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THERMODYNAMIC PARAMETERS AND DYEING KINETICS OF WOOL YARN WITH AQUEOUS EXTRACT OF RUBIA TINCTORUM L.

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ABSTRACT

Wool yarn have been dyed with colorant extracted from of Rubia tinctorum L in the absence and presence of potassium aluminum sulphate and acetic acid mordant and under the optimum conditions (Dyeing of wool yarn under the optimum conditions natural pH, treatment time 1 hour, and temperature 94-98^{o}C). It is found that the producing shades of the small different colours, ranging from red to dark red. The Kinetic and thermodynamic studies on the uptake by wool yarn have also been carried out. It is observed that this dyeing process is endothermic and spontaneous adsorption. During the dyeing process the ΔH is positive that this implies an uniform ordered distribution of dye on wool yarn.

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KEY WORDS

Natural dyes, Mordant, CIE L a* b*, Colour, Rubia tinctorum L, Dyeing kinetics, Wool Yarn*

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[I] INTRODUCTION

Natural dyes have been a part of human life since time immemorial and before the turn of the century dyes were the only source of colour available and , therefore they were widely used and traded [1]. Natural dyes are obtained from plants, minerals and animals, According to the chemical structure, the natural plant dye can be divided into indigo type, anthraquinone type, flavone type, alkaloids type, multi-hydroxybenzene type, diketone type, benzopyran type, and carotenoid type [2].

Natural dyes are known for their use in coloring of food substrate, leather as well as natural protein fibers like wool, silk and cotton as major areas of application since pre-historic times. Since the advent of widely available and cheaper synthetic dyes in 1856 having moderate to excellent color fastness properties the use of natural dyes having poor to moderate wash and light fastness has declined to a great extent. However, recently there has been revival of the growing interest on the application of natural dye [3]. Also, the use of non-allergic, non toxic and eco friendly natural dyes on textiles has become a matter of significant importance due to the increased environmental awareness in order to avoid some hazardous synthetic dyes, and produce skin allergy, toxic wastes and other harmfulness to human body. At the same time, synthetic dyes are widely available at an economical price and produce a wide variety of colours. Although the better performance of synthetic dyes than natural dyes recently the use of natural dyes on textile materials has been attracting for study on this due to the reasons which is non- toxic, non -allergic effects dyes, and specialty colors, restoration of heritage of old textiles etc [4].

So much has been reported in literature about the naturel dyes. such as, dyeing process variables, the effect of dye extraction, extraction time, dyeing time, mordant concentration and methods of mordanting reported [5, 6]. Studied are also reported on the optimum dyeing technique for dyeing wool [7, 8].

Reports on the effect of process variables on dyeing with selective natural dyes are available [9, 10]. It has been found that required scientific studies and systematic reports on dyeing of textiles with natural dyes are still insufficient [11].

Common madder (*Rubia tinctorum* L.) produces anthraquinone pigments in its roots, one of them being alizarin (1,2 dihydroxy anthaquinone) which has been used for dying textiles since 2000 B.C.

In the present study a try out has been made to dye wool yarns with *Rubia tinctorum* L, and CIE L* a* b* values, thermodynamic parameters and kinetics of dyeing.

[II] MATERIALS AND METHODS

2.1. Plant materials

Dried root material of *Rubia tinctorum* L. was obtained from the Gürpınar region of Van/Turkey. Wool yarns of Nm 2.5 were used for dyeing and wool yarns were provided by Van Textile Fabrics (Van/Turkey) All other chemicals including mordants (potash alum sulfate and acetic acid) used were of laboratory grade.

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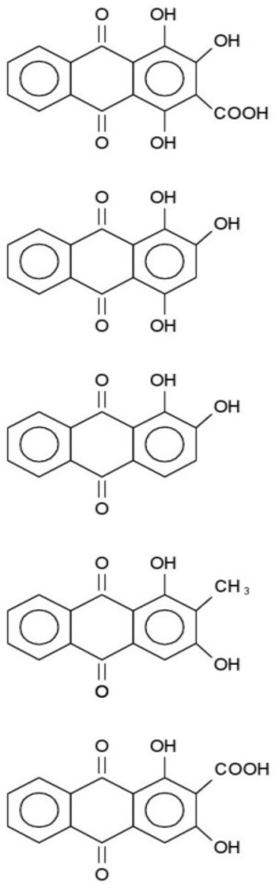

Pseudopurpurin

Purpurin

Alizarin

Rubiadin

Munjistin

Fig:1. Chemical structure of *Rubia tinctorum* L.

2.2 Extraction of dye

Rubia tinctorum L. was ground to a coarse powder and extracted with water in 500 ml-Erlenmayer flasks at 90^{0}C till the colour was extracted. The colored aqueous solution was filtered for dyeing woolen yarn samples. For the kinetics, *Rubia tinctorum* L. extracted with n-Hexane in soxhlet apparatus at 50^{0}C. The semi-dry mass of the dye was obtained after evaporation of solvent.

2.3. Dyeing of woolen yarns

The woolen yarns were dyed at pH 5.0 in a bath containing extracted *Rubia tinctorum* L. dye solution at 1:100 M:L ratio. The dyeing process was started initially at 25^{0}C and the temperature was gradually raised till boiling point (94^{0}C-98 ^{0}C) and dyeing was continued for 45 minutes. The dyed woolen yarns were washed with tap water and dried in shade at room temperature.

2.4. Kinetic dyeing

The kinetic studies were carried out for the time periods ranging from 15 minutes to 1h, keeping the material- to- liquor ration 1:100 at 95^{0}C. The concentration of the dye in the aqueous solutions after dyed yarns was measured by using the Uv-Vis spectrophotometer. (Cintra 202 Duble Beam) q_t, the amounts of dyed woolen yarn at various time periods were determined using the following equation:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

where C_i and C_t is the initial concentration of dye and the aqueous solution after t min. V is the volume of dye solution (L), and m is the mass of wool yarn

2.5. Thermodynamic studies

The thermodynamic parameters such as standard affinity ($\Delta\mu^0$), the entropy of dyeing (ΔS^0) and enthalpy (ΔH^0) were calculated using the following equation [12; 13; 4].

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 = \quad (2)$$

$$-\Delta\mu^0 = RT \ln \frac{D_f}{V} x D_s = RT\ln K_d \quad (3)$$

$$K_d = \frac{C_i - C_e}{C_e} x \frac{V}{m} \quad (4)$$

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

Where, K_d is the equilibrium constant, Ci is the initial dye concentration (g/dm^3), Ce is the equilibrium dye concentration, V is the volume (ml) and m is the mass of the wool yarn (g) R is the gas constant (8.314 J mol-1 K^{-1}), T is the absolute temperature (in Kelvin). The various of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of the plot of ln K_d versus 1/T are linear, respectively.

[III] RESULTS AND DISCUSSION

3.1. Dyeing of woolen yarns

CIE L* a* b* values of the samples dyed with mordanting are found to be higher to that observed without mordanting. **Table–1** shows the CIE L* a* b* values and colours properties of the samples dyed. Potash alum sulfate and acetic acid mordanted samples result in deeper shades are observed after than without mordanting. Best results were obtained in case of simultaneous mordanting method.

Table: 1. Observed colour and CEI L* a* b* values of wool yarn samples dyed with *Rubia tinctorum* L

	Observed Colour	L*	a*	b*
Without Mordanting	Red	40	28	10
Simultaneous Mordanting				
Potash alum sulphate	Dark Red	41	38	19
Acetic asic	Light Red	46	30	13

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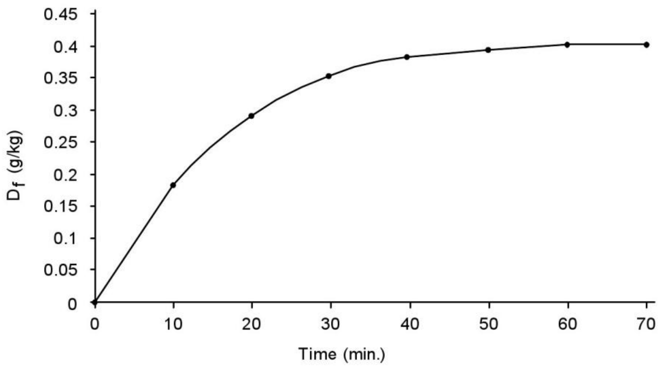

Fig: 2. Plots of dye uptake with respect to time for wool yarn

3.2. Kinetic studies

The dye exhaustion by wool yarn dyed at 95^{0}C for various time periods has been carried out. The time of dyeing is calculated as 45 min. It is observed that as the time of dyeing increases from 30 min after than that the equilibrium is achieved. Similar trend was reported for the kinetics and thermodynamics of dye extracted from Arnebia nobilis Rech.f.on wool [14] and colouration of wool and silk with *Rheum emodi* [15]. Kinetic parameters were calculated using the following equation: [16]

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{1}{q_e} t \qquad (7)$$

The k_1 and q_e have been calculated from the slope and intercept of plots of log (q_e-q_t) versus t according to pseudo-first - order model **[Figure-2]** and versus t according to pseudo-second -order model **[Figure–3]** q_e and k_2 from the slope and intercept have been calculated. The kinetic parameters have been given in **Table–2**. as table the correlation coefficient values for the pseudo-second-order rate equation 0.97 was found to be higher than the pseudo-first-order rate equation 0.90. This indicates that dyeing process can be explained with pseudo-second-order equation.

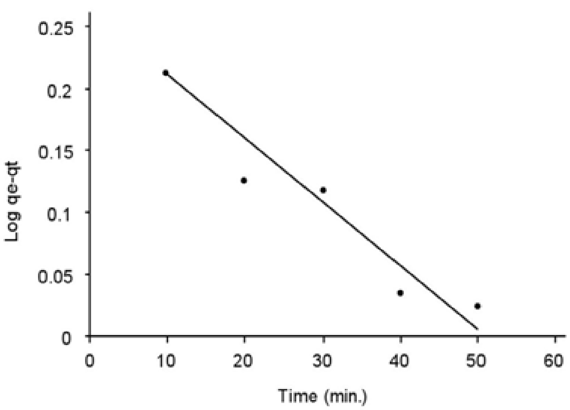

Fig: 3. Pseudo-first-order plots for wool yarn dyed

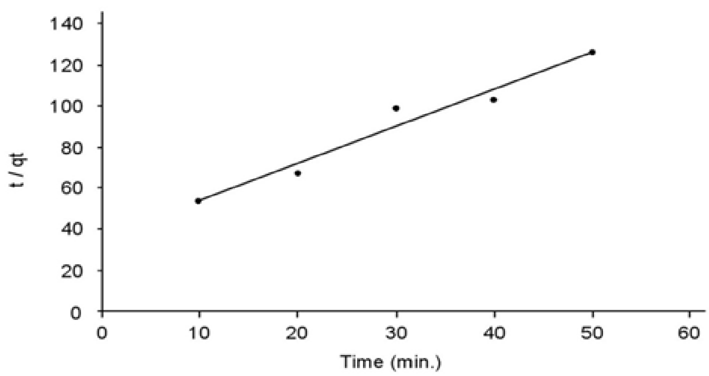

Fig: 4. Pseudo-second-order plots for wool yarn dyed

Table: 2. Kinetic parameters for dyed wool yarn with *Rubia tinctorum* L.

Pseudo-fist-order	k_1 1x10^{-2} (min^{-1})
	q_e 2.6 (mg g^{-1})
	R^2 0.90
Pseudo-seconder-order	k_2 1.8 x10^{-1} (g mg^{-1} min^{-1})
	q_e 3.6 (mg g^{-1})
	R^2 0.97

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3.3. Thermodynamic parameters

The thermodynamic parameters are given in **Table-3**. It is clear from the table that the enthalpy change (ΔH^0) has been found to be positive, indicating that the dyeing in case is an endothermic process. So, the increasing of the dyeing temperature will lead to higher dye affinity up to a certain temperature limit, above which the uptake will gradually reduce or levels off, and in this case means attached to dye fibers, In other words practically there is a decrease in dye affinity. The negative values of ΔG^0 where the dyeing process is spontaneous and the negative values of ΔG side with rise in temperature. However, there are little or almost no significant changes in dye affinity with increase of dyeing temperature. Similar results were reported earlier in similar studies [17-19].

Table: 3. Thermodynamic parameters for dyeing of wool yarns with *Rubia tinctorum* L.

Temperature (K)	ΔH0 (kJ/mol)	ΔS0 (kJ/mol K)	ΔG0 (kJ/mol)
343	20.68	23.61	-12.58
358	19.75	22.74	-11.61
368	23.65	32.11	-11.83

[IV] CONCLUTIONS

1. With the increase in dyeing time the dye uptake increases on wool yarn upto 60min of dyeing time and then gradually slows down and dyeing process becomes stable.
2. The dye extracted from *Rubia tinctorum* L. is found to be at natural pH and different mordanting with the colors ranging from Red and light red to dark red at different pH. The dye extracted from *Rubia tinctorum* L.
3. The kinetics of dyeing can be fitted by pseudo-second-order model as a correlation coefficient values.
4. The thermodynamics parameters of dyeing are endothermic and spontaneous. Therefore, there will be increase in dye absorption with increase in temperature of dyeing after then dyeing process slowed and dye adsorption at a certain temperature where equilibrium of dyeing is achieved.

CONFLICT OF INTEREST

Author declares no conflict of interest.

FINANCIAL DISCLOSURE

The work is not supported by any grant.

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