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A Comprehensive Study on the Kinetics and Thermodynamic Aspects of CI Acid Red 1 Dyeing on Wool

F. S. Fattahi *

Department of Textile Engineering, Isfahan University of Technology, P.O. Box: 8415683111, Isfahan, Iran

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ABSTRACT

In the present investigation, the physicochemical parameters of dyeing woolen yarn with the CI Acid Red 1 dye in terms of the kinetics and thermodynamic of adsorption were studied. Different models (Zero order, First order, Second order, Parabolic, Cegarra–Puente and modified Cegarra–Puente models) were employed to discover a suitable dyeing apparatus. It was found that the modified Cegarra-Puente model best fitted to the investigational data with the maximum correlation ($R^2 \geq 0.99$). The dyeing-rate constant, half dyeing times, rise time and fixation time were then calculated. Thermodynamic parameters, for instance the Gibbs free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$), and the activation energy (E_a), were considered. The thermodynamic parameters imply that the dying procedure could be improved by increasing the system temperature. Also, dyeing woolen yarns with CI Acid Red 1 decreases randomness and enhances the order of reaction systems by immobilizing dye molecules onto the solid fiber surface.

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1. Introduction

Dyes are part of a significant class of complexes extensively applied in various fields like textile, dye, plastic, paper, leather, rubber and cosmetic [1]. The process of dyeing materials is a challenging procedure, containing the diffusion of dyes in solutions and the adsorption of dyes to fibers [2]. Studies on the principles of dyeing have been carried out to develop the quality of dyed materials and save water and energy [3]. Dyeing kinetics is adapted to examine the rate of dye adsorption reactions throughout the dyeing route. The investigation of the dyeing kinetics is important and can aid recognize the dyeing apparatuses and advance the knowledge of dyeing fabrics [4]. A kinetic model which include the surface adsorption and diffusion into the pores is related to the motion of material bodies and forces and the

*Corresponding author: fattahi_farnaz@yahoo.com (F. S. Fattahi)

associated energy [5, 6]. Moreover, the adsorptions revealed by the mass transfer, diffusion control, and chemical reaction are essential for investigating the dyeing procedures [7]. It is well known that the Dyeing process takes place in three phases [8]:

1) Transfer of dye molecules from the solution to the external surface of the fiber [9];
2) Adsorption of the dye at the external surface of the fiber [10];
3) Diffusion of the dye from the external surface to the inner parts of the fiber [11].

Dyeing kinetics in Physics is the branch of mechanics that deals with the activities of energies in generating or varying the motion of dye molecules in the above 3 phases [12, 13]. The adsorption kinetics is explored to know the reaction between dyes and yarns in the adsorption procedure [14].

It is stated that, in a new effort in 2022, the kinetics, thermodynamics and synergistic effects of the reaction on the co-pyrolysis of cotton fibers were studied [15, 16]. In another work, the kinetics and thermodynamics of the cationic dye adsorption onto the carboxymethyl cotton fabric were investigated [17]. Rabiei et al., examined the kinetic and thermodynamic parameters of dyeing polypropylene/Clay fibers using the disperse dye [18].

In a novel work in 2022, Jiang et al., explored the mechanism, isotherm, kinetics, and thermodynamics of the absorption accelerating behavior of the surface modification of wool [19]. Islam et al. studied the ultrasonic effects on the kinetics and thermodynamics of dyeing Wool fibers with reactive dyes [20]. Mirnezhad et al., investigated the kinetic, equilibrium, and thermodynamic adsorption of the cochineal natural dye on wool fibers [21]. Ajmal et al., analyzed the effect of the mordanting process on the adsorption thermodynamics and kinetics of cochineal for wool [22]. Shen et al., explored the kinetics and thermodynamics of the monascus red dye on wool [23]. Tang et al., stated the kinetics and thermodynamics of the gas adsorption on wool fibers [24]. Also, the dyeing thermodynamics of Lac Red on wool fibers were considered [25]. Tang et al., studied the kinetics of dyeing wool fibers with silver nanoparticles [2]. In a different work, the dyeing thermodynamics of Luteolin on wool fabrics was explored [26]. In another research, the kinetic model and adsorption isotherm of natural Indigo and Madder colorants for dyeing wool in one and two dye baths were studied [27].

This research was started with a work to explore the kinetic and thermodynamic aspects of dyeing woolen yarns with CI Acid Red 1(A milling acid dye, see Table 1). Also, from this aspect, to the best knowledge of the author, there could not be found any papers among the literatures on the kinetic and thermodynamic parameters of applying CI Acid red 1 dye on woolen substrates. Consequently, part of this exploration was devoted to considering a simple route for studying the kinetics and thermodynamics of dyeing wool with CI Acid Red 1.

2. Experimental section

2.1. Materials

2.1.1. Woolen yarns

The dyeing material was a single thread 100 % plain woven grey woolen yarn with a yarn count of 102/18 twist /m, which was acquired from a retail store in Isfahan, Iran. Wool carpet yarns are natural protein-based

yarns, which have been used in Persian carpets or rugs for thousands of years. The woolen yarns were scoured to eliminate any probable impurities which could possibly affect the subsequent surface treatment. Unprocessed woolen yarns were pre-scoured in a bath having 2 g/l of Diadavin Ewnol (non-ionic surfactant, Saveh Rezin) and at 60 °C for 15 min, using the liquor-to-materials ratio (LMR) of 40:1. After scouring, the samples were rinsed with water and then dried under ambient conditions overnight.

2.1.2. Acid dye

CI Acid Red 1 (Eriofloxine 2GN, 100 % purity) (chemical formula, $C_{18}H_{13}N_3Na_2O_8S_2$), ($M_{wt}$ = 509.43 g/mol, λ_{max} = 540 nm) was purchased from Alvan Sabet Co. (Iran) (Table 2).

The respective molecular construction of C.I. Acid red 1 is displayed in Figure 1.

Table 1
Properties of CI Acid red 1.

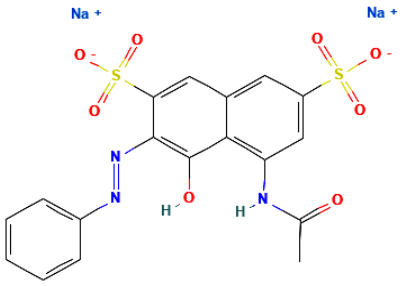
Chemical configuration		
Molecular formulation	$C_{18}H_{13}N_3Na_2O_8S_2$	
	Atoms: 46	Bonds: 46
Color index name	Acid Red 1	
Commercial name	Eriofloxine 2GN	
Color index number	18050	
CAS number	3734-67-6	
E number	E128 (Red)	
ECHA InfoCard	100.020.999	
λ_{max} (nm)	540	
M_w (g/mol)	509.43	
Mono-isotopic mass (g/mol)	508.99394529	

Table 2
Physical and chemical aspects of CI Acid red 1.

Phisycal state (At room temperature)	Powder
Chemical formula	Benzeneazo-8-acetylamino-1-naphthol-3,6-disulfonic acid, sodium salt
Rotatable bond count	3
Defined bond stereo-center count	1
Solubility in water, g/100 mL	18 (at 20 °C)
Solubility in glycerol, g/100 mL	1
Solubility in ethanol	Negligible in ethanol

Figure 1. A) Molecular construction of C.I. Acid Red 1 (Space-filling model), Color cypher: Carbon, C: black, Hydrogen, H: white, Oxygen, O: red, Nitrogen, N: blue, Sodium, Na: lilac, Sulfur, S: yellow; B) The optimized structure of C.I. Acid Red 1 (3D Model by JSmol software).

2.2. Instruments

A UV/VIS spectrophotometer (Jenway AVR 2000 over the range of 380 to 720 nm) was applied to calculate the absorbance of the dye bath solution.

2.3. Dyeing process

Dyeing wool yarns was done in a solution media using the L:R ratio of 40:1 at 1 % on the weight of fiber (o.w.f). The pH of the dyeing bath was adjusted to 3.5-4 using a Sulphoric Acid/Sodium Sulphate buffer solution. As it is shown in Figure 2, the dyeing started at 40 °C, and then ramped to the dyeing temperature of 90 °C, at 2 °C per minute and held this temperature for 60 minutes. After dyeing, the yarns were rinsed with warm water for five minutes and with cold water two minutes and then air-dried at room temperature.

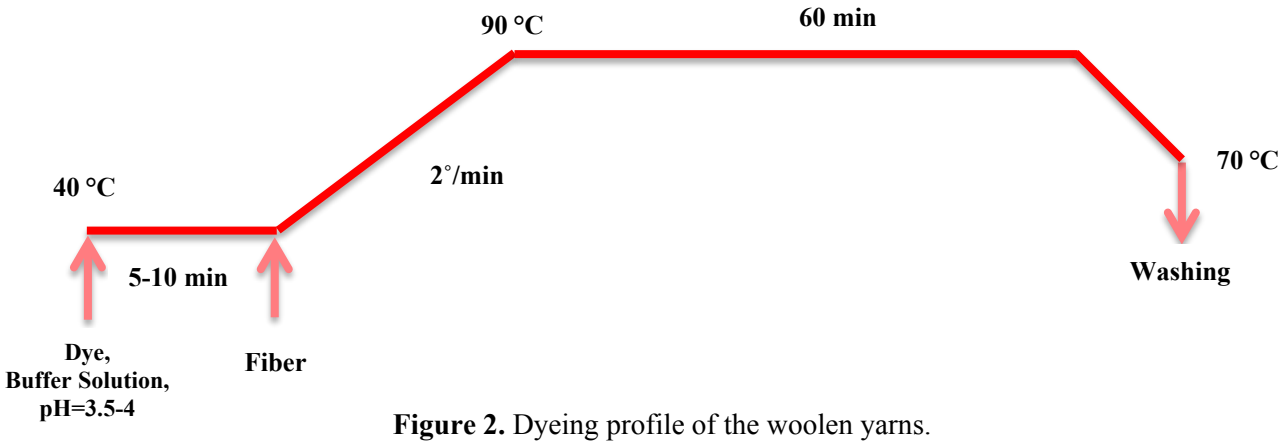


Figure 2. Dyeing profile of the woolen yarns.

2.4. Kinetic studies

2.4.1. The Definition of the dye bath exhaustion

At the end of the dyeing procedure, the amount of the dye bath exhaustion E (%) is specified by the following equation:

$$\text{Exhaustion (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial concentration of CI Acid Red 1 in the dye bath before dyeing (mgL^{-1}), and C_t is the residual concentration of CI Acid Red 1 in the dye bath after dyeing (mgL^{-1}).

2.4.2. Defining the dyeing kinetics

The kinetics of adsorption offers valuable and helpful data about the adsorption rate of the procedure and possible rate controlling phase. For this purpose, various kinetic models listed in Table 3 were used.

Table 3
Linearized form of the used kinetic models.

Kinetic model	Linearized form	Ref.
Zero order	$C_t - C_0 = K_0 t$	[28]
First order	$\ln\frac{C_0}{C_t} = K_1 t$	[7]
Second order	$\frac{1}{C_t} - \frac{1}{C_0} = K_2 t$	[29]
Parabolic	$C_t = k\sqrt{t}$	[30]
Cegarra-Puente	$\ln\left(1 - \frac{{C_t}^2}{{C_\infty}^2}\right) = -K_{CP} t$	[31]
Modified Cegarra-Puente	$\ln\left[-\ln\left(1 - \frac{{C_t}^2}{{C_\infty}^2}\right)\right] = a\ln t + a\ln K_{1CP}$	[32]

2.4.3. Validity of the kinetic model

The validity of the dyeing data (which were fitted to the kinetic models) was compared with adjudging from the R^2 values [33].

2.5. Determining the thermodynamic parameter

2.5.1. Arrhenius-equation

The apparent activation energy can be estimated with the Arrhenius equation as specified in Equation (2), where K is the absorption rate constant at temperature T, E is the apparent activation energy, A is the frequency factor, R is the gas constant (R = 1.9858 cal/molK) and T is the absolute temperature (K) [34].

$$K = A * \exp^{\left(-E_a/R*T\right)} \quad (2)$$

3. Results and discussion

3.1. Extinction coefficient of CI Acid Red 1

The kinetics of the dye relates to the determination of the concentration of the dye in the bath in a period of time. The molar extinction coefficient of the Beer–Lambert law (Equation 3) permits the association of the absorbance of the solution with the consistent concentration of the dye to be estimated [22]:

$$A = \varepsilon \times C \times l \quad (3)$$

where ε is the molar extinction coefficient that is dependent on the material and its wavelength, l is the path length, and C is the concentration of the dye in the solution. For determining this, the absorbance of solutions holding various concentrations of CI Acid Red 1 was quantified at maximum wavelength values (540 nm). Figure 3 displays the Beer–Lambert law plot of CI Acid Red 1.

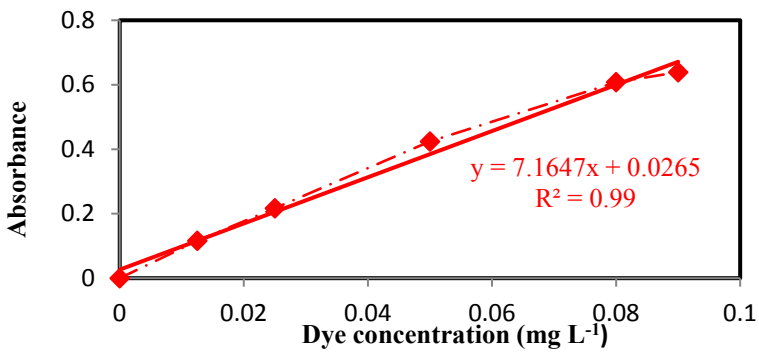


Figure 3. Beer–Lambert law plot of the CI Acid Red 1 dye (at λ_{max} = 540 nm).

Table 4 shows the extinction coefficient of CI Acid Red 1 and its relative correlation coefficients.

3.2. Exhaust dyeing process

The exhaust technique is the most common method of applying dyes, as it is resistant to small changes in system variables. The procedure involves gradually transferring the dye from a dye bath to the textile material using the dyeing equipment. This study set the dyeing condition at 338-363 K for 2-100 min.

Table 4
Extinction coefficient of the CI Acid Red 1 dye.

Dye	λ_{max}, nm	ϵ , L mg^{-1} cm^{-1}	R^2
CI Acid Red 1	540	7.1647	0.99

3.2.1. Exhaustion curves

All of the dyeing procedure in this step of work was carried out using the yarns (2.5 g) that had been wetted out in tap water, in stainless steel dye containers housed in a research laboratory scale dyeing instrument with a 1 % on weight of the fiber (o.w.f), and a liquor ratio of 40:1. To study the curves of dyeing woolen yarns with CI Acid Red 1, the exhaustion (%) of the dye bath was quantified at different periods throughout the dyeing procedure (2, 5,10, 15, 30, 50, 80, 90 and 100 minute). Figure 4 displays the curves of the kinetics of the dyeing process at 338 K, 348 K and 363 K.

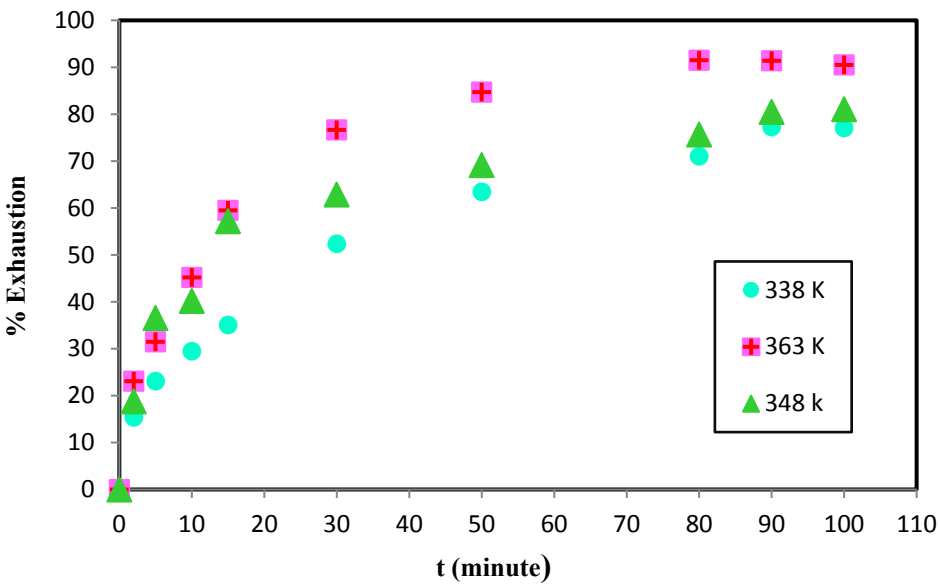


Figure 4. Curves of the kinetics for dyeing woolen fibers with Acid Red 1 : Plot of the exhaustion percentage against the dyeing time at various process temperatures (338 K, 348 K and 363 K).

From the consequences observed, it can be realized that the forms of the various curves were alike. However, in the procedures at higher temperatures, a time of 40 minute was essential to get the extreme values of the dye bath exhaustion. The maximum values of the dye bath exhaustion, the half-dyeing time, the rise-time and the fixation-time of the dyeing

procedure were assessed as presented in Table 5. The half-dyeing time (signified as $t_{\frac{1}{2}}$) matches up to the time taken the woolen yarns to absorb half of the quantity of CI Acid Red 1 that it will have absorbed when the equilibrium is reached. Moreover, the shorter the half-dyeing time; the faster the dyeing speeds, and consequently, the greater the diffusion coefficient [35]. The fixation-time is the essential period for the dye to be adsorbed, then diffused and lastly fixed to the amorphous regions of the yarns [36].

Table 5
Various dyeing times of CI Acid Red 1.

Temperature (K)	Half-dyeing time [a] (minute)	Rise-time [b] (minute)	Fixation-time [c] (minute)	% Exhaustion at E_m
338	20	40	80	~ 77
348	11	22	44	~ 80.5
363	10	20	40	~ 91

[a] The half-dyeing time $t_{\frac{1}{2}}$ is the period necessary to reach 50 % of the exhaustion-time. [b] The rise-time = 2 × $t_{\frac{1}{2}}$. [c] The fixation-time = 4 × $t_{\frac{1}{2}}$

3.3. Studying dyeing kinetics

The kinetic studies predict the progress of the adsorption of dyes during the dyeing procedure to reach the equilibrium [37, 38]. Dyeing kinetic investigations are vital in enhancing the procedure condition for the adsorption of dyes on the textile yarns [39]. The kinetic data obtained at 338 K, 348 K and 363 K were analyzed using various models to collect information about their effect on the dyeing rate.

3.3.1. Kinetic models

In this research, a kinetic model of the dyeing process was investigated by zero order, first order, second order, Parabolic, Cegarra–Puente and modified Cegarra–Puente models. Firstly, three common kinetic models were selected in this investigation to describe the dyeing process: the zero order, first order and second order [40].

a) Zero order equation

$$C_t - C_0 = K_0 t \quad (4)$$

wherever C_o and C_t (mg/L) are the concentrations of the dye at the primary time and at time t, k_0 (L/min) is the rate constant of the zero order kinetics [20, 40].

b) First order equation

$$\ln \frac{C_0}{C_t} = K_1 t \quad (5)$$

wherever C_o and C_t (mg/L) are the concentrations of the dye at the primary time and at time t, k_1 (L/min) is the rate constant of the first order kinetics [13, 41].

c) Second order equation

$$\frac{1}{C_t} - \frac{1}{C_0} = K_2 t \quad (6)$$

wherever C_o and C_t (mg/L) are the concentrations of the dye at the primary time and at time t, k_2 (Lmg/min) is the rate constant of the second-order kinetics [42].

d) Parabolic equation

In theory, this equation is adapted to the outcomes of the investigation only from the start of the dyeing procedure to half the dyeing period, even though in several cases it

can also be applied well beyond the half time while the exhaustion levels are great [26].

$$C_t = K_P\sqrt{t} \quad (7)$$

C_t is the concentration of the dye at time t, 'K' is the dyeing rate constant and 't' is the dyeing period [43].

e) Cegarra–Puente equation

This equation is appropriate for dyeing in baths at constant concentrations [44].

$$\ln\left(1 - \frac{{C_t}^2}{{C_\infty}^2}\right) = -K_{CP}t \quad (8)$$

where C_t is the concentration of the dye at time t, C_∞ is the concentration of the dye at the equilibrium, K is the absorption rate constant and t is the dyeing period [6, 14].

f) Modified-Cegarra–Puente equation

Eq. (6) is deduced for baths with constant concentrations. On the other hand, it can be reformed to baths by the variable exhaustion, presenting the suitable modification, wherever 'a' is the coefficient dependent on the exhaustion [45, 46]. The modified equation is:

$$\ln\left[-\ln\left(1 - \frac{{C_t}^2}{{C_\infty}^2}\right)\right] = a\ln t + a\ln K_{1CP} \quad (9)$$

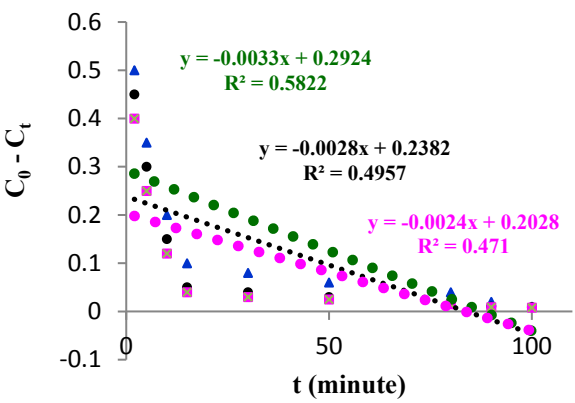
3.3.2. Determination of dyeing kinetics

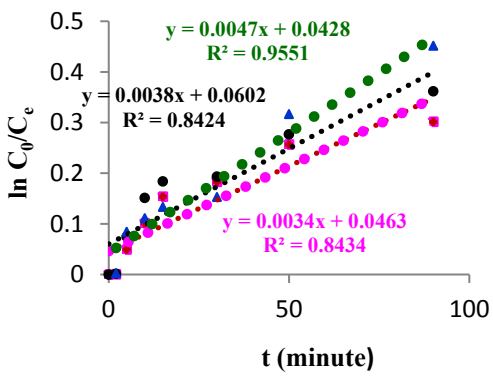
The experimental data were analyzed by zero order, first order, second order, Cegarra–Puente and modified-Cegarra–Puente kinetic model equations given in Table 6.

Figure 5 shows plots for the kinetic models for different dyeing temperatures.

Table 6
Plots, slopes and intercepts of the used kinetic models.

Kinetic model	Plot	Slopes	Intercepts
Zero order	$C_0 - C_t$ vs t	K_0	----
First order	$\ln\frac{C_0}{C_t}$ vs t	K_1	----
Second order	$\frac{1}{C_t} - \frac{1}{C_0}$ vs t	K_2	----
Parabolic	C_t vs $\sqrt{t}$	K_P	-----
Cegarra–Puente	$\ln\left(1 - \frac{{C_t}^2}{{C_\infty}^2}\right)$ vs t	$-K_{CP}$	----
Modified-Cegarra–Puente	$\mathrm{Ln}\left[-\ln\left(1 - \frac{{C_t}^2}{{C_\infty}^2}\right)\right]$ vs ln t	a	$a\ln K_{1CP}$





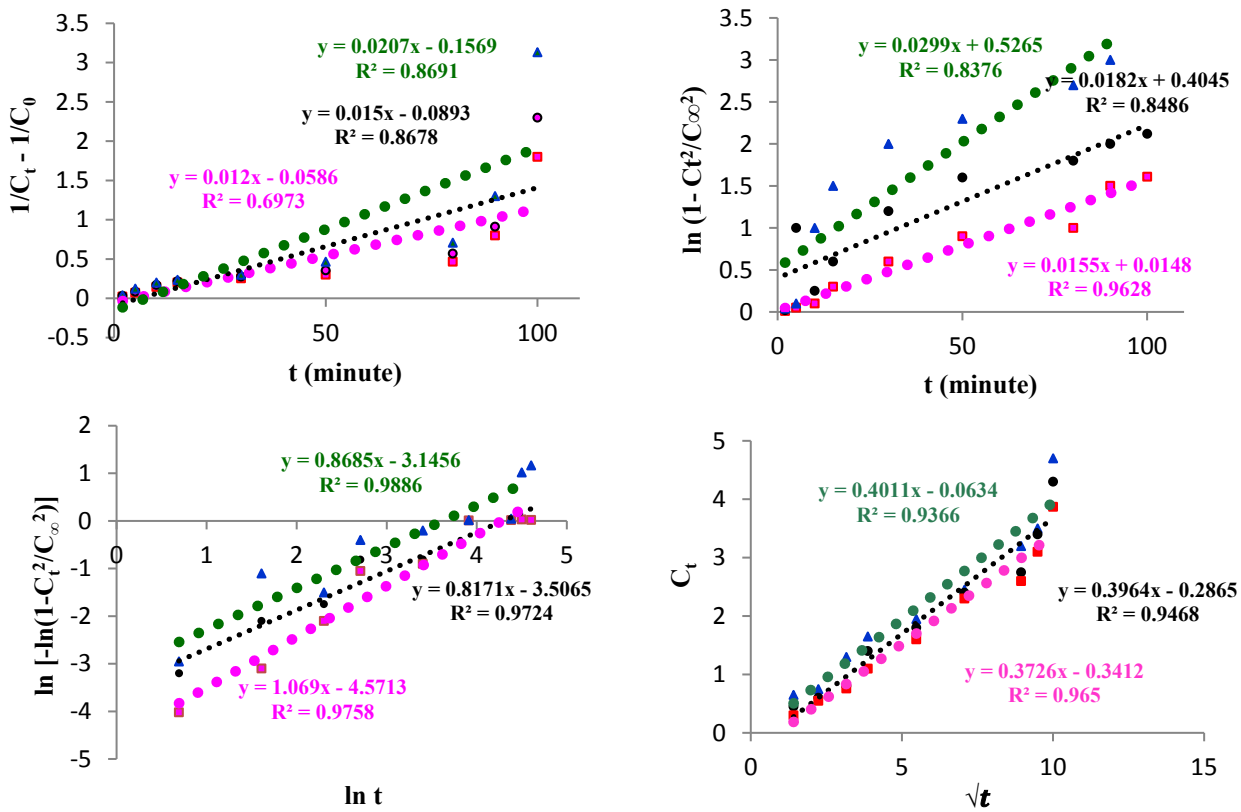


Figure 5. Kinetic data fitted to zero order , first order, second order, Cegarra–Puente , modified Cegarra–Puente and Parabolic models at different temperatures (338 K ■, 348 K ● and 363 K ▲).

The model being widely used to analyze the adsorption of the dye through the material surface means that the coefficient of determination (R^2) can be examined to test the authenticity of the selected model [6, 24, 47].

3.3. Absorption rate constants

The parameters were analyzed by linear analyses (MS Excel 2010), and the results are presented in Table 7.

Table 7

Kinetic rate constants and correlation coefficients obtained for the adsorption of CI Acid Red 1 dye on wool.

Kinetics model	Rate constant	338 K	348 K	363 K
Zero order	$K_0(min^{-1})$	0.5822	0.4957	0.471
First order	$K_1(min^{-1})$	0.8434	0.8424	0.9551
Second order	K_2 ($mgL^{-1}min$)	0.8973	0.8678	0.8691
Parabolic	K_p($mg\ g^{-1}\ min^{-1}$)	0.965	0.946	0.936
Cegarra–Puente	K_{CP} (min^{-1})	0.9628	0.8486	0.8376
Modified Cegarra–Puente	$K_{mCP}(min^{-1})$	0.9758	0.9824	0.9986

The correlation coefficients (R^2) were highest in the Cegarra–Puente model (in the range of 0.97-0.99). The results show that dyeing woolen substrates with the CI Acid Red 1 dye follows the Cegarra–Puente kinetic model. This result is completely consistent with the outcomes of the work done by Riva et al., who explored the kinetic model for the

dyeing process of woolen fabrics with acid dyes [48]. The absorption rate constant (K) for dyeing woo1 with CI Acid Red 1 is given in Table 8.

Table 8
Absorption rate constant obtained for the adsorption of CI Acid Red 1 dye on wool at different temperatures.

Temperature (K)	338 K	348 K	363 K
K (min^{-1})	0.042	0.051	0.065

3.4. Thermodynamic investigations

Thermodynamic investigations were carried out while the system reached the equilibrium, to explore the energy changes associated with the adsorption procedure, to evaluate the nature and possibility of the adsorption procedure, and to determine the category of the adsorption procedure (physical, chemical or endothermic, exothermic) [49]. Thermodynamic parameters are essential to our understanding of the effect of temperature on the dyeing process [50, 51].

The activation energy (E_a) is a vital kinetic factor [52]. According to Arrhenius law (Equation 2), to determine the activation energy (E_a) for the dyeing process, the plot of the ln of k vs 1/T, the resultant straight line will have a slope equal to E_a/R (Figure 6, Table 9). The obtained E_a value was equal to 17.7661 kJ/mol. Table 10 compares the outcomes of the kinetics in this investigation with other researches. The difference in values is probably due to the chemical and physical structures of the acid dyes.

3.4.1. Activation parameters

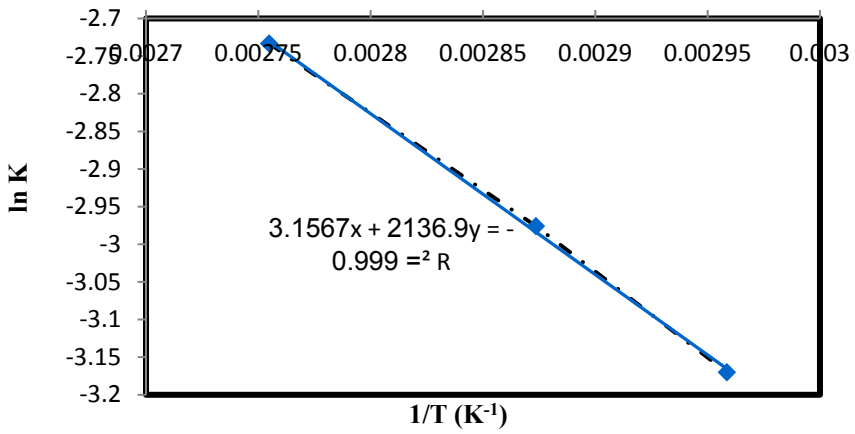


Figure 6. Plot of the ln of K (modified Cegarra–Puente kinetic constant) versus $^{1}/_{T(K)}$ to define the activation energy of the dyeing procedure.

Table 9
Activation parameters from kinetic data for the CI Acid Red 1 dye adsorption onto wool.

Temperature (K)	ln A	E_a ($kJmol^{-1}$)	R^2
338			
348	3.1567	17.7661	0.999
363			

Table 10
Absorption rate constants and activation energy for dyeing wool with acid dyes at 348 K.

ACID DYE	K (min^{-1})	E_a ($kJmol^{-1}$)	Reference
CI Acid Red 1	0.0580	17.7661	This research
CI Acid Blue 80	0.0650	15.078	[53]
CI Acid Black 194	0.0771	24.491	[48]

3.4.2. Gibbs free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$)

The free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$), and entropy ($\Delta S^{\#}$) of the activation of dying process was calculated based on the Eyring-equation as follows [54]:

$$\ln\left(\frac{K}{T}\right) = \ln\left(\frac{K_b}{h}\right) + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \quad (10)$$

wherever K_b is the Boltzmann constant (1.3807×10^{-23} JK^{-1}), h is the Planck constant (6.6261×10^{-34} Js), k is the modified Cegarra–Puente kinetic constant [31]. The plots of $\ln(K/T)$ vs. $1/T$ are in agreement with Equation (10) for the dyeing process which are represented in Figure 7.

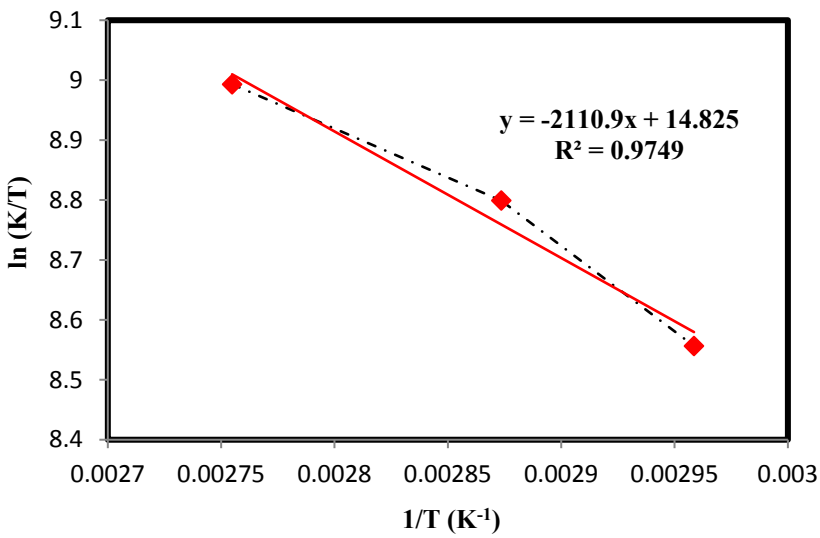


Figure 7. Modified Cegarra–Puente dyeing kinetic models of dyeing wool fibers with CI Acid Red 1; Plots of ln (k/T) as functions of $1/T(^{\circ}K)$.

The amounts of $\Delta H^{\#}$ and $\Delta S^{\#}$ of dyeing procedures were evaluated in the light of the slope and intercept of a plot of ln (K/T) against $\frac{1}{T}$ (Table 10). Besides, $\Delta G^{\#}$ can be determined by means of the enthalpy and entropy of the activation as stated by Equation (11) [1].

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad (11)$$

The positive amount of $\Delta G^{\#}$ at a certain temperature indicates that the procedures of dyeing woolen fibers with CI Acid Red 1 are not spontaneous [55]. The amounts of $\Delta G^{\#}$ improved with temperature and were positive, signifying that the adsorption reaction needs energy. Extra energy is required during the interaction between CI Acid Red 1 and woolen fibers.

Table 11
Thermodynamic parameters for the adsorption of CI Acid Red 1 dye onto wool.

$\Delta H^{\#}$ (KJ mol^{-1})	$\Delta S^{\#}$ (KJ mol^{-1} T^{-1})	$\Delta G^{\#}$ (KJ mol^{-1})		
		338 K	348 K	363 K
17.55002	-0.07428	42.6566	43.3994	44.5136

The positive value of $\Delta H^{\#}$ ($\Delta H^{\#} > 0$) indicates that the dying process was endothermic [56, 57]. Energy was required for the adsorption of CI Acid Red 1 onto woolen fibers. The dyeing procedure can be improved by increasing the system temperature [58]. The negative $\Delta S^{\#}$ amounts expose that the dyeing woolen yarns with CI Acid Red 1 decreases randomness and enhances the order of reaction systems by immobilizing the CI Acid Red 1 dye molecules onto the solid fiber surface.

3.5. Proposed dyeing mechanism

The schematic representation of the proposed mechanism for dyeing wool with CI Acid Red 1 can be seen in Figure 8.

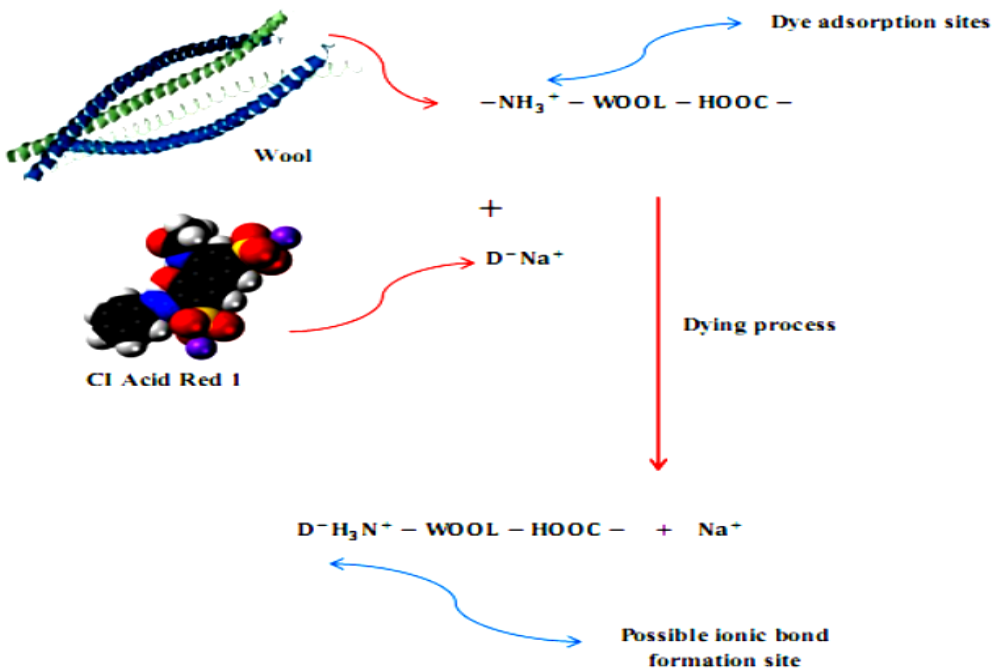


Figure 8. Schematic representation of the proposed mechanism for dyeing wool with CI Acid Red 1.

4. Conclusions

In the present investigation, the physicochemical parameters of the process of dyeing woolen yarn with CI Acid Red 1 dye in terms of the kinetics and thermodynamic of adsorption were studied. The main results are as follows:

- It was found that the modified Cegarra-Puente model best fitted to the experimental data with the highest correlation ($R^2 \geq 0.99$).
- The dyeing rate constant, half dyeing times, rise time and fixation time were then calculated (K (min^{-1}) as 338 K, 348 K and 363 K: 0.042, 0.051 and 0.065).

❖ The thermodynamic parameters, such as the Gibbs free energy ($\Delta G^{\#}$), enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$), and the activation energy (E_a) were considered ($\Delta G^{\#}$ at 338 K, 348 K and 363 K: 42.6566, 43.3994 and 44.5136 KJ mol^{-1}, $\Delta H^{\#}$: 17.55002 KJ mol^{-1}, $\Delta S^{\#}$: -0.07428 KJ mol^{-1} T^{-1}, E_a: 17.7661 $kJmol^{-1}$).

❖ The thermodynamic parameters imply that the dyeing procedure can be improved by increasing the system temperature. Furthermore, this dyeing process decreases randomness and enhances the order of reaction systems by immobilizing dye molecules onto the solid fiber surface.

5. Outlook and future perspectives

Investigating the kinetics and thermodynamics of chemical reactions is one of the important topics of chemical engineering. Today, the process of dyeing textiles, especially woolen clothes, is one of the most important issues in the textile industry, and the approach of researchers in this field is to optimize this procedure via the application of novel techniques (such as UV/O_3 irradiation). Therefore, it seems that the future horizon of research in this field is the thermodynamic and kinetic investigation of dyeing woolen textiles (fibers, yarns and fabrics) with various dyes after enzymatic or radiation treatment.

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Nomenclature

R^2	correlation coefficient.
C_o	initial concentration [mg L^{-1}].
C_e	equilibrium concentration [mg L^{-1}].
$t_{1/2}$	half dyeing times [min].
K_0	kinetic rate constant of Zero order model [min^{-1}].
K_1	kinetic rate constant of First order model [min^{-1}].
K_2	kinetic rate constant of Second order model [$mgL^{-1}min$].
K_p	kinetic rate constant of Parabolic model [mg g^{-1} min^{-1}].
K_{cp}	kinetic rate constant of Cegarra–Puente model [min^{-1}].
K_{mCP}	kinetic rate constant of modified Cegarra–Puente model [min^{-1}].
E_a	activation energy [kJ mol^{-1}].
$\Delta H^{\#}$	enthalpy [J].
$\Delta S^{\#}$	entropy [J K^{-1}].
$\Delta G^{\#}$	Gibbs free energy [kJ mol^{-1}].
K	absorption rate constant [min^{-1}].
E	Apparent activation energy [kJ mol^{-1}].
A	Frequency factor [L mol^{-1} s^{-1}].
R	Gas constant [JK^{-1} mol^{-1}].
T	Absolute temperature [K].

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