Chemical auxiliaries free dyeing of cationized cotton with 1:2 metal complex dye

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Application of 1:2 metal complex dyes on pre-cationized cotton has been studied. This unconventional process avoids the use of electrolyte required as exhausting agent in conventional dyeing of cotton fabric. Indeed, when we use a large amount of salt, the discharged wastewater from dye house creates unavoidable environmental threats. The dyeing has been carried out at the liquor ratio of 1:40 in a sealed stainless steel dyebath housed on the Ahiba Nuance speed varying temperature, contact time and sulphate concentration. Optimal conditions are determined using the experimental designs method. The results show the possibility of chemical auxiliaries free dyeing of cotton fabrics with 1:2 metal complex dye at 75°C for 15 min by treating them with cationizer prior to dyeing. Adsorption kinetic and isotherm are also studied and the parallel exponential model is shown to fit experimental data with higher average regression coefficients.

Keywords: Cationized cotton, Dyeing, Experimental designs method, Metal complex dye, PEK model

1 Introduction

The popularity of pure cotton and cotton blend fabrics have been increasing in recent years[1,2]. Firstly, the natural fibres have become more prevalent in fashion over the last 10 years. Secondly, the blending natural and man-made fibres have the particular advantage of successfully combining the good properties of both fibre components[3], such as comfort, resistance, and the easiness of dyeing & finishing.

In industry, the selection of dyestuff to be used is determined by the specific fibre being dyed and by the fastness properties desired. In every case, there must exist some types of affinity between the fibre and the dyestuff. This affinity depends on the chemical and physical nature of the fibre and the dye. For example, 1:2 metal complex dye shows an affinity for wool, silk and nylon, but no affinity for cotton. However, the available synthetic dye classes for dyeing of cellulosic fibres are the direct and the reactive dyes which are water soluble anionic dyes, the vat and sulphur dyes categorized as nonionic as they are water insoluble in their original form. All of these dye classes have some advantages but also some limitations[4,5].

The polymer chain of the cotton which is a natural cellulosic fibre consists of several number of β-D-glucose units linked to each other. The cotton fibres gain anionic surface charge when immersed in water, and the direct and the reactive dyes are anionic as cited above; hence the charge repulsion adversely affects the dye bath exhaustion. To overcome this problem, large quantities of electrolyte must be added to the dye bath[6]. These electrolytes lead to enormous environmental problems[7]. That's why many researchers study the possibility to minimize or to eliminate the use of electrolyte in cotton reactive dyeing[8-10]. They were looking into the modification of cotton by anchoring with positive charges to increase reactivity with anionic dyes, direct and reactive. Because of [...] dyes have low wet fastness. However, the reactive dye, which is sensitive to sodium hypochlorite and characterized by a low exhaustion, forms a chemical bond to the cotton fibre which determines both the fixing properties and the wet fastness of the dyed material.

From the above discussion, it can be concluded that the cationization of the cotton fibre contributes to the possibility to make a dye which is not substantive to the material to become substantive without electrolyte with desired level exhaustion. This chemical modification allows superficial dyeing using anionic dyes as 1:2 metal complex dyes, direct and reactive. The present

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study includes investigation on the dyeability of pre-cationized cotton fabric using cationic resin without any chemical auxiliaries. Also, the optimization of the dyeing process using experimental design method, adsorption kinetic of molecules dyes and adsorption isotherm is studied.

2 Materials and Methods

2.1 Preparation and Dyeing of Cotton Fabric

Experiments were carried out on cotton woven fabrics (twill 3-1, warp count 44 yarns /cm, weft count 32 yarns/cm and fabric weight ratio 283 g/m²). Prior to dyeing, desizing and scouring treatments were applied to remove glue added to warp before weaving, and waxes and oils attached to greige fabric. The fabric was then bleached at 90°C for 30 min with 4mL/L of hydrogen peroxide (35%), 2g/L of sodium carbonate and 2g/L of sodium silicate[5,11]. After that the prepared fabric was cationized using 7% Resicrom SG resin at 60°C for 30 min using pH 11 by adding caustic soda. The Resicrom resin is a commercial epoxy compound derivatives containing reactive group with cationic character. The epoxy group reacts with the hydroxyl group of the cellulose in an alkaline medium with the formation of a covalent bond. The cationic groups can decrease the negatively charged barrier between cotton fibre and anionic dyes. As shown in Fig. 1, cationization using Resicrom resin imparts a surface positive charge to the cotton cellulose which makes the modified fabric susceptible to the anionic dyes.

The dyeing was carried out in laboratory apparatus (Ahiba Nuance, DataColor), with liquor-to-fibre ratio of 40:1. The commercial 1:2 metal complex dye used in this study was the Rosso Infalan SDRL. The UV-visible absorption spectrum in water of this dye was recorded using Biochrom spectrophotometry. Its absorption spectrum shows that the maximum adsorption wavelength of this dye is 500 nm.
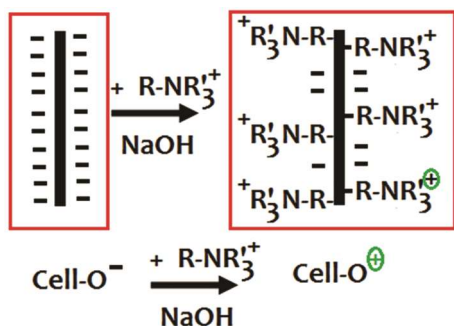

Fig. 1 — Resicrom reacts with cotton fibre

2.2 Determination of Dye Concentration

At each time, the dye concentration was determined using UV-visible absorption Biochrom Spectrophotometry. Quartz cells of path length of 1cm were used to do absorbance measurements at the characteristic maximum wavelength. The main principle in the quantitative UV-visible technique is the linear relation between absorbance at the wavelength of 500 nm and concentration, as given by the Beer Lambert law. The calibration curve of the used dye at the wavelength of the maximum absorption was drawn, whose equation and correlation coefficient (R^2) are determined. The equation was Abs=0.0454 [Dye] with regression coefficient (R^2) of 0.9936. After any dyeing, the dye concentration was calculated according this equation[11].

2.3 Color Strength Measurements of Dyed Fabrics

Reflectance values and curves of the dyed fabrics were measured in the visible portion of the spectrum (380-780 nm) using a reflectance spectrophotometer (Datacolor 660 Plus) and the standard illuminant was D65 with 10° standard observer. The measurements were taken in four different places making four folds of each samples and their average was taken for the analysis of each result. Color strengths (K/S) values of dyed fabrics were calculated using Kubelka-Munk equation[12,13].

2.4 Equilibrium Experiments

The cotton fabric (1g) was immersed in the dyebath which contains only the water (35 mL) for 10 min. Then, the 1:2 metal complex dye, which has been dissolved in water to the required concentrations, was added to the dye bath (5 mL). The cotton samples were then rapidly withdrawn after different immersion times. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at λ_{max} 500nm versus dye concentration in standard 1:2 metal complex dye solutions. The amount of dye adsorbed per gram of cotton (mg/g cotton) at any time (Q_t) was calculated using the following masse balance relationship:

$$Q_t = (C_0 - C_t)\frac{V}{W}$$

where C_t is the liquid phase concentration of dye at any time; C_0, is the initial concentration of the dye in solution; V, the volume of the solution; and W, the mass of the dry adsorbent (g).

To study the isotherm, the amount of equilibrium [Q_e (mg/g)] was calculated using the following formula:

$$Q_e = (C_0 - C_e)\frac{V}{W}$$

where C_0 and C_e are the liquid phase concentrations of dye initially and at equilibrium.

2.5 Experimental Design

The factorial experimental design was used in this study. This method can reduce the number of experiments and minimizes the number of parameter combinations required to investigate the effects of chosen factors on the response. In this work, temperature, dyeing duration and sodium sulphate concentration were adopted as three controllable variables. Table 1 gives the factors and their different levels for experimentation. The experimental analysis of variance (ANOVA) and the response surface were carried out using the statistical software package Minitab 14. This software was used for the regression analysis of the experimental data and to plot the contour graph. The quality of fit of the mathematical model was expressed via coefficient of determination (R²), the adjusted R² adj and the p-values.

3 Results and Discussion

3.1 Optimization of Dyeing Conditions

The initial main purpose of this study is to determine optimum and robust cationized cotton dyeing process conditions by using the response surface methodology. The RSM output data are obtained by conducting tests of dyed fibre for the indication of color value at spectrophotometer machine. It includes measuring the color strength value, as defined above, at the wavelength of 500 nm. Factors that influence the color strength of dyed

Table 1 — Control factors and their level

Factor	Level 1	Level 2	Level 3
Temperature, °C	75	82.5	90
Duration, min	15	30	-
[Sodium sulphate], g/L	0	5	-

fabrics are evaluated by using factorial plots: main effects and interactions. Main effects of each parameter (temperature, duration and concentration of the sodium sulphate) on color strength of dyed fabrics are displayed in Fig. 2.

The main effect plots are generated to represent the results of the regression analysis. The main effects represent deviations of the average between the high and the low levels for each factor. As shown in Fig.2, the effect of duration factor is positive; *K/S* increases as this factor changes from 15 to 30 min. In contrast, the effects of temperature and sodium sulphate concentration factors are negative; a decrease of *K/S* is observed when factors change from low to high. Both, temperature and sodium sulphate concentration factors result in a higher mean *K/S* at their low level, compared to that at the high level. For the duration factor, the opposite is true.

In addition, sodium sulphate concentration has a greater effect on *K/S*, as is evident by the longer vertical line. It is observed that the colour strength decreases when we use sodium sulphate in dyebath because of the electrostatic attraction between the (SO_4^{2-}) of sodium sulphate and the positive charge on surface due the catonic group of the Resicrom SG Resin. Then, the negative charges of (SO_4^{2-}) fixed on the surface of cotton cellulose repel anionic dyes, and thus, the affinity between dye and cationized cellulose decreases. The higher colour strength of the dyed fabric is observed when the sodium sulphate is not used. In the absence of sodium sulphate, the surface of the cotton may become more positively charged and the affinity increases.

The interaction between each factors and its effects on color strength of dyed fabrics are displayed in Fig. 3. Indeed, an interaction between two factors is considered as effective when the change in the response from low to high levels of the first factor is dependent on the level of the second factor, i.e. when the lines do not run parallel.
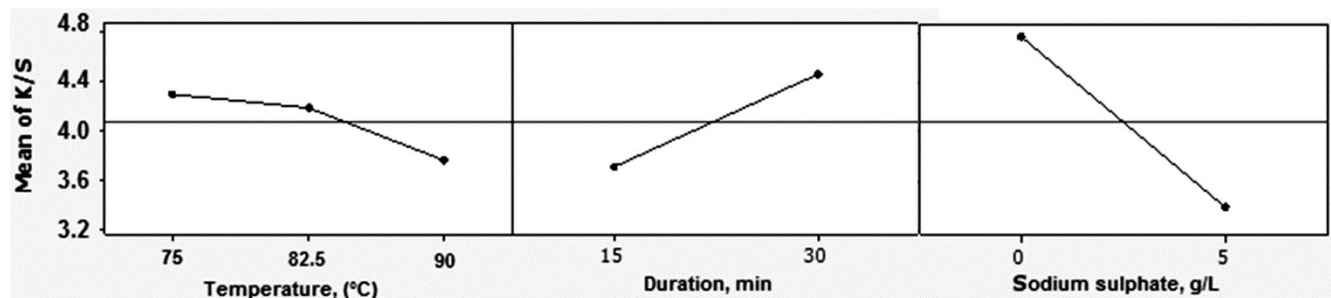

Fig. 2 — Main effects diagram for colour strength *(K/S)*

These plots (Fig. 3) clearly indicate that interaction between temperature and duration is stronger than that between duration and sodium sulphate concentration which is much small. The interaction between temperature and sodium sulphate is statistically not significant, expressed by parallel lines.

Main interaction effect coefficients of the model, standard deviation of each coefficient, and probability for the full factorial designs are studied using Minitab 17. The significance of the regression coefficients is determined by applying a "Student's t-test". It is found that with the exception of interactions (P-values > 0.05), all other effects are found significant with 95% confidence level. For these reason, we have not considered the interactions in the fitted model (Fig. 4). In addition, the linear regression model shows a square correlation coefficient (R^2) of 92.2%, fitting the statistical model quite well. In this way, the colour strength could be expressed using the following equation (Fig. 4):

$$K / S = 6.63 - 0.362 \text{ Temperature} + 0.0506 \text{ Duration} - 0.279 \text{ [Sulphate]}$$

…(3)

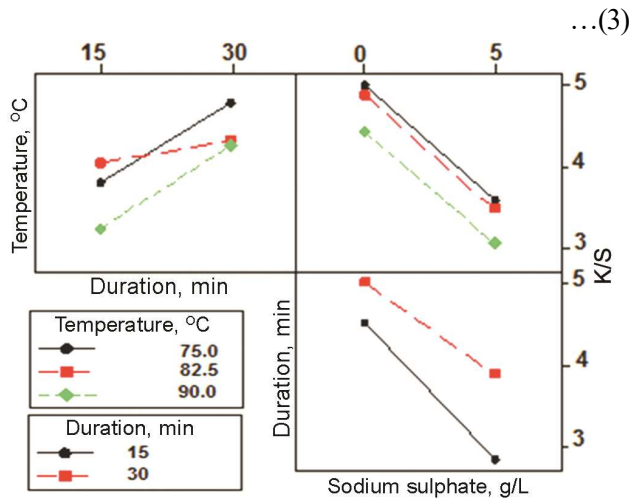This mathematical function describes how the experimental variables influence the colour strength and confirm the results found by the main effects diagram. The sodium sulphate concentration has the greatest effect on K/S, followed by the duration and the temperature.

The response surface plots are reported in Fig. 5 for the average K/S. Figure 5 illustrates the response surface contour plots when sodium sulphate concentration is kept constant (0 g/L). From three surface plots, maximum values of K/S require lower temperature and higher duration, in agreement with the main effects diagram.

One of the main objectives of RSM is the determination of optimum settings of the control variables (temperature, duration and sulphate concentration). Using Minitab, the optimal value of every variable is determined to have the maximum response. As shown in Fig. 6, when the cationized cotton is dyed at 75°C for 15 min without sulphate, the K/S attains its maximal value, which is equal to 5.4304.
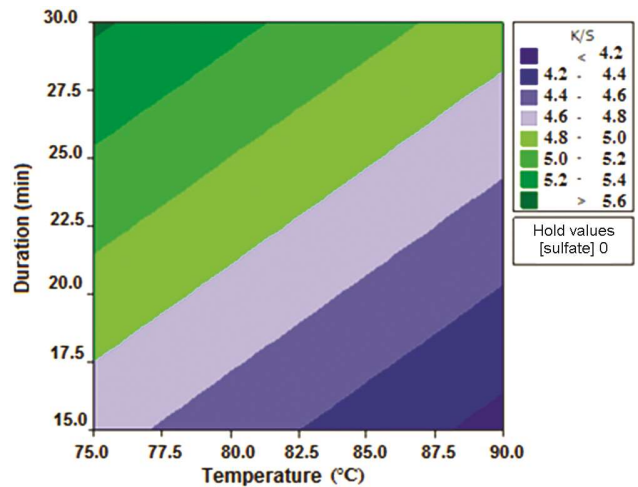

Fig. 3 — Interaction diagram

Fig. 5 — Contour plot of K/S response function

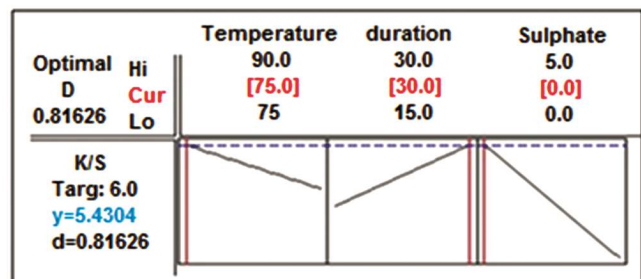Fig. 4 — ANOVA results for fitted linear regression model

Fig. 6 — Optimal conditions to have the maximum value of K/S

3.2 Adsorption of Dyes

To study the adsorption processes of the cationized cotton dyeing with 1:2 metal complex dye at optimal conditions (75°C temperature, 30 min duration and without chemical auxiliaries), it is important to establish the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium and at constant temperature.

To establish a mathematical model following the adsorption capacity of 1:2 metal complex dye by the cationized cotton fibre, the experimental data are curve fitted using MatLab to the parallel exponential kinetic model[14], as shown below:

$$Q_e = Q_{1\infty}[1 - \exp(-A_1 C_b)] + Q_{2\infty}[1 - \exp(-A_2 C_b)]$$
$$\ldots (4)$$

where Q_e is the adsorbed dye amount of equilibrium; $Q_{1\infty}$ and $Q_{2\infty}$, the adsorbed dye amount of equilibrium associated respectively with the low residual concentration of the dye in solution and high residual concentration of the dye in solution; A_1 and A_2, the adsorption coefficient of dye molecules respectively at the first concentration interval (low residual concentration) and the second one (high residual concentration); and C_b, the liquid phase concentration of dye at equilibrium.

In Fig. 7, the line is the best fitted for the PEK model to the experimental data. The validity of the
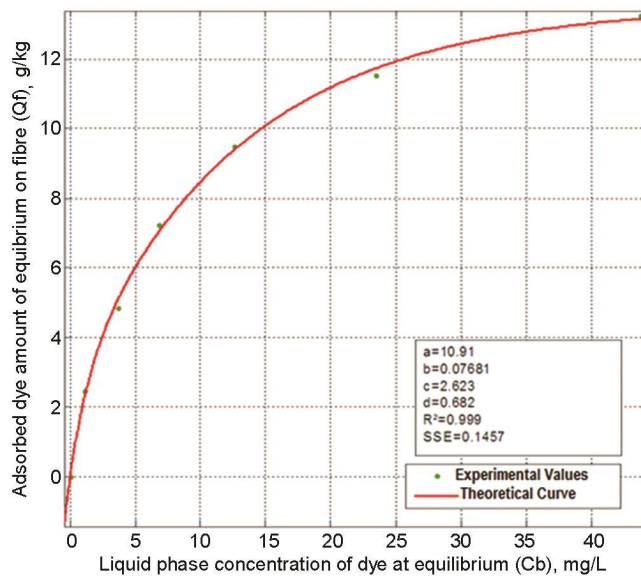

Fig. 7 — Fitted adsorption isotherm model of 1:2 metal complex dye on cationized cotton fabric

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 our case, the high R^2 value (0.999) and the law SSE value (0.01457) indicate that the experimental data are well correlated to the PEK equation. From the PEK model, it could be found that the values of A_1 (b in Fig. 7) and A_2 (d in Fig. 7) are 0.07681 L/mg and 0.682 L/mg respectively. So, it is observed that $A_1 \lll A_2$, which means that the second term of the model can be neglected.

3.3 Kinetic Model

The result indicates that the curve is composed essentially of two stages. In the first stage, the amount of the adsorbed dye on the cationized cotton fabric increases rapidly during a few minutes. Then, after 4-5 min, the amount of dye adsorbed on the textile continues to increase slowly until the equilibrium state is reached at ~ 30 min. This result indicates that the evolution of 1:2 metal complex dye adsorption 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.

The experimental data of the dye adsorption onto the cationized cotton at each time are curve fitted using MatLab to the parallel exponential kinetics model. PEK model has a double exponential form as given by the following equation[5,14-16]:

$$Q_e(t) = Q_{1\infty}[1 - \exp(-K_1 t)] + Q_{2\infty}[1 - \exp(-K_2 t)]$$
$$\ldots (5)$$

where Q_e is the adsorbed dye amount of equilibrium after dyeing time t; $Q_{1\infty}$ and $Q_{2\infty}$, the adsorbed dye amount of equilibrium after an infinite time of dyeing associated respectively with the fast and slow processes; and K_1 and K_2 are the adsorption kinetic of dye molecules respectively at the fast and the slow processes.

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 our case, the high R^2 value (0.9998) and the law SSE value (0.01145) indicate that the experimental data are well correlated to the PEK equation. From the PEK model, it could be found that the equilibrium adsorbed dye amount associated with the fast and slow processes are 7.059 g/kg and 2.306 g/kg respectively. The kinetic parameters K1 and K2 are found to be 7.479 min^{-1} and 0.1354 min^{-1} respectively. It is observed

that K1 >>>K2, which means that adsorption of dye molecules onto cationized cotton is very rapid.

3.4 Fastness Testing

The dyed samples are tested for fastness properties according to standard methods, such as for colour fastness to washing ISO 105–C02, colour fastness to chlorinated water ISO 105-E03: 2010 and colour fastness to artificial light ISO 105-B02[17]. Results show that colour fastness to washing are 4 and 3/4 respectively at 40°C and 60°C. The colour fastness to artificial light fastness is 3/4 and to chlorinated water is 3.

4 Conclusion

Treatment of cotton fabric with Resicrom SG Resin created cationic sites on the fibre polymer that results in higher absorption of the 1:2 metal complex dyes which have good fastness to sodium hypochlorite. This unconventional process using 7% resin at 60°C for 30 min at pH 11 by adding caustic sodium, avoids the use of electrolyte, which is required as exhausting agent in conventional dyeing of cotton fabrics. As demonstrated by the response surface methodology, the maximum absorption ability of the cationized fabric is obtained at 75°C for only 15 min without any chemical auxiliaries.

Also, in the second part of this study, mathematical models to describe respectively, the adsorption isotherm and the adsorption kinetic of the used dye on the cotton fabric are established and have been demonstrated to be satisfactory. In fact, the experimental data have been interpreted using double-exponential model (DEM) and the simulation curves show good fits with the experimental data.

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