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Dual-Mode Adsorption of Cochineal Natural Dye on Wool Fibers: Kinetic, Equilibrium, and Thermodynamic Studies

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Abstract: The dual-mode adsorption model was used to investigate the adsorption behavior of cochineal natural dye on wool fibers. Kinetic, thermodynamic, and equilibrium characteristics were investigated in terms of the adsorption isotherm, affinity, enthalpy and entropy changes, dyeing rate, diffusion coefficient, and activation energy of dye diffusion. The results revealed the prominent role of dyeing pH in determination of dyeing mechanism and dye adsorption isotherm type. At pH 4, dual Langmuir-Nernst model with the highest correlation coefficient was found as the most appropriate isotherm model to describe the adsorption behavior of cochineal onto wool fibers while at pH 6, the adsorption isotherm was the Nernst type. Cochineal adsorption onto wool was exothermic which resulted in progressive fall in affinity and equilibrium dye up-take values with increasing temperature. Moreover, dyeing rate steadily increased with temperature. At pH 4, affinity, dyeing rate, and diffusion coefficient demonstrated higher values compared to pH 6 whereas enthalpy and entropy changes, and activation energy showed lower values. Additionally, negative value for activation energy was obtained at pH 6. The results are deliberated based on the different possible interactions between cochineal dye and wool fiber.

Keywords: Cochineal, Wool dyeing, Thermodynamic parameters, Kinetic parameters, Adsorption

Introduction

Many years ago, natural sources were used in dyeing of textiles all around the world. After discovery of the first synthetic dye in 1856 and its industrialization in the late of nineteenth century, the producers preferred using synthetic dyes due to their ability to easily match a favorite color, extensive gamut, high purity, economical facts, and easy processing ability [1]. Due to toxic and harmful effects associated with the synthetic dyes, a ban has been imposed by countries on the use of synthetic dyes in textile garments exported into their countries. Moreover, increasing awareness of the environmental and health hazards associated with the synthesis, processing and the use of some synthetic dyes has created a worldwide interest in textiles dyed with natural dyes [2].

Due to the current eco-consciousness, the researcher's attention has been shifted to the use of natural dyes for dyeing of textile materials and today craftsmen in various parts of the world desire to revive the old tradition of using natural dyes as these dyes produce beautiful and attractive shades. The use of natural dyes can significantly minimize the volume of the toxic effluent resulting from the conventional dyeing process [3]. At present, the textile products dyed and finished with natural products have won the favor of the consumers who are quite aware of environmental problems, and their market is therefore steadily increasing [4].

Cochineal (C.I. Natural Red 4; C.I. 75470) is a natural dye of animal (insect) origin that has been used for centuries in natural dyeing of textiles. The main source of dye is the dried bodies of the females of the *coccus cacti* scales which live on a species of cactus (Nopaleacoccinellifera) mainly in central America and Mexico [5]. The main coloring component in cochineal is an anthraquinone derivative, so called carminic acid. The chemical structure of carminic acid is shown in Figure 1. Cochineal can be used as a mordant dye with the carbonyl and the adjacent hydroxyl groups participating in the fiber-mordant-dye complex formation [5-7]. Currently, cosmetic, food and pharmaceutical and textile applications are the major uses of the cochineal [5].

Generally, the variation in dyeability of fibers has been examined by measuring the surface reflectance function of the colored fibers, i.e., color strength, expressed in term of *K/S* value [8-13]. Nevertheless, *K/S* sounds not to be a suitable criterion for analytical evaluation of the dyeing systems since it is a coarse parameter which does not necessarily reflect the analytical aspects of the dyeing system. The study about the isotherms of cochineal adsorption on wool can assist to realize its adsorption mechanism and thus to control the process of its dyeing. However, few

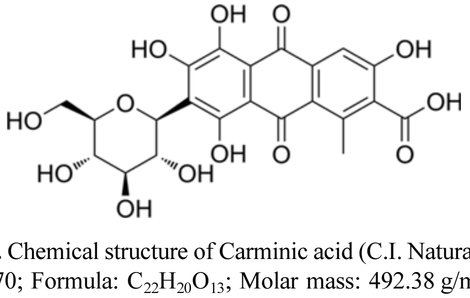

Figure 1. Chemical structure of Carminic acid (C.I. Natural Red 4; C.I. 75470; Formula: $C_{22}H_{20}O_{13}$; Molar mass: 492.38 g/mol), the main coloring component of cochineal.

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*Corresponding author: s.safapour@tabriziau.ac.ir researches have been performed on the mechanism of cochineal dye adsorption on the wool [4], and thus the adsorption thermodynamics remain somewhat obscure.

To the best of our knowledge, thus far, sparse data are available in the published literatures concerning the adsorption kinetic and thermodynamic characteristics of the wool dyeing process with cochineal natural dye. Therefore, in this study, with the aim of finding the most appropriate model to describe the adsorption behavior of the cochineal on wool, the equilibrium adsorption isotherms of the cochineal at pH values of 4 and 6 were investigated at different temperatures and fitted using Langmuir, Frundlich, Nernst, and dual Langmuir-Nernst models. In addition, some of the physicochemical properties of dyeing such as equilibrium adsorption isotherm, affinity, enthalpy and entropy changes, diffusion parameters (i.e. diffusion coefficient and activation energy of diffusion) and the adsorption rate, which have not been already reported by other researchers, have been investigated, and the thermodynamics of adsorption of cochineal on wool in two different pH values were compared and deliberated.

Experimental

Materials

A commercial material of cochineal dye, purchased from local natural dyeing workshop, was used without further purification. The scoured 100 % woolen yarn (200 tex/ 4 fold) was used for dyeing trials. The nonionic detergent used for the scouring of wool was obtained from the Shirley Development Ltd. Acetic acid was supplied by Merck. All other chemical reagents used for preparation of solutions were of analytical reagent grade. Also, all solutions were prepared with double-distilled water.

Scouring Method

Wool fibers were first scoured in a solution containing 2 g/*l* nonionic detergent, and 1 g/*l* sodium carbonate, at 70 °C, for 30 min, and liquor ratio (L.R) of 50:1. Then, the scoured wool was rinsed thoroughly with distilled water, and air-dried.

Dyeing Equilibrium Parameters

Dye adsorption isotherms as well as the commonly used dyeing equilibrium parameters, i.e., the affinity, enthalpy, and entropy changes were determined.

Dyeing

To study the adsorption isotherm of the dye on the wool, dyeing processes were performed in dyeing equilibrium time using a laboratory HT dyeing machine. All dyeing trials were performed using buffer solutions prepared from the mixture of the appropriate amount of citric acid solution (0.1 M) and disodium hydrogen phosphate (0.2 M) solution depending on the pH required. Different concentrations of the dye in buffer solution (0.05, 0.1, 0.3, 0.5, 0.7, and 0.9 g/*l*) were prepared, and then wool samples (1 g) were dyed at pHs 4 and 6 and various temperatures of 60, 80 and 100 °C using the liquor ratio (L.R) 100:1. In the experiments, equilibrium was generally obtained within 1-2 h. Nonetheless, to assure the achievement of the equilibrium, dyeing of fibers was prolonged at the desired temperatures for 4 h. Absorption values of dyeing solutions were measured in the visible range using a UV-Vis Cecil 9200 double beam spectrophotometer. Maximum absorption wavelength of the colored solutions was identified to be in pH 4: λ_{max}=492 nm and pH 6: λ_{max}=535 nm. Dye exhaustion was measured by sampling the dye solution before and during the dyeing process. The percentage dye exhaustion (*E%*) was then calculated by equation (1):

$$\%E = \frac{(A_1 - A_2)}{A_1} \times 100 \tag{1}$$

where, A_1 and A_2 are the concentration of the solution at the beginning of dyeing, and at any given time, respectively.

Affinity

Partitioning coefficient (K) and affinity ($\Delta\mu^o$) of the dye between the fiber ($[D]_f$), and the dyeing solution ($[D]_s$) were calculated from the adsorption isotherm. The affinity of the dye was calculated using equation (2):

$$-\Delta\mu^o = RT\ln\frac{[D]_f}{[D]_s} = RT\ln K \tag{2}$$

where $-\Delta\mu^o$ is the affinity of dye molecules to the fiber (cal/mol), R is the gas constant (1.9872 cal/mol·K), T absolute temperature (K); $[D]_f$, dye concentration in the fiber (g/kg); $[D]_s$, dye concentration in the solution (g/*l*) at equilibrium and K is the partitioning coefficient of dyeing.

$[D]_f$ was obtained using the calibration curve established by proper dilutions of stock dye solution (0.5 g/*l*). The linear regression calibration equation at pHs 4 and 6 was obtained using a linear equation obtained from regression equations as follows:

at pH 4: A=6.00×C, (R^2=0.995); and
at pH 6: A=7.74×C, (R^2=0.993)

where, A is the absorbance and C is the concentration of dyeing solution (g/*l*).

Enthalpy Change

The enthalpy change (ΔH^o) was obtained from the empirical plot that shows the relationship between $-\Delta\mu^o/T$ and $1/T$, from the slopes of the straight lines, the enthalpy change can be calculated using equations (3) and (4):

$$\Delta H^o = d(\Delta\mu^o/T)/d(1/T) \tag{3}$$

$$-\Delta\mu^o/T = -\Delta H^o/T + C \tag{4}$$

where, ΔH^o and C are the heat of dyeing (cal/mol) at T absolute temperature (K) and the integration constant, respectively.

Entropy Change

The entropy change (ΔS^{o}) was determined from the slope of $-\Delta\mu^{o}$ versus T plots using equation (5):

$$-\Delta\mu^{o} = \Delta H^{o} - T\Delta S^{o} \tag{5}$$

where $-\Delta\mu^{o}$ is affinity (cal/mol), ΔH^{o} is heat of dyeing (cal/mol); ΔS^{o} is the change in entropy (cal/mol·K); and T is absolute temperature (K).

Adsorption Isotherm Models

Nernst Isotherm

The simplest type of adsorption isotherm is the Nernst model which includes only one parameter according to equation (6):

$$[D]_f = K_N[D]_s \tag{6}$$

where K_N is the partitioning coefficient.

Langmuir Isotherm

Langmuir adsorption isotherm is one of the most successful isotherms for real systems obtained about gas molecules adsorption on the surface in relation to the solid [14-16]. This model can be applied to the cases in which the number of positions in the sorbent is limited and also when in each position of the adsorption, only a single molecule is adsorbed. So, according to this theory, a certain amount of substance can be adsorbed and after reaching the saturation point (the point after which there is no possibility of adsorption), the increase in self-adsorbed material will not result in increase in adsorption [17]. The expression for the widely used Langmuir isotherm is equation (7):

$$[D]_f = \frac{SK_L[D]_s}{1+K_L[D]_s} \tag{7}$$

where $[D]_f$ (mg/g) and $[D]_s$ (mg/*l*) are the concentrations of cochineal dye on wool fiber and in the solution at equilibrium, respectively; S is the saturation concentration of cochineal dye on wool fiber (g/*l*); K_L is the Langmuir affinity constant.

Freundlich Isotherm

Another experimental adsorption isotherm which is important in investigation of the dyeing behavior of textile fibers using different dyestuffs has been expressed by Freundlich in 1907 [14]. This type of isotherm can be applied to dye adsorption in unlimited situations. In fact, this type of adsorption isotherm is used for the levels which have non-homogeneous surface energy. In these adsorption isotherms, at first, dye adsorption increases quickly, as the initial concentration increases and after occupation a considerable number of adsorption positions in the fiber, the adsorption speed declines [18,19].

The empirical Freundlich isotherm is expressed with equation (8):

$$[D]_f = K_f[D]_s^{1/n} \tag{8}$$

where K_f is the Freundlich affinity constant, and n is an indicator of adsorption intensity or surface heterogeneity.

Langmuir-Nernst Dual Isotherm

The Langmuir-Nernst dual model containing electrostatic (Langmuir) and non-electrostatic (partitioning) modes can be described by equation (9) [20]:

$$[D]_f = C_N + C_L = K_N[D]_S + \frac{SK_L[D]_S}{1+K_L[D]_S} \tag{9}$$

where C_N and C_L are the concentrations of dye on wool fiber by Nernst type partitioning and Langmuir adsorption, respectively; S is the saturation concentration of dye on wool fiber by Langmuir adsorption; K_N and K_L are the partitioning coefficient and the Langmuir affinity constant, respectively.

Dyeing Rate Parameters

The rate of adsorption of dye by fibers has been studied by several fundamental physicochemical parameters. In this study, the most practical parameters, i.e., dyeing rate constant (k), diffusion coefficient (D_T) and the activation energy of the diffusion (E_a) were determined.

The Rate Constant of Dyeing (k)

To determine the dyeing rates, wool samples were dyed in bath containing 0.3 and 0.5 g/*l* of the dye at the temperatures of 60, 80, and 100 °C and the L:R of 100:1. The dyebaths were heated to the dyeing temperature before the fibers were immersed into the dyebath. The Vickerstaff's hyperbolic rate equation, equation (10), was employed to calculate the rate constant of dyeing (k) [21].

$$k.t = (1/(C_\infty - C_t) - (1/C_\infty) \tag{10}$$

where C_∞ is the dye uptake (g/kg fiber) at equilibrium and C_t is the dye uptake (g/kg fiber) at time t.

Diffusion Coefficient

Different methods have been suggested to calculate the diffusion coefficient (D_T) of dye into the fiber in the dyeing process depending on the dyeing procedure and the physical shape of material used. In this study, the Hill's equation was employed to determine the diffusion coefficient of dye [21]. According to Hill's equation, the diffusion coefficient was calculated by plotting C_t/C_∞ versus $t^{1/2}$ for the early stages of dyeing, using equation (11):

$$C_t/C_\infty = 4(Dt/\pi r^2)^{1/2} \tag{11}$$

where r is the radius of the cylindrical fiber in centimeter.

Activation Energy of the Diffusion

The activation energy of the diffusion was calculated from the relationship between ln D_T and $1/T$ (Arrhenius equation) (equation (12)). Plotting the rate of adsorption against the reciprocal temperature gives a reasonably straight line, the gradient of which is $-E_a/R$ [21].

$$\ln D_T = \ln D_0 - (E_a/RT) \tag{12}$$

where D_T: diffusion coefficient at a temperature (cm^2/min); D_0: constant; E_a: activation energy; R: gas constant (1.9872 cal/mol K); and T: absolute temperature (K).

FTIR Analyses

Fourier transform infrared (FTIR) spectra of the samples were recorded in a Nicolet FTIR spectrophotometer, Madison, USA. 2 mg of each sample was grinded with 100 mg dry potassium bromide (KBr), and pressed into a mold in a uniaxial hydraulic press under a load of 0.9 MPa to obtain IR-transparent pellets. The spectra were then collected in transmittance mode in the region of 4000-400 cm^{-1} with resolution of 4 cm^{-1}.

Colorimetric Measurements

Colorimetric parameters of the dyed samples were measured through Color-Eye XTH Spectrophotometer, X-Rite Inc., USA under D65 illumination, 10° standard observer. The spectrophotometer was equipped with software able to automatically calculate CIEL*a*b*, color difference and color strength (*K/S*) values from the reflectance values at the appropriate wavelength for each dyed sample. The colors are given in CIEL*a*b* coordinates: L* corresponding to the brightness (100=white, 0=black), a* to the red-green coordinate (positive=red, negative=green), b* to the yellow-blue coordinate (positive=yellow, negative=blue), C* to chroma or color purity or vividness-dullness (100=vivid, 0=dull) and h° to hue angle. The color strength (*K/S*) is directly proportional to the concentration of colorant within the substrate.

Fastness Properties

Wash fastness was measured by the standard ISO 105 C06 C2S:1994 (E) method. The washing was conducted for 30 min at 60 °C, rinsed with cold water, air dried, and analyzed with grey scale. Light fastness test ISO 105 B02:1988 (E) was evaluated with the xenon arc lamp using blue reference samples. The rub fastness test was performed according to ISO 105-X12:1993 (E) standard using a crockmeter. For the wet rub test, the testing squares were thoroughly immersed in distilled water; the rest of the procedure was the same as in the dry test. The staining on the white test cloth was evaluated according to the gray scale.

Results and Discussion

Dyeing Equilibrium

Adsorption Isotherm of the Cochineal Dye on the Wool

In this study, four isotherm models, namely, Langmuir, Nernst, Freundlich, and Langmuir-Nernst (the dual adsorption equation consisting of the partitioning and Langmuir models) were employed in order to compare the adsorption equilibrium of cochineal dye on the wool. The adsorption isotherms of cochineal natural dye on the wool fibers at two dyeing pH values of 4 and 6 are shown in Figure 2.

To find out the most appropriate model and describe the adsorption behaviors of cochineal on wool at pH 4, different isotherm models were fitted using the nonlinear least-squares fitting procedure, and thus the parameters described in equations (6)-(9) were obtained. The adsorption parameters for the Nernst, Langmuir, Freundlich, and Langmuir-Nernst models have been summarized in Table 1. The normalized deviations (*ND*) of the experimental values, calculated according to equation (13), have also been listed in Table 1 and used to evaluate the degree of fitting [20].

$$\%ND = 100 \times \frac{1}{N}\sum_{i=1}^{N}\left(\frac{\left|C_{f,i}^{expt} - C_{f,i}^{calcd}\right|}{C_{f,i}^{expt}}\right) \tag{13}$$

where the superscripts *expt* and *calcd* refer to the experimental and calculated values, respectively; the latter is a result of calculation using equations (6)-(9) on the basis of the parameters, which were obtained by the fitting procedure; the index *i* refers to the sequence number of adsorption data; *N* is the total number of data sets.

The parameters in equations (6)-(9) obtained from nonlinear least-squares curve fitting of four isotherm models are

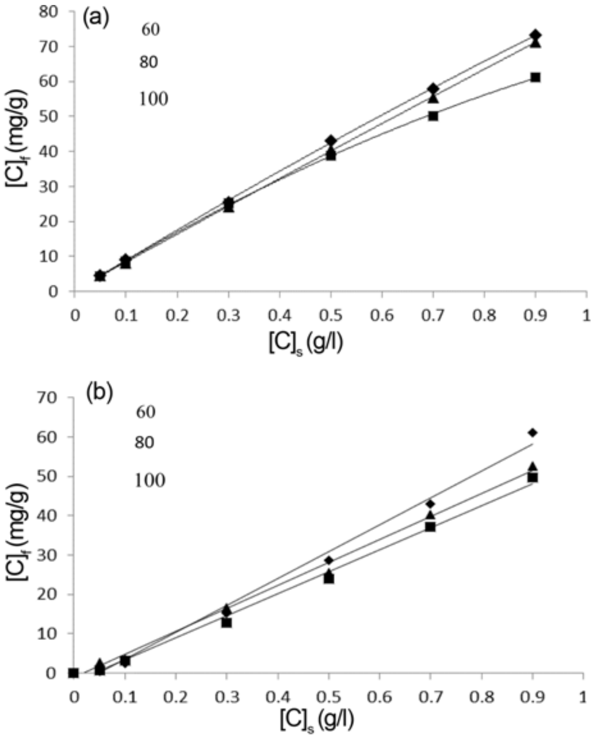


Figure 2. Adsorption isotherms of cochineal on wool fiber at different temperatures; (a) pH 4 and (b) pH 6.

Table 1. The correlation coefficient (R^2) and normalized deviation (ND) of isotherm models at pH 4

Temperature (^{o}C)	R^2				ND (%)			
	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
60	0.972	0.994	0.979	0.993	12.38	7.68	41.98	2.32
80	0.995	0.917	0.977	0.999	0.42	4.63	38.70	0.71
100	0.930	0.995	0.993	0.999	4.18	2.47	44.58	8.67

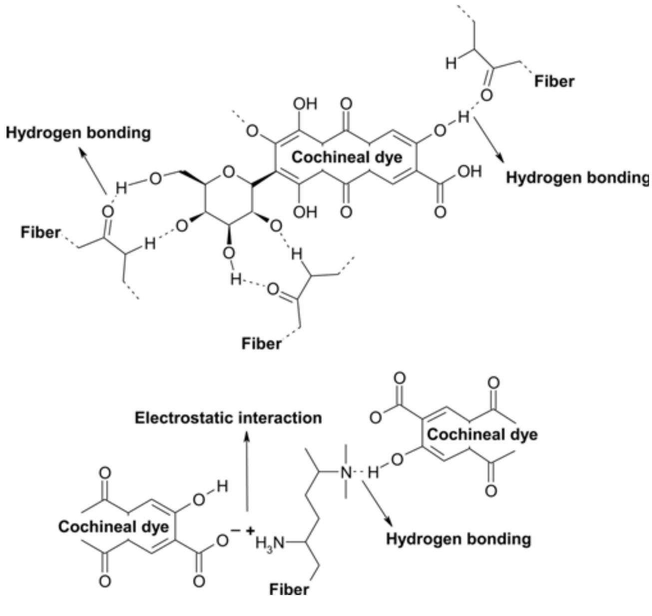
Models for the adsorption: (a) Nernst, (b) Langmuir, (c) Freundlich, and (d) Langmuir-Nernst.

presented in Table 1. According to this table's data, the Langmuir-Nernst model gave the best fit to the adsorption isotherms since it had the lowest normalized deviation and the highest correlation coefficient (R^2) suggesting that the Langmuir-Nernst dual isotherm is the most appropriate model to describe the adsorption behavior of cochineal dye on the wool fiber at pH 4. Therefore, it can be concluded that the uptake of cochineal dye by the wool fiber is the consequence of contribution of both Langmuir and Nernst adsorptions. It seems that the electrostatic interactions operating between the cochineal dye molecules and the amino groups in wool fiber participate to Langmuir adsorption, whereas the non-electrostatic interactions between cochineal dye and wool fiber contribute to partitioning adsorption.

Nonetheless, as the dyeing pH increased to 6, the Nernst curve almost passed through all the experimental data exactly, demonstrating a precise fitting to the experimental data. Hence, partitioning adsorption was identified as the best model to describe the adsorption behavior of cochineal dye on wool at pH 6. This behavior may rely on the fact that at higher pH the wool fiber becomes less protonated, and less positively charged, thus leading to the lowered extent of the electrostatic interaction between wool fiber and cochineal dye. Consequently, non-electrostatic interactions (hydrogen bonding, van der Waals forces and hydrophobic interaction) between the cochineal dye and the wool fiber contributed to partitioning adsorption (Nernst isotherm) at pH 6. The interactions between cochineal dye and wool fiber is schematically shown in Scheme 1.

In Table 2, the adsorption parameters for the Langmuir-Nernst model have been summarized. Remarkable variations in isotherm model parameters with temperature were observed. The Langmuir affinity constant (K_L) values steadily increased with increasing temperature, whereas the partitioning coefficient (K_N) values decreased. The increasing K_L values may be the consequence of heat consumption for the disassociation of cochineal dye aggregates and the swelling of wool structure that accompanied an increase in temperature. Additionally, an appreciable decrease in saturation concentration of dye on wool by Langmuir adsorption (S) values with increasing temperature may be ascribed to a decrease in the contribution of Langmuir adsorption to total adsorption that accompanied an increase in temperature [20].

Such peculiar behavior in the adsorption of cochineal dye onto wool fiber, which is dependent strongly on the dyeing pH, can be explained in detail by taking into account the chemical structures and molecular characteristics of cochineal dye and wool fiber, and the reciprocal interactions which are likely to take place, as described in the following.



Scheme 1. Schematic representation of the interactions between cochineal dye and wool fiber.

Table 2. Parameters in Langmuir-Nernst, and Nernst models for the adsorption of cochineal dye on wool at pH values of 4 and 6

Temperature (^{o}C)	pH 4			pH 6		
	K_L (10^{-3} l·mg^{-1})	$\Delta\mu^o_{L+N}$	S (mg·g^{-1})	K_N (10^{-3} l·g^{-1})	$-\Delta\mu^o$	K_N
60	7.66	7979.46	86.95	80.83	2794.315	68.21
80	18.83	5730.70	53.19	77.00	2692.402	58.48
100	30.30	5106.32	41.32	75.20	2662.816	55.92

Wool, indeed, has a complicated chemical structure which is composed of a protein so-called keratin. The main chains in wool are cross-linked with cystine (-S-S-) residues and contain a variety of side chains, some basic and some acidic, depending on the side-chain groups present. From a structural viewpoint, the main part of the wool is the cylindrical core of the fiber, which is called the cortex and is divided into ortho and para segments. Surrounding the cortex is a cuticle made up of an outmost scale layer and a thin outer layer (epicuticle). Both layers have a tremendous impact on dye penetration and dyeing behavior owing to their hydrophobic nature. The cuticle is separated from the underlying cortex by the intercellular material and consists of non-keratinous proteins and lipids. The hydrophobic nature of wool is known to be due to the special properties of the exocuticle and epicuticle. The exocuticle is hydrophobic because it contains a high degree of disulfite cross-linkage. The epicuticle surrounds each cuticle cell of the wool fiber, and it contains fatty acid and protein. The major component of the fatty acid fraction is 18-methyleicosanoic acid, which is oriented away from the fiber to produce a polyethylene-like layer at the fiber surface, and this makes the epicuticle hydrophobic and resistant to the attack of different agents. This is the reason that wool is known to have a hydrophobic water-repellent surface even after the removal of wool grease by aqueous scouring or a solvent treatment [22].

Numerous amine (-NH_2), amide (-NH-CO-), carboxyl (-COOH), and numerous hydroxyl (-OH) groups of wool are very prone to from hydrogen bonds with multiple hydroxyl and carbonyl groups of cochineal. Furthermore, hydrophobic parts of wool fiber such as non-polar amino acid residues and the aromatic ring-containing amino acid residues can interact with the hydrophobic aromatic rings of cochineal by hydrophobic interaction [5,13,23]. Previous researchers have reported that the colorants like cochineal which contain carboxylic acid groups demonstrated significantly higher adsorption over the colorants having similar chemical structure but no carboxyl groups [5]. Cochineal has one carboxyl group in its structure (see Figure 1). The pK_a value of the carboxyl group of cochineal (carminic acid) is 2.81 [24], indicating carminic acid would exist in carboxylate anion form at both pH values investigated in this study. Consequently, it is reasonable to assume the cochineal as an acid dye which would interact electro-statically with protonated amino groups of wool. Nevertheless, the numbers of protonated amino groups within wool, being responsible for electrostatic interaction with anionic carboxyl groups of dye, are crucial in dye adsorption and are primarily changed by dyeing pH.

It is well accepted that the pH is an important factor which controls the adsorption of anionic dyes onto wool [25]. Considering iso-electric point of wool (pH 4.2), below this point, wool is positively charged principally whereas above that point carboxyl groups render a net negative charge on the wool. At pH 4, more amine groups (NH_2) inside the wool would be present in protonated amino form (NH_3^+) and the net charge of wool fiber is positive [25]. Consequently, in acidic dyeing condition, the adsorption of cochineal onto wool arises from both electrostatic (Langmuir isotherm model) and no-electrostatic interaction (Nernst isotherm model). Merging the Nernst model to Langmuir model (dual Langmuir-Nernst isotherm model) is therefore recognized as the proper model to evaluate balance dyeing behavior and absorption mechanism of cochineal dye-wool fiber system in acidic dyeing conditions [20,26]. Thus, it can be concluded that the proposed dual mode mechanism for cochineal dye adsorption by wool fibers in acidic media, obtained in this study, is more precise than previously suggested either Langmuir or Freundlich models [4]. Nonetheless, increasing of pH to 6 leads to substantial decreasing in the amount of amino groups, and accordingly, the share of the ionic forces in dye adsorption process decreases. As a result, non-electrostatic dye-fiber interactions become dominant and Nernst model is the most appropriate isotherm model at pH 6.

Affinity

The most significant thermodynamic parameter is $\Delta\mu^o$ which is defined as the difference between the chemical potential of the dye in the dyeing solution and the chemical potential of the dye within textile. This factor is a criterion of the affinity of the dye to transfer from the dye bath solution toward the textile [27]. From Table 2, affinity values in all temperatures and pH values demonstrated that adsorption of cochineal dye on wool fiber was an exothermic reaction process. Due to this fact, as the temperature increased, the partitioning coefficient (K_N) of dye decreased for both pH values since the thermodynamic adsorption or the partition coefficient could be negatively influenced by using the higher dyeing temperature [28]. It is also clear that the affinity of the affinity of cochineal dye at pH 4 was markedly higher than pH 6.

Enthalpy and Entropy Change

As mentioned earlier, the cochineal dye adsorption onto wool is an exothermic reaction process and releases thermal energy. The amount of exothermic energy released depends mainly on the dyeing conditions, such as fibers, dyes, dyeing media, and etc. In addition, ΔH^o is considered as the measure of the adsorption strength of dyes. Meanwhile, ΔS^o in dyeing represents the entropy difference of the dye molecules within the fiber [21]. Figure 3(a) demonstrates the linear relationship between $-\Delta\mu^o/T$ and $1/T$ on enthalpy change. The enthalpy changes at different pH values have been summarized in Table 3.

It is clearly observed that the enthalpy change (ΔH^o) is mainly affected by dyeing pH. Comparatively higher ΔH^o values at pH 6 in comparison with corresponding values at pH 4 suggests that the amount of exothermic energy arisen out of the interaction between the polymeric chains of wool and cochineal dye molecules is remarkably higher when the wool is dyed at pH 6. Consequently, it can be concluded that

Table 3. The enthalpy and the entropy changes of cochineal on wool at different pH values

Parameters	pH	
	4	6
ΔH^o (cal/mol)	-3856.10	-4388.00
ΔS^o (cal/mol·K)	-2.86	-4.77

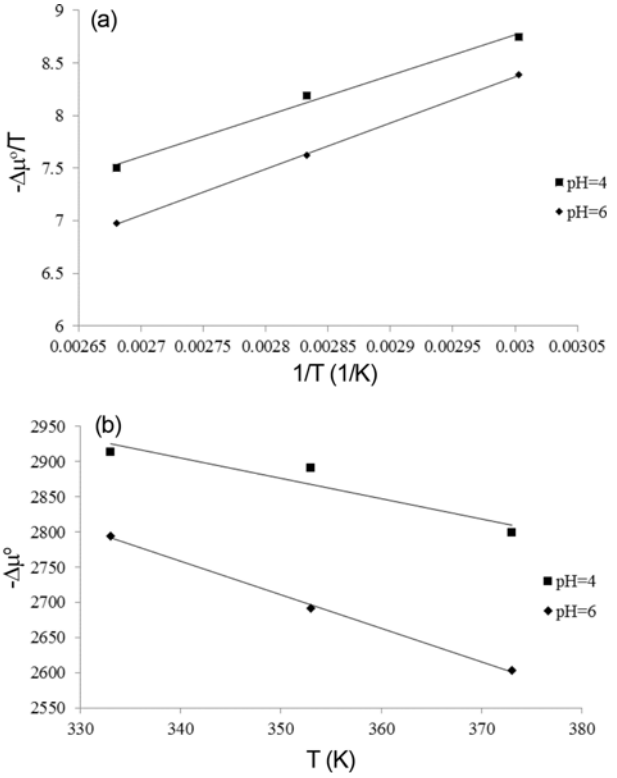


Figure 3. Relationships between (a) $-\Delta\mu^o/T$ and $1/T$ on enthalpy change, and (b) $-\Delta\mu^o$ and T on entropy change.

the more energy and heat is required for wool dyeing at pH 6 in comparison with pH 4.

In most dyeing processes, the entropy change (ΔS^o) demonstrates negative values. This behavior can be attributed to the adsorbed dyes which become more restrained inside fiber than the dyeing solution. In other words, the value of the entropy change could be regarded as the ratio of immobility of dyes within the fibers. However, entropy cannot be directly calculated owing to the complication of the dyeing process. Therefore, the calculation of this term can be used for comparison purposes. Figure 3(b) demonstrates the linear relationship between $-\Delta\mu^o$ and T. The slope of the line was calculated as ΔS^o, and the results at different pH values have been presented in Table 3. Relatively higher ΔS^o values at pH 6 demonstrates higher extent of the reduced freedom of dye molecules after the completion of dyeing, and thus stronger bonding of fiber with the dye and more orientation of dye inside the wool fiber [29].

Dyeing Rate

It is generally agreed that dyeing process involves three continuous steps. The first step is the diffusion of dye through the aqueous dye-bath onto the fiber. The second step is the adsorption of dye into the outer layer of the fiber and the last step is the diffusion of dye into the fiber inside from the adsorbed surface. The second step, the actual adsorption process, is generally assumed to be much faster than either of the other diffusion steps. Of the two diffusion steps, the diffusion into the inner layer is much slower than the movement of dye through the aqueous solution due to the physical obstruction of dye diffusion presented by the network of fiber molecules [21,29].

Dyeing Rate Constant

Figure 4(a-c) demonstrates the dyeing rate curves for different cochineal dye concentrations (0.3 and 0.5 g/*l*) and

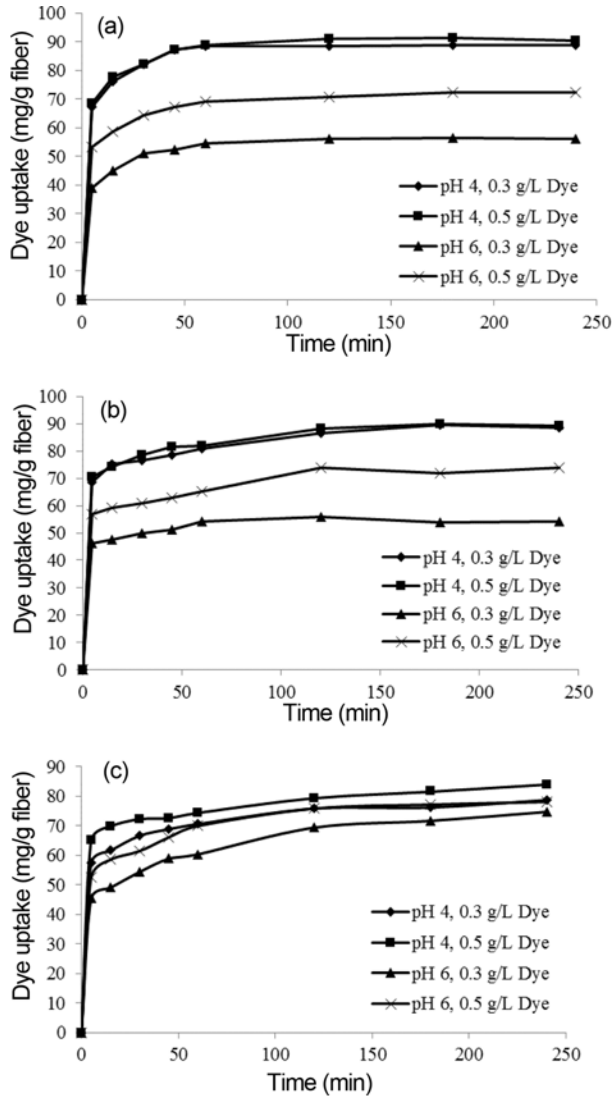


Figure 4. The rate of dye uptake against dyeing time for cochineal at (a) 60 °C, (b) 80 °C, and (c) 100 °C at pHs 4 and 6.

Table 4. Dyeing rate constants (k) in wool dyeing with cochineal

Temperature (°C)	k (min^{-1})			
	pH 4		pH 6	
	C_{dye} 0.3 (g/l)	C_{dye} 0.5 (g/l)	C_{dye} 0.3 (g/l)	C_{dye} 0.5 (g/l)
60	0.006	0.007	0.003	0.004
80	0.007	0.013	0.005	0.006
100	0.012	0.022	0.011	0.013

temperatures (60, 80, and 100 °C). The dyeing rate constant (k) was calculated by means of least squares fit of experimental data using equation (10) at different temperatures and the results are shown in presented in Table 4. According to the results, dyeing rate constant increases with the increase in dye concentration and dyeing temperature. The highest rate constant is obtained at pH 4 and 100 °C.

Diffusion Coefficient and Activation Energy of Diffusion

In the literature, diffusion coefficient (D_T/r^2) is practically calculated from Hills' equation (equation (11)) to describe the diffusion ability of dyes into the textile fiber. The relationship between C_t/C_∞ and $t^{1/2}$ for wool dyeing with cochineal at three different temperatures and two dye concentrations are shown in Figures 5 and Figure 6, respectively. The corresponding calculated coefficient (D_T/r^2) values are also presented in Table 5.

According to Table 5 data, there is a direct relationship between diffusion coefficient of dye and dye concentration, i.e., the diffusion coefficient increases as the dye concentration increases. Nontheles, temperature has negative impact on diffusion coefficient in which furthur raise in temperature results in lower diffusion coefficient. Moreover, the diffusion coefficient values at pH 4 are substantially higher than those values at pH 6 at any given temperature and dye concentarion. Since the method of calculation of the diffusion coefficient of dye into fiber is strongly related to the amount of dye uptake, which is time-dependant, by fiber in the early stage of dyeing, it seems acceptable that the ability of fiber to hold and gain dye molecules in the early stage of dyeing plays a crucial, final role in the value of this kinetic parameter. Hill's equation demonstrates that the amount of C_t/C_∞ is proportional to D_T/r^2. In fact, the calculated D_T/r^2 has an apparent meaning because the sum of the adsorbed dye by the wool fiber at a certain time of dyeing represents an integral of concentration profiles. It seems that the reason for the above mentioned trend originates from the ability of wool fiber to mainatin dye molecules within its polymeric matrix [20].

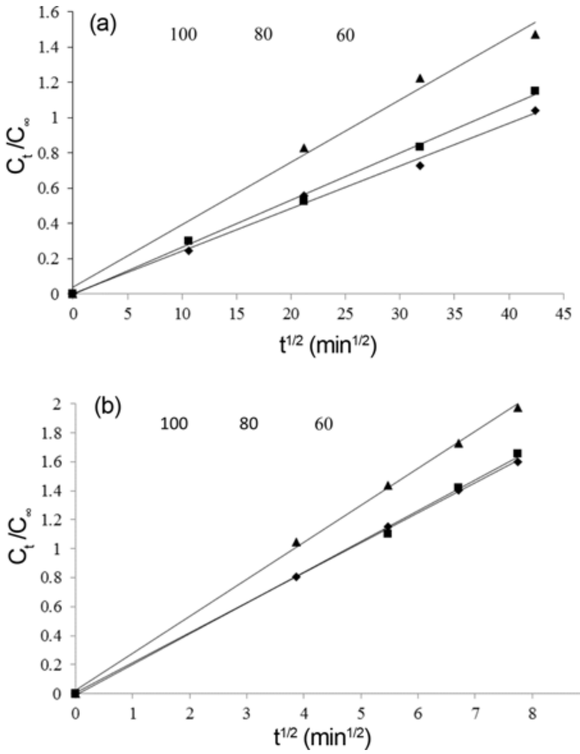


Figure 5. Variation of C_t/C_∞ against $t^{1/2}$ for determination of diffusion coefficient at (a) pH 6 and (b) pH 4 (0.3 g/l dye).

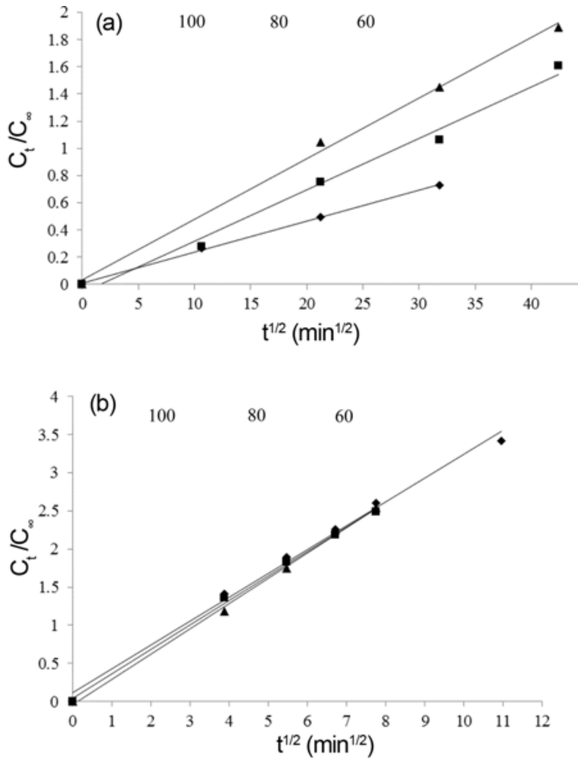


Figure 6. Variation of C_t/C_∞ against $t^{1/2}$ for determination of diffusion coefficient at (a) pH 6 and (b) pH 4 (0.5 g/l dye).

The appreciable difference between the diffusion coefficient values at two different pH values can be explained by the forces participating in dye-fiber interaction and dye adsorption process. As described earlier, indeed, at pH 4 where the amine groups (-NH$_2$) within wool are fully protonated and present in amino (-NH$_3^+$) form, the combination of electorstatic and non-electrostatic forces are responsible for dye adsorption

Table 5. The diffusion coefficient of the cochineal on wool at various temperatures

Temperature (°C)	$D_T/r^2 \times 1000$ (min^{-1})			
	pH 4		pH 6	
	C_{dye} 0.3 (g/l)	C_{dye} 0.5 (g/l)	C_{dye} 0.3 (g/l)	C_{dye} 0.5 (g/l)
60	0.255	0.332	0.035	0.044
80	0.212	0.321	0.026	0.037
100	0.207	0.312	0.024	0.022

which favor dye uptake by wool. However, at pH 6, due to substantial decrease in the number of active protonated amino groups, the possibility of ionic interactions is remarkably decreased. So, dye molecules are mostly adsorbed by dominant non-ionic weaker forces being more temperature sensitive and thus an appreciable decrease in the values of diffusion coefficient occurres.

Table 5 data also show that the maitaining ability of dye molecules by wool fiber at lower temperatures is greater than that at higher temperatures, the matter which is more pronounced at at pH 6. In fact, when the temperature increases, the level of kinetic energy of dye molecules increases correspondingly that can lead to desorption of dye molecules due to lower stability of non-electorstatic forces at higher temperatures. Due to higher sensitivity and less stability of non-ionic interactions to temperature changes, e.g. hydrogen bonds which may be broken down much faster and more easily at higher temperatures, the rate of dye desorption at pH 6 from wool matrix with temperature rise would therefore be faster. Since this rate determines the value of dye diffusion coefficient into wool fiber, the parameter decreases at higher temperature resulting in negative activation energy (see Table 6 data).

The activation energy of the diffusion describes the dependence of the diffusion coefficient on the dyeing temperature and also stands for the energy barrier that a dye molecule should overcome to diffuse into the polymer molecules [30]. The activation energy of the diffusion can be obtained from the slope in the linear relationship between the ln(D_T/r^2) and $1/T$, as shown in Figure 7. The corresponding calculated activation energy data are presented in Table 6.

In wool dyeing at pH 4, at lower temperatures, it seems that dye molecules have lower kinetic energy for diffusion, and therefore the penetration of dye molecules take place more slowly into the wool fiber.

At pH 6, nonetheless, negative activation energy of diffusion is obtained. This finding may be explained by the kinetic energy of dye molecules to diffuse into wool fiber. Actually, the level of kinetic energy of dye molecules at low temperatures, e.g. 60 °C, to diffuse into wool fiber is enough. Owing to increasing in the level of kinetic energy of adsorbed dye molecules inside the wool, as the temperature increases, desorption of dye molecules occurs. In other words, as the temperature increases the value of diffusion coefficient which is related to the value of (C_t/C_∞) decreases. Therefore, the negative value for this parameter is achieved due to the diffusion rate decrease. In fact, this behavior clearly indicates that desorption of dye molecules from wool fiber is more sensitive to temperature than the adsorption process of the dye molecules. Consequently, the rate increases steeply as the temperature is raised, and depletes the steady-state concentration [21]. This peculiar behavior arises very likely from the lowered stability of weaker non-ionic forces at higher temperatures to hold high kinetic energy level dye molecules within wool polymeric matrix that could be re-approved by the decreased share of ionic interactions and consequent dominant role of non-ionic interactions at pH 6 between the dye molecules and the polymeric chains of wool.

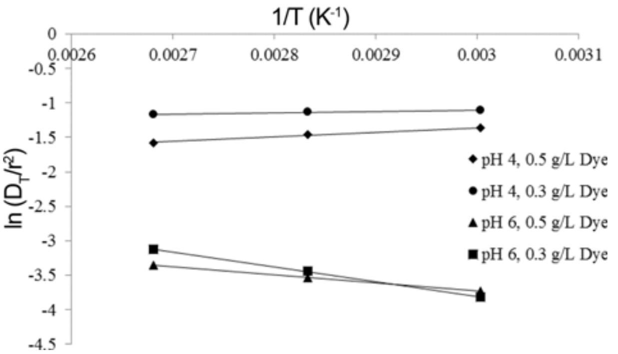


Figure 7. Plot of ln (D_T/r^2) against $1/T$ for determination of activation energy at pH values of 4 and 6.

Table 6. The activation energy of diffusion (E_a) for cochineal on wool

Parameter	pH 4		pH 6	
	C_{dye} (g/l)		C_{dye} (g/l)	
	0.3	0.5	0.3	0.5
E_a (kcal/mol)	193.0	645.7	-2153.0	-1170.0

Adsorption parameters for the dyeing of textile fiber with natural dyes have been shown in Table 7. Data in Table 7 show the equilibrium capacity of cochineal dye on wool yarn is almost similar to other natural dyes on the fibers.

FTIR Analysis

FTIR spectra of woolen yarn, cochineal dye extract and wool dyed with cochineal extract are shown in Figure 8. FTIR spectrum of wool is characterized by strong bands at 3000-3600 cm^{-1} (O-H and N-H stretching vibrations) and various amide peaks in the range of 1600-1700 cm^{-1} which are characteristic of polypeptides and proteins which is indicative of alpha-helical structures [31,32].

As mentioned earlier, cochineal contains carminic acid as

Table 7. Adsorption parameters for dyeing of fibers using natural dyes

Dye	Fiber	Temperature (°C)	K_L	S	K_N	Reference
Tea polyphenols	Wool	60	4.64	27.07	12.63	[3]
		70	1.66	51.89	17.66	[3]
		80	2.65	41.35	27.24	[3]
		90	3.59	34.50	28.39	[3]
Tea polyphenols	Silk	60	1.01	36.67	16.13	[3]
		70	1.46	18.90	15.01	[3]
		80	2.87	10.25	15.20	[3]
		90	3.78	8.86	12.29	[3]
Lac	Chitosan	40	12.91	33.53	88.30	[20]
		50	40.52	18.78	90.65	[20]
		60	52.74	13.84	85.90	[20]
Cochineal	Wool	60	7.66	86.95	80.83	Present study
		80	18.83	53.19	77.00	Present study
		100	30.30	41.32	75.20	Present study

the principal colouring matter. Theoretical values for carminic acid are [33]: OH to 3600-3000 cm^{-1} (stretching, carboxylic acids), C=O to 1730-1700 cm^{-1} (stretching, carboxylic acids), C-O to 1400 cm^{-1} (stretching, carboxylic acids), O-H to 1590 cm^{-1} (bending, carboxylic acids); C=O to 1715 cm^{-1} (stretching, ketone), C-C to 1300-1100 cm^{-1} (stretching, ketone); C-O-C to 1715 cm^{-1} (stretching diaryl ether); C-H to 3100-3000 cm^{-1} (stretching, aromatic), C=C to 1600-1475 cm^{-1} (stretching, aromatic). The FTIR spectrum of carminic acid in Figure 8 is similar to those reported in literature [33] with somewhat differences possibly due to likely differences in coloring matter ratios and contents.

FTIR spectrum of wool dyed with cochineal showed major changes as compared to un-dyed wool which confirmed the presense of cochineal on the wool as well as new interactions between wool macromolecular chain with cochineal dye like ionic interaction, hydrogen bonding, etc.

Colorimetric and Fastness Properties

Color strength (*K/S*) values of woolen yarns dyed with cochineal at pH values of 4 and 6 are given in Table 8. Wool dyed at pH 4 posssessd appreciably higher *K/S* values than wool dyed at pH 6. In general, higher *K/S* at pH 4 could be attributed to the structural features of the dye and wool. In addition, the electrostatic forces between the positively charged terminal amino groups of the polymeric chains of wool and dye molecules seems to play a dominant role in the increasing of the dyeing ability. For better evaluation of dyed wool samples, their color quality was reported in the CIE $L^*a^*b^*$ color coordinate. Data show lower lightness (L^*) values were obtained for dyed wool at pH 4 as compared to that dyed at pH 6. Further, appreciably different color shades were resulted at two different pH values of dyeing.

The results of color fastness tests of cochineal natural dye on woolen yarns are given in Table 9. Good washing fastness

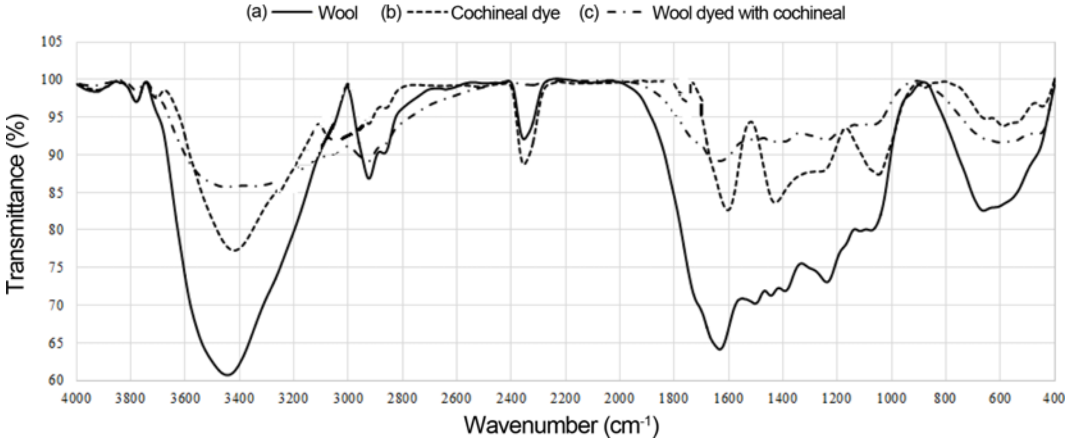


Figure 8. FTIR spectra of (a) wool, (b) cochineal extract, and (c) wool dyed with cochineal extract.

Table 8. Colorometric parameters of dyed wool with cochineal (dye concentration: 20 %owf; dyeing temperature=100 °C; dyeing time: 60 min)

pH	L^*	a^*	b^*	C^*	h^o	K/S
4	25.73	26.15	0.85	26.16	1.87	17.33
6	42.23	26.78	-7.15	27.72	345.05	4.90

Table 9. Fastness properties of cochineal dyed wool (dye concentration: 20 %owf, T=100 °C, dyeing time: 60 min)

pH	Wash fastness			Light fastness	Rub fastness	
	CC*	SC*	SW*		Dry	Wet
4	3-4	3	4-5	7	4	4
6	3-4	3	4-5	7	4	4

*CC: color change, SC: staining on cotton, SW: staining on wool.

rating (3-4) was obtained for both dyed substrates. Moreover, light fastness rating of 7 demonstrated very good rating for the stability of cochineal dye on woolen yarn against irradiated light.

Conclusion

The results of this study revealed that the kinetic, equilibrium, thermodynamic, and dyeing properties of wool fibers with cochineal natural dye were significantly affected by dyeing variables such as pH, temperature, and dye concentration. Cochineal dye adsorption onto wool fiber was strongly pH dependent. Of the various isotherm models evaluated, the dual adsorption isotherm consisting of partitioning (Nernst) and Langmuir type models were best fitted by the experimental data obtained at pH 4. The analysis of adsorption mechanism suggested that the electrostatic interactions operating between cochineal and wool contributed to Langmuir adsorption whereas non-electrostatic such as hydrogen bonding, hydrophobic interaction and van der Waals forces, contributed to Nernst adsorption. Nevertheless, at pH 6, dye adsorption process was governed by non-electrostatic interactions and thus the contribution of Langmuir adsorption to total adsorption decreased to a great extent so that the most appropriate isotherm became the Nernst type. Because of higher affinity at pH 4, cochineal exhibited better build-up properties. The increase in dyeing temperature had negative impact on equilibrium dye up-take due to lowered affinity of dye at higher temperatures. Negative enthalpy changes emphasized that the adsorption of cochineal onto wool fiber was an exothermic process. In addition, higher negative values for enthalpy and entropy changes were obtained at pH 6. Dyeing rate increased with the raise in dyeing temperature. At pH 4, diffusion coefficient of dye was appreciably higher than that of pH 6 which decreased with the increase in dyeing temperature. Although the activation energy of diffusion at pH 6 was negative due to the peculiar dye adsorption/desorption, its value was comparatively higher than the corresponding value at pH 4.

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