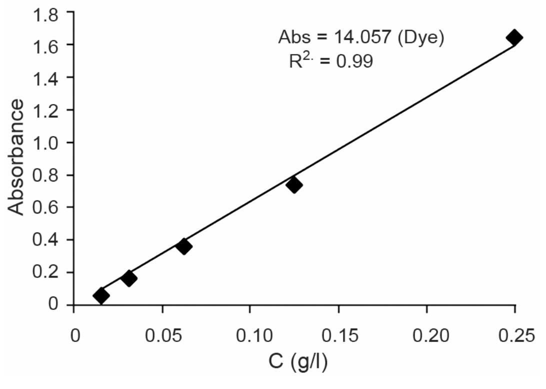

Fig. 2—Calibration curve of blue dye at the wavelength of 594 nm

The wavelength of the maximum absorption ($\lambda_{\max}$) for determination of residual dye concentration of the used dye was 594 nm. Using this wavelength, a calibration curve was drawn, whose equation and correlation coefficient (R^2) are presented in Fig. 2.

2.2 Determination of Dye Exhaustion

After dyeing, the per cent dye exhaustion (E%) values were determined by calculating the dye concentration before adding fabric into the dyebath (C_0) and after dyeing (C_f) according to calibration curve. The percentage of dye exhaustion was calculated using the following equation[11]:

$$E\% = \frac{C_0 - C_f}{C_0} \times 100 \qquad \ldots (1)$$

3 Results and Discussion

3.1 Experimental Data Treatment

In this section, the exhaustion of the blue reactive dye with time (t) has been discussed. The dye bath contains an initial dye concentration of 1% o.w.f and an auxiliary concentration as given in Table 1. The dyeing process was carried out according to the procedure outlined in Fig. 1.

The evolution of the experimental data of the exhaustion as a function of time has been studied. In a first stage, the percentage of the dye molecules adsorbed on the textile fabric increases rapidly during a few minutes. The dyebath exhaustion at the end of this phase is called the primary exhaustion. When alkali is added to the dyebath to raise the pH to the point where the dye begin to react the hydroxyl groups of the cotton fibre, more reactive dye is absorbed from the bath and the exhaustion continues

Table 1—Amount of salt, alkali and auxiliary used for dyeing

Process step	Content	Amount
A	Salt	40 g/L
	Sera Lube	2 mL/L
B	Dye	x%
C	Sodium carbonate	5 g/L
D	Soda	0.5 – 1.2 mL/L
E	Acetic acid	1 mL/L
F	Detergent	2 m/L
G	Softener	mL/L

to increase slowly until the equilibrium state is reached at ~ 80 min. The exhaustion of the dyebath at the end of the second process (when alkali is added) is called the secondary exhaustion. This result indicates that the evolution of the blue reactive dye exhaustion as a function of time can be modeled by two parallel independent processes. The first one is the rapid phase and the second one is the slow phase.

3.2 Kinetic Model

In order to better understand the adsorption kinetics of dye molecules onto the cotton fabric, the experimental data of exhaustion of dyebath at each time were curve fitted using MatLab to the Parallel Exponential Kinetics model. PEK model has a double exponential form as given by the following equation[12]:

$$E_t = E_{1\infty}[1 - \exp(-K_1 t)] + E_{2\infty}[1 - \exp(-K_2 t)] \quad \dots (2)$$

where E_t is the exhaustion of the dyebath at time *t*. As discussed earlier, the adsorption kinetic is composed essentially of two exponential terms which represent both a fast and slow process respectively. So the terms $E_{1\infty}$ and $E_{2\infty}$ are the exhaustion of the dyebath at an infinite time associated respectively with the fast and slow processes (Fig. 3). K_1 and K_2 are the adsorption kinetic of dye molecules respectively at the fast and slow processes.

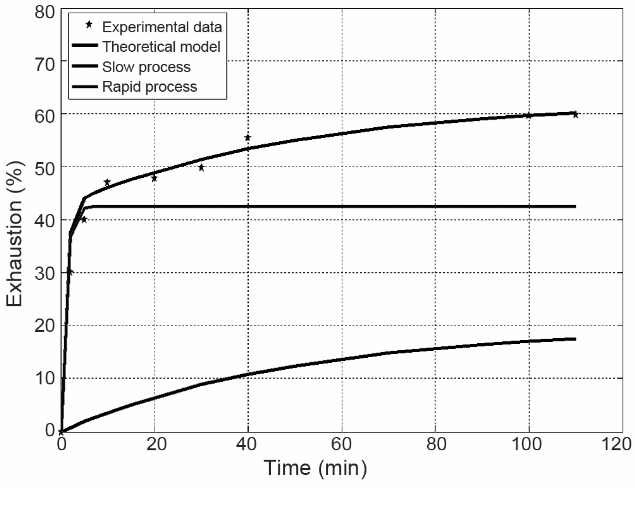

Fig. 3—Fitted curves of exhaustion reactive dye bath at 60°C

The model proposed to describe the dye uptake is tested by comparing the theoretical curves with the experimental one. In Fig. 3, the lines are the best fitted for the PEK model to the experimental data. The validity of the PEK model in describing the kinetic data is checked by the correlation coefficient (R^2) and the Sum of Square due to Error (SSE). In case of blue reactive dye, the high R^2 value (0.9966) and the law SSE value (8.970) indicate that the experimental data are well correlated to the PEK equation.

From the PEK model, it could be found that the equilibrium exhaustion associated with the fast and slow processes are 42.53% and 19.77% respectively. It is observed that at lower time of dyeing (after 8 min), the dye exhaustion was fairly achieved but at higher time of dyeing (after 110 min) the exhaustion is fully achieved. The kinetic parameters K_1 (min^{-1}) and K_2 (min^{-1}) are found to be 0.995 min^{-1} and 0.01993 min^{-1} respectively. It is observed that $K_1 >> K_2$, which means that the rapid process can be assumed to be negligible on the overall adsorption kinetics and very short.

3.3 Influence of Temperature on Adsorption Kinetic

To study the influence of temperature on the exhaustion of dyebath and the adsorption kinetic parameters, the dyeing process of the cotton fabric using Levafix blue reactive dye has been studied at different temperatures (50, 60 and 70°C) and under the same conditions of time, *p*H, liquor ratio and initial dye concentration in each case. Table 2 summarizes the PEK model fitting parameters ($E_{1\infty}, E_{2\infty}$, K_1 and K_2), the R^2 and the SSE coefficients at different temperatures.

Based on the R^2 values (> 0.99 in all cases) (Table 2), it can be said that experimental data are well correlated to the PEK equation for the three tested temperatures. It can be observed that 'K_1' values are greater than 'K_2' for the three tested temperatures. Also, it can be demonstrated that more than 42% of the dye amount initially used in the dye

Table 2—Influence of temperature on exhaustion and kinetic parameters

Temperature °C	$E_{1\infty}$, %	$E_{2\infty}$, %	K_1, min^{-1}	K_2, min^{-1}	SSE	R^2
50	43.52	18.11	0.740	0.02310	1.479	0.9995
60	42.53	19.77	0.995	0.01993	8.970	0.9966
70	42.17	19.37	0.732	0.02799	6.836	0.9977

bath is adsorbed in a short time (almost 8 - 10 min). Then, only 19% of the initial dye amount used in the dyebath needs more than 90 min to be fully exhausted.

As shown in Table 2, it is clear that the temperature affects lightly the dye bath exhaustion and the kinetic parameters of PEK model. But, the more important dye bath exhaustion is attained at 60°C ($E_{1\infty}+E_{2\infty}$=62.3%) against 61.63% and 61.54% at 50°C and 70°C respectively. Also, it is observed that the adsorption kinetic of the dye molecules associated with the rapid process is more important at 60°C.

4 Conclusion

The simulation curves show good fits with experimental data of the exhaustion rates, suggesting that the adsorption of reactive dye molecules onto cotton fabrics could be divided into two steps, namely rapid phase and slow phase. For each temperature, the adsorption kinetic coefficients K_1 for the rapid process (short duration) and K_2 for the slow process (longer duration) have been determined. Using the PEK model, one can also determine the exhaustion of the dye bath at an infinite time associated respectively, with the fast and slow processes. The values obtained for exhaustion of dye bath and adsorption kinetic at different temperatures show that at lower duration of dyeing the exhaustion is fairly achieved but at higher time of dyeing the exhaustion is fully achieved. Also, it is observed that K_1 is higher than K_2, which means that the rapid process can be assumed to be very short and negligible on the overall adsorption kinetics.

References

1 Khatri A, *Pad-steam dyeing of cotton with reactive dyes using biodegradable alkaline organic salts*, thesis, School of Fashion and Textiles, RMIT University, 2010.

2 Gordon S & Hsieh Y L, *Cotton: Science and Technology*, Ist edn (Woodhead Publishing Limited*)*, 2007.

3 Borland V S, *Text World*, 160 (2010).

4 Hembree B, *World Cotton Demand Remains Strong* (Southeast Farm Press), 2010.

5 Fayala F, Hamdaoui M, Perré P & Ben Nasrallah S, *J Porous Media*, 11 (3) (2008) 231.

6 Hamdaoui M, Fayala F, Perré P & Ben Nasrallah S, *AUTEX Res J*, 8 (2) (2008) 44.

7 Shore J, *Cellulosics Dyeing*, Ist edn (Society of Dyers and Colourists), 1995.

8 King D, Dyeing of cotton and cotton products, in *Cotton: Science and Technology*, edited by S Gordon and Y L Hsieh, Ist edn (Woodhead Publishing Limited), 2007, 353.

9 Ribitsh V & Stana-Kleinscheck K, *Text Res J*, 68 (1998) 701.

10 Gohl E P G and Vilensky L D, *Textile Science: An Explanation of Fibre Properties,* 2nd edn (Longman Chashire, Melbourne), 1983.

11 Hamdaoui M, Turki S, Romdhani Z & Halaoua S, *Indian J Fibre Text Res*, 38 (2013) 405.

12 Hamdaoui M, Achour N S & Ben Nasrallah S, *J Eng Fibers Fabrics*, 9 (1) (2014) 101.