

Extraction, Identification and Sorption Studies of Dyes from Madder on Wool

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ABSTRACT: Since the last decade, the application of natural dyes on textile materials is gaining popularity all over the world, possibly because of increasing awareness of environment, ecology, and pollution control. In this research, extraction of dyes from madder at different conditions has been studied. The extracted dyes from madder were examined by TLC and HPLC. The adsorption properties of the dyes extracted from madder on natural polyamide fibers (wool) were also determined. The rate of dyeing at different temperatures, as well as the values of

standard affinity, entropy, and enthalpy was calculated. The results indicated that increase of temperature leads to decrease the values of partition ratio and affinity. The adsorption isotherm was tested by fitting the adsorption data with Langmuir, Freundlich, BET, and Temkin isotherms. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3799–3808, 2009

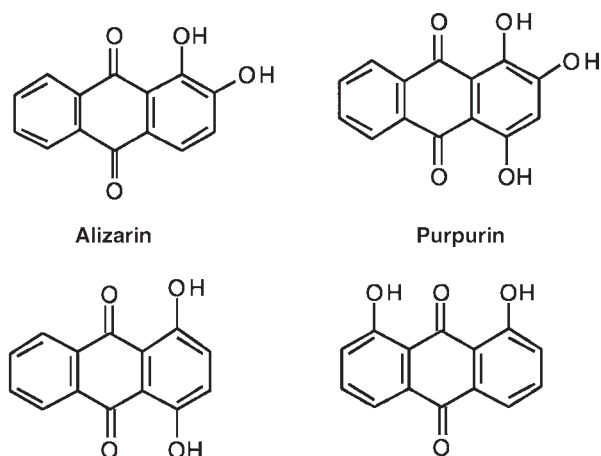
Key words: madder; chromatography; wool; thermodynamics; adsorption isotherm; dyeing

INTRODUCTION

Natural dyes have become a part of human life since time immemorial. People used to try to dye carpet, rug, and cloth by using roots, stems, barks, leaves, berries, and flowers of various dye plants.¹ Since the last decade, application of natural dyes on textile materials is gaining popularity all over the world, possibly because of increasing awareness of environment, ecology, and pollution control. In the present context of eco preservation, natural dyes have acquired tremendous commercial potential as some of the synthetic dyes are associated with the release of enormous amount of hazardous chemicals into the environment. Though vegetable dyes cannot replace synthetic dyes, they have several advantages over synthetic dyes with regard to health, safety, and ecology. Natural dyes exhibit better biodegradability and generally have a better compatibility with the environment.^{1–10} Madder is a source of a natural dye producing a variety of anthraquinone pigments in its roots and rhizomes. The main components are di- and trihydroxyanthraquinones, alizarin, and purpurin and their derivatives, ruberythric acid (alizarin – primeveroside), psedopurpurin, and lucidin – primeveroside. Rubiadin, munjisti, quinizarin, lucidin, and 1,8-dihydroxy-anthraquinone are

also identified from plant tissues.¹¹ Madder is an old and famous dye for dyeing wool, silk, and cotton fibers. Banyai et al. determined amount of alizarin and purpurin in Madder. Also, they reported that 1,4-dihydroxyanthraquinone and 1,8-dihydroxyanthraquinone in not identify in their samples.¹¹ The chemical structure of more important coloring compounds i.e. alizarin and purpurin presented in Figure 1. Grygar et al. identified alizarin and purpurin as the main components in madder by TLC analysis.¹² Recently, the thermodynamic and kinetic study of natural dyes on textile fibers is an important issue. It has been reported that dyeing of wool fibers using natural dyes follow the same mechanism as disperse dyes.¹³ According to previous studies, it was indicated that adsorption isotherm of natural dyes on wool and silk fibers fitted to the Langmuir and Freundlich isotherm.^{14–16} In this research, we decided to identify and determine amount of coloring compounds in madder produced in Iran by TLC and HPLC. It is known that madder produced in different area has various amounts of dyes. Knowing the coloring compounds in madder produced in Iran specially Fars province helps to analyze the adsorption data of madder on wool samples. In Iranian workshops, the dyers have used madder for dyeing wool (carpet yarns) by traditional methods. There is no scientific data (i.e. thermodynamic properties) of dyeing of wool with madder. This research work also aims to study the thermodynamic properties of adsorption of madder on wool fibers.

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1,4-dihydroxyanthraquinone 1,8-dihydroxyanthraquinone

Figure 1 Chemical structure of main compounds of madder.

EXPERIMENTAL

Materials

Wool

To evaluate the reflectance data on samples, we applied fabric in this study. Woven wool fabric with the following characteristics was gifted from Iran Merino: weight 205 g/m², 72 ends inch, 64 picks per inch. Before being used, the fabric was treated with a solution containing 2 g/L non-ionic detergent, 1 g/L sodium carbonate at 70°C for 30 min and L : G 50 : 1. Then, the fabric was thoroughly washed with water and air dried at room temperature.

Natural dye

Madder was purchased from Fars province, Iran and was finely powdered in a mill.

Chemicals

For HPLC analysis, alizarin, purpurin, quinizarin (1,4-dihydroxyanthraquinone), and 1,8-dihydroxyanthraquinone were purchased from Fluka. Acetonitrile and methanol of HPLC grade were prepared from Merk. Ammonium formate, trifluoroacetic acid powders were purchased from Sigma-Aldrich. Ethyl acetate and methanol and other solvents for TLC analysis purchased from Merk. A TLC paper (silica gel 60 F₂₅₄) was used for identification of coloring compounds in madder.

HPLC conditions

Chromatography was performed using a Spectra Physics (Fremont, CA) system consisting of a P4000 quaternary gradient pump, a FOCUS scanning UV-

VIS detector. The volume injected was 20 μL. Quantitative determination of alizarin and purpurin was performed at 254 nm on a 5 μm ECLIPSE XDB-C8, 150 × 4.6 mm² I.D. (Phenomenex, Torrance, CA) with an eluent of a 45 : 55 (v/v) mixture of acetonitrile: 20 mM ammonium formate (pH 3). The flow-rate was 1 mL/min. The solvent was filtered through a nylon membrane (0.45 μm × 47 mm; Supelco) and degassed by sonication before use. Peaks were identified by adding authentic standards and diode-array detection. Peak purity testing was performed and all peaks were found pure, both up, and down the peaks. A similarity test of alizarin and purpurin in a sample was performed by comparing the similarity of peaks in a sample track to that of a library maintained for the anthraquinones. The peak homogeneity was tested by examining the UV spectrum for different points on the emerging peaks.

Calibration of HPLC

Standard solutions of alizarin, purpurin, quinizarin (1,4-dihydroxyanthraquinone), and 1,8-dihydroxyanthraquinone at 1, 5, 15, 30, and 100 μg/mL were prepared in methanol. A 20 μL volume of each standard solution was injected in triplicate onto the HPLC column. The calibration graphs were constructed by plotting the peak areas of alizarin, purpurin, quinizarin (1,4-dihydroxyanthraquinone), and 1,8-dihydroxyanthraquinone versus their concentrations.

Instrumentation

A Unico 4802 UV-Visible spectrophotometer was used for absorbance measurements using quartz cell of 1 cm path length. A Shimadzu 1601 PC UV-Visible spectrophotometer was used for measuring of color strength (K/S). A pH meter (Metrohm 691) was used to measure the pH values of the dyeing bath. A shaker bath equipped with thermostat (SDL-D403/1-3) operated at 75 rpm, was used to study the adsorption and kinetics of madder dye onto wool sample.

METHODS

Dye extraction

Dye extraction was carried out in 100 mL distilled water at different pH (3,7, and 8) and temperatures (60 and 100°C) using varying amount of the dye materials (1–8 g dye in 100 mL water) for different time intervals (15–180 min). The aqueous solution was filtered and the filtrate concentrated under reduced pressure (rotary evaporator) to give a crude madder dye extract.

Dyeing

Dyeing wool samples was carried out in a dye bath containing different dye solution, which were extracted at different pH (3, 7, and 8), temperatures (60 and 100°C), times (30–180), and dye materials (1–8 g dye in 100 mL water) with L : G 100 : 1. The dyed samples were rinsed with cold water and finally dried at ambient temperature.

Kinetic studies

One gram of wool sample was dyed with madder at 40, 60, and 100°C and pH 3 at different times, keeping the L : G 100 : 1 and an initial dye concentration of 4160 mg/L. The quantity of dye adsorbed on wool samples were estimated using the following eq. (1):

$$q_t = (C_0 - C_t)V/W, \quad (1)$$

where, q_t is the quantity of dye adsorbed on wool samples (mg/g wool) at any time, C_0 and C_t are the initial and dye concentrations (mg/L) after dyeing time t , respectively. V is the volume of dye bath (mL) and W is the weight of wool sample (g).

The madder concentrations graph for standard solution versus absorbance at 430 nm wavelength, at where the maximum absorbance was reached, was prepared and used to determine the concentration of an unknown solution. For each dyeing, the absorbance of dye solution was monitored until it was unchanged. Then, the equilibrium concentrations of madder in the residual bath and the dye uptake were calculated using the standard graph. Subsequently, the dyeing rate of madder on wool was plotted.

Equilibrium studies

One gram of wool sample was dyed with different dye concentrations at 40, 60, and 100°C, pH 3 for 120 min. The quantity of dye adsorbed on wool samples at equilibrium were estimated using the following eq. (2):

$$q_e = (C_0 - C_e)V/W, \quad (2)$$

where, q_e is the quantity of dye adsorbed on wool samples (mg/g wool) at equilibrium, C_0 and C_e are the initial and equilibrium dye concentrations (mg/L), respectively. V is the volume of dye bath (mL) and W is the weight of wool sample (g).

K/S

K/S values of the dyed samples were measured and the K/S values were assessed using the Kubelka-Munk eq. (3)¹⁷:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (3)$$

where, R is the observed reflectance, K the absorption coefficient, and S the light scattering coefficient.

RESULTS AND DISCUSSION

Dye extraction

Effect of extraction time and temperature on absorption, K/S, and yield

To extract high amounts of dyes from Iranian madder, different extraction methods studied. Extraction carried using 1 g madder in 100 mL water in different conditions. The results of K/S, absorbance, and yield are presented in Table I. It can be inferred that an increase of extraction time at 60 and 100°C, causes increase in dye yield. However, the yield increase rate decreases after 120 min at 60°C and 90 min of extraction at 100°C. The results also show that K/S values of dyed samples with dye solution extracted at different temperatures and times are similar to yield results. The absorbance values of extracted dye solution at different temperatures and times at 430 nm confirm the above results. It can be seen that several increases of time different times lead to higher absorbance for extracted dye for 90 min at 100°C and 120 min at 60°C. After these times, the absorbance increase rate lowers. Increasing of yield, absorbance, and K/S with increasing time can be attributed to more possible contact between coloring compounds and water. Also, according to obtained results, it can be suggested that increasing of temperature causes an increase in activation energy.

Effect of pH on absorption, K/S, and yield

The extraction of madder (1 g/100 mL water) was carried out at different pH of 3, 7, and 8. The results show that yield, absorbance, and K/S values of dyed samples with extracted dye solution increases with the increasing of pH (Table I).

Effect of dye weight in 100 mL water on absorption, K/S, and yield

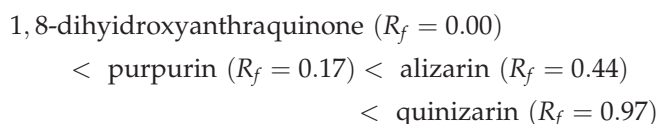
The results in Table I show that increase in dye weight in 100 mL water leads to increase in the yield of the extracted dye. The maximum extraction was attained with 6 g/100 mL of water and increasing of dye percent does not affect on yield of extracted dye. In fact, with 6 g/100 mL of water the solution saturated. The results of absorbance and K/S values in Table I confirmed that the maximum extractability attained with 6 g/100 mL of water. Results show that increase in dye percentage leads to obtain a higher absorbance to 6 g/100 mL of water. With higher dye weights, there is no considerable change in the absorbance.

TABLE I
Effect of Extraction Parameters (Time, Temperature, pH, and Dye Weight in 100 mL water) on absorbance, K/S, and yield

Parameters	60°C			100°C		
	Absorbance	K/S	Yield (g)	Absorbance	K/S	Yield (g)
Time (min)						
30	0.232	3.210	0.170	0.342	3.730	0.235
60	0.249	3.480	0.187	0.400	4.930	0.271
90	0.280	4.120	0.218	0.479	6.680	0.311
120	0.284	4.350	0.221	0.491	6.760	0.320
150	0.290	4.700	0.223	0.502	6.800	0.327
180	0.302	4.920	0.224	0.510	6.880	0.329
pH						
3	0.256	3.620	0.203	0.430	3.100	0.299
7	0.284	4.350	0.221	0.491	6.760	0.320
8	0.321	5.517	0.248	0.599	7.540	0.341
Dye weight (g/100 mL water)						
1	0.284	4.350	0.221	0.491	6.760	0.320
2	0.295	4.610	0.382	0.559	7.740	0.600
4	0.337	5.102	0.526	0.597	8.360	0.812
6	0.382	5.510	0.775	0.710	9.050	1.104
8	0.394	5.570	0.780	0.730	9.130	1.110

Identification of dyes in madder

To identify the main components in madder the TLC analysis was used. In this analysis, the mobile phase was ethyl acetate–methanol–acetic acid (90–9–1). Three spots were identified in the TLC paper with different R_f . The order of increase in R_f is:



The mixture of pure alizarin, purpurin, 1,4-dihydroxyanthraquinone, and 1,8-dihydroxyanthraquinone was monitored by TLC with the same solvent and the behavior of these chemicals was compared to madder. The results revealed that the main components in madder are the same as three of four pure chemicals. Therefore, those three spots seems to be alizarin, purpurin, and 1,4-dihydroxyanthraquinone. According to values of R_f , it can be observed that the highest R_f belongs to the 1,4-dihydroxyanthraquinone.

The results of HPLC analysis for extracted madder solution at different times (30 and 120 min) and temperatures (60 and 100°C) are shown in Figure 2 and Table II. According to Figure 2 and Table II, an increase in time and temperature leads to an increase in the alizarin and purpurin content. It can be concluded that in all samples, the amount of alizarin and purpurin extracted in madder solution are different but the amount of 1,4-dihydroxyanthraquinone is constant. In fact, time and temperature changes have no influences on this compound. Having more alizarin and purpurin with increasing of

extraction time and temperature confirm by HPLC. The absorbance values in Table I also confirm the results of HPLC as the absorbance values increase with increasing of alizarin and purpurin compounds prior to longer time and higher temperature.

Dyeing

The effect of dye bath pH

The pH is an important factor that controls the adsorption of dyes from aqueous solution onto wool samples.¹⁵ Therefore, the effect of pH on the adsorption of madder on wool was studied in range of 3–6 because of normal wool dyeing at this range. Figure 3 shows that the dyeing pH has a considerable effect on the adsorption of madder. It can be seen that the highest adsorption value of dye is obtained at pH 3. The effect of pH can be attributed to the chemical structure of madder, wool fiber, and the correlation between dye and wool fiber. Because madder used is soluble in water at high temperature and it has carbonyl and hydroxyl groups, the carbonyl groups of madder in acidic media can adsorb hydrogen atoms and change to enol isomer (Keto-enol tautomerism) that leads to higher hydrogen bonding with carboxyl groups of wool fibers. By decreasing pH, the adsorption of dye on wool increases. Also, K/S values increase with decreasing of pH and the highest K/S values which were obtained at pH 3 (Fig. 4). According to these results, the pH of dye bath in all experiments was fixed at 3.

Rate of dyeing

Determining of equilibrium time is one of the most important characteristics which represent the

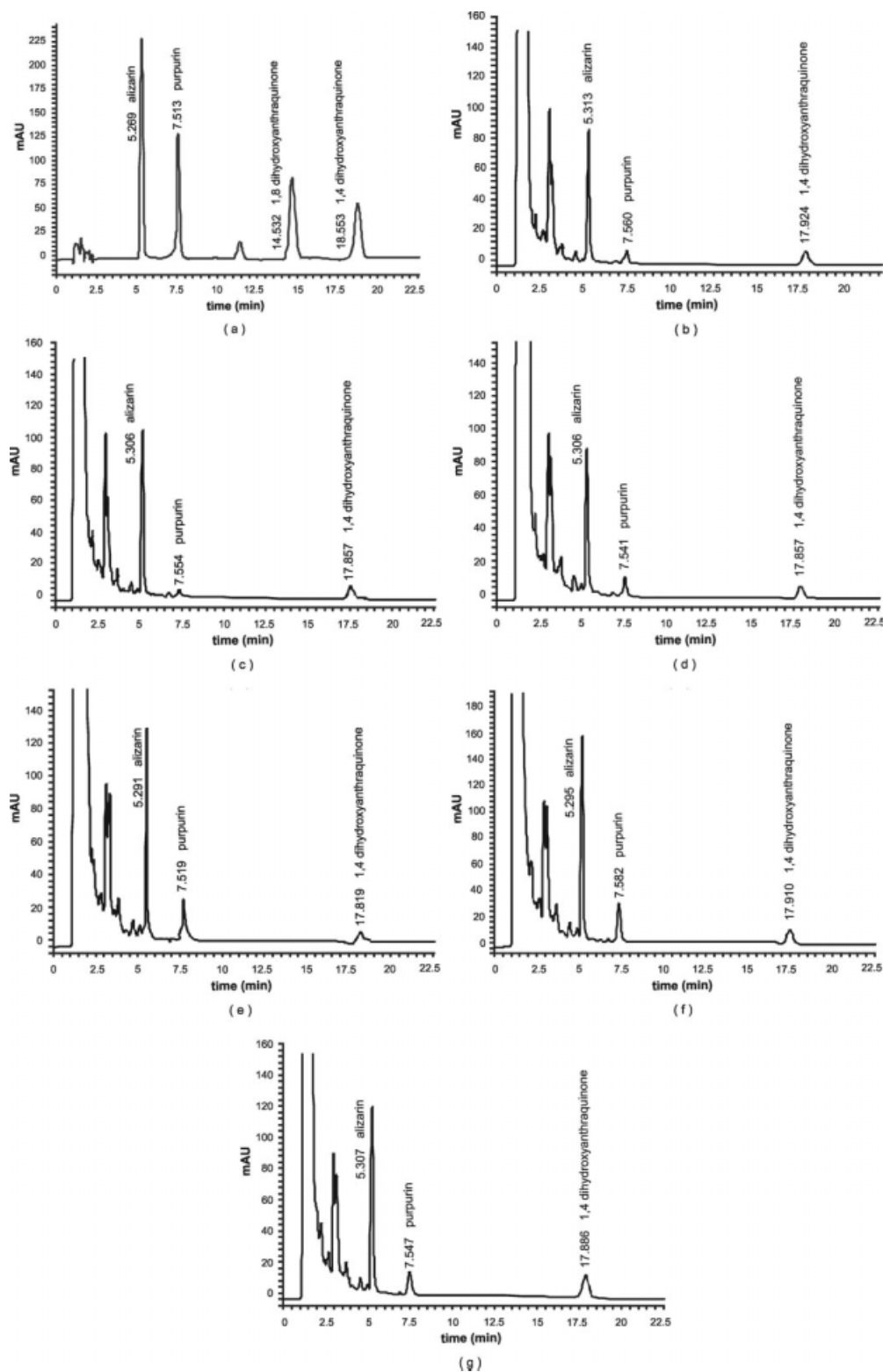


Figure 2 HPLC chromatogram of dye extracted at different times, temperatures and pH. (a) Standard chemicals. (b) Extraction at 60°C for 30 min. (c) Extraction at 60°C for 120 min. (d) Extraction at 100°C for 30 min. (e) Extraction at 100°C for 120 min and pH 7. (f) Extraction at pH 3. (g) Extraction at pH 8. HPLC conditions: ECLIPSE XDB-C8 column (150 × 4.6 mm² I.D.; 5 μm); mobile phase: 45 : 55 (v/v) mixture of acetonitrile: 20 mM ammonium formate (pH 3); the flow-rate; 1 mL/min; detection: λ = 254 nm.

adsorption of madder on wool. According to Figure 5, the dye adsorption increases with increasing of time to 120 min of dyeing. Longer time has no influ-

ence on dye adsorption. This means that the dye adsorption reaches to equilibrium for different temperatures. The results show that temperature is an

TABLE II
Influence of Extraction Parameters (Time, Temperature, and pH) on Amount of Alizarin and Purpurin in Madder by HPLC

Parameters	60°C		100°C	
	Alizarin (mg/L)	Purpurin (mg/L)	Alizarin (mg/L)	Purpurin (mg/L)
Time (min)				
30	4.1	1.4	6.2	2.6
120	5.6	1.8	9.7	4.5
pH				
3	–	–	8.9	4.1
7	–	–	9.7	4.5
8	–	–	10.3	4.7

important factor in adsorption and increases by decreasing the temperature. It is clear that the adsorption of madder on wool was controlled by an exothermic process. The adsorption of madder on wool fabric at different dye concentrations is shown in Figure 5(b). The results show that increasing of dye concentrations leads to increase in madder adsorbed on wool fabric. The maximum adsorption of madder on wool fabric reaches at 4160 mg/L. According to Figure 5, although dye concentrations may has an important role to dyeing process, but also the results show that dye concentrations has not main role to rate of dyeing and determine of equilibrium time. The results show that using different initial dye concentrations in 40°C showed similar trends. As it is shown in Figure 6, K/S values obtained increases as the time increases to 120 min and afterwards the K/S remains constant. This means that dyeing for 120 min give a high K/S value. Therefore, time of dyeing was set at 120 min.

Adsorption isotherms

Several models have been published for describe adsorption isotherms. The Langmuir and Freundlich

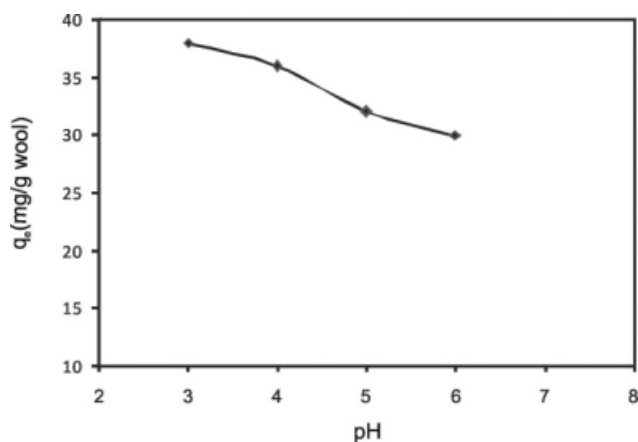


Figure 3 Effect of pH on adsorption of madder on wool. Dyeing conditions: initial dye concentration 112 mg/L, L : G 100 : 1, temperature of dyeing 40°C, and time of dyeing 120 min.

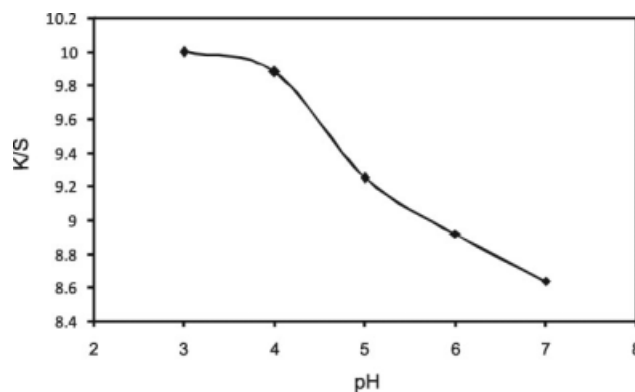


Figure 4 Effect of pH on K/S wool dyed samples with madder. Dyeing conditions: initial dye concentration 12 mg/L, L : G 100 : 1 temperature of dyeing 40°C, and time of dyeing 120 min.

models are the most frequently used models.¹⁸ In this research, for describe the relation between the amount of dye adsorbed on wool and the amount of dye in residual dyeing bath at different temperatures (40, 60, and 100°C), Langmuir, Freundlich, BET, and

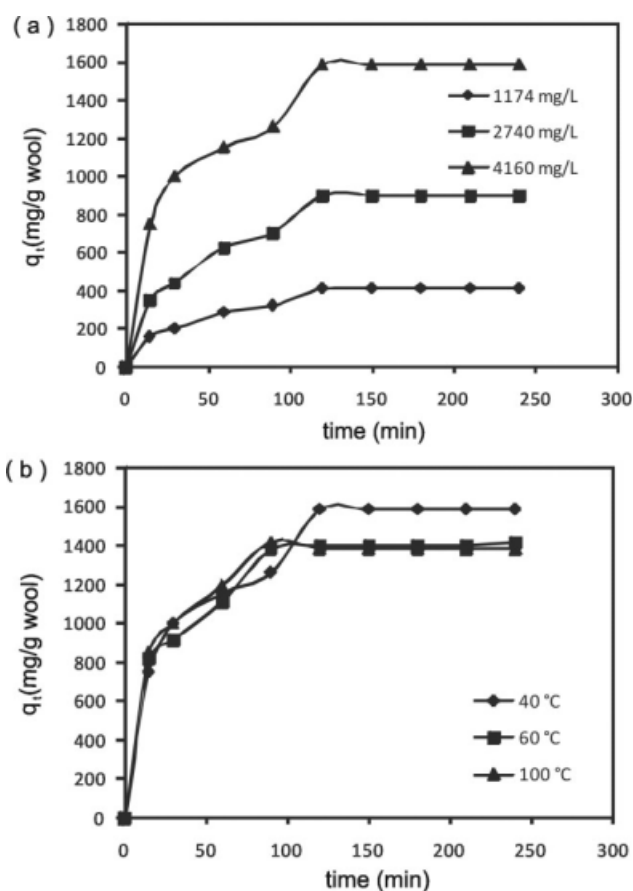


Figure 5 Effect of time and temperature of wool dyeing with madder. (a) Dyeing conditions: different initial dye concentrations (1174 – 4160 mg/L), L : G 100 : 1, and pH 3. (b) Dyeing conditions: initial dye concentration 4160 mg/L, L : G 100 : 1, and pH 3.

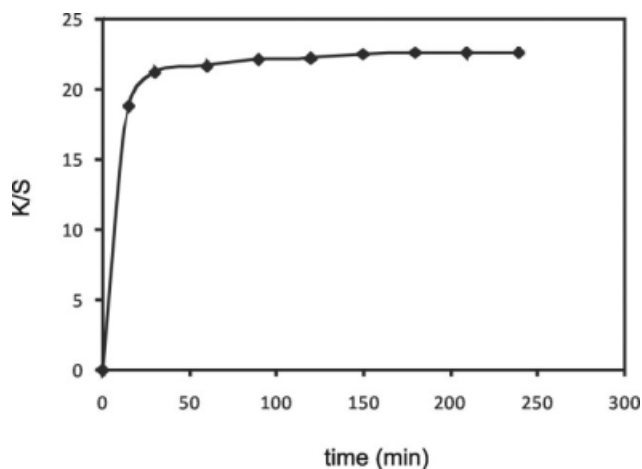


Figure 6 Effect of time of wool dyeing with madder on K/S values. Dyeing conditions: initial dye concentration 4160 mg/L, L : G 100 : 1, temperature of dyeing 40°C, and pH 3.

Temkin models were used. The most widely used equation describing the adsorption process is Langmuir equation, which has the linear form eq. (4)¹⁶:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e. \quad (4)$$

For lower concentrations, the following form of the Langmuir equation is found to be more satisfactory [eq. (5)]^{15,16}:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{QbC_e}, \quad (5)$$

where, Q is the maximum amount of the dye adsorbed on wool fibers to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e , q_e is the amount of dye adsorbed on wool fibers at equilibrium, and b is Langmuir constant related to the affinity of the binding sites. The value of Q represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and assists in the comparison of adsorption performance. The values of Q and b can be calculated from intercepts and slopes of the straight lines of plot of $1/q$ against $1/C_e$.^{15,16} The values of Q and b listed in Table III. Correlation coefficients are near to 1 which means that experimental data fitted this model well. According to the results, it can be seen that temperature increases led to decreases adsorption of dye on wool samples and it means that adsorption of madder on wool samples are exothermic. Also, results show that Q and b values increased with decreasing temperature and it can be seen from the b values that the wool samples have a maximum affinity for madder at lower temperature.

The Freundlich equation is another model which is often used to describe adsorption data. The linear

form of the Freundlich isotherm can be represented in the following eq. (6):

$$\ln q_e = \ln Q_f + \frac{1}{n} \ln C_e, \quad (6)$$

where, Q_f is roughly an indicator of the adsorption capacity and $1/n$ is the adsorption intensity. Therefore, Q_f and $1/n$ can be determined from the linear plot of $\ln q_e$ against $\ln C_e$. The Q_f and n values are listed in Table III. Results show that increases temperature led to decreases Q_f and which means that adsorption of madder on wool fibers is exothermic process. Correlation coefficients are near to 1 and means that experimental data fitted to this model as well as Langmuir model. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption conditions.¹⁵

The BET equation is another model which is often used to describe adsorption data for multilayer systems. The linear form of the BET isotherm can be represented in the following eq. (7)¹⁹:

$$\frac{C_e}{Q_e(1 - C_e)} = \frac{1}{X_m K_B} + \frac{K_B - 1}{X_m K_B}, \quad (7)$$

where, X_m is roughly an indicator of the adsorption capacity, K_B is the adsorption constant, C_e and Q_e are equilibrium dye concentrations in solution and wool, respectively. Therefore, X_m and K_B can be determined from the linear plot of $\frac{C_e}{Q_e(1 - C_e)}$ against C_e . The X_m and K_B values are listed in Table III. The correlation coefficients of this model are above 0.99. However, the regression coefficients obtained by

TABLE III
Langmuir, Freundlich, BET, and Temkin Values of Adsorption of Madder on Wool at Different Temperatures

Adsorption isotherm	Temperature (°C)		
	40	60	100
Langmuir			
Q	21.37	18.73	18.59
b	0.17	0.15	0.12
R^2	0.997	0.998	0.997
Freundlich			
Q_f	3.23	2.49	1.96
n	1.06	1.09	1.06
R^2	0.996	0.997	0.996
BET			
X_m	194.93	251.83	987.95
K_B	0.018	0.011	0.0021
R^2	0.992	0.996	0.998
Temkin			
b	1939.11	2324.57	2761.46
K_{T_e}	8.39	2.86	5.69
R^2	0.956	0.968	0.97

TABLE IV
The Values of the Pseudo First Order and Pseudo Second Order Models for Adsorption of Madder on Wool

Temperature (°C)	$q_{e,exp}$ (mg/g wool)	pseudo first-order			pseudo second-order		
		k_1 (min ⁻¹)	q_e (mg/g wool)	R^2	K_2 (min ⁻¹)	q_e (mg/g wool)	R^2
40	45.25	0.0120	918.83	0.962	0.000025	1666.67	0.987
60	39.15	0.0165	735.09	0.993	0.000049	1428.57	0.997
100	38.54	0.0218	820.57	0.997	0.000068	1388.89	0.998

Dyeing conditions: Initial dye concentration 4160 mg/L, L : G 100 : 1, and pH 3.

Langmuir and Freundlich are higher than BET. This means that experimental data does not fitted well to the BET model.

Another popular equation for the analysis of isotherms of a high degree of rectangularity is that proposed by Temkin isotherm as follows eq. (8)²⁰:

$$q_e = \frac{RT}{b} \ln(K_{Te}C_e), \quad (8)$$

where, RT/b and K_{Te} can be determined from the linear plot of q_e against $\ln C_e$. The b and K_{Te} values are listed in Table III.

The correlation coefficients obtained by this model are above 0.95. This shows that the experimental data does not fit well to this model.

Kinetics of adsorption

To investigate the mechanism of adsorption process of madder on wool samples pseudo- first- order and pseudo- second-order models were used. These models are two of the most commonly models used to describe the sorption of dyes on textile fibers.¹⁵

Pseudo-first-order

A simple kinetic analysis of adsorption is the Lagergren equation, a pseudo-first-order equation,

describes the kinetics of the adsorption process as follows [eq. (9)]¹⁵:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (9)$$

where, k_1 is the rate constant of pseudo-first-order adsorption (s⁻¹), and q_e and q_t is the amount of dye adsorbed on wool samples (mg/g wool) at equilibrium and at time t . In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over only the initial stage of the adsorption.²¹ After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, eq. (10) becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t. \quad (10)$$

Linear plot feature of $\ln(q_e - q_t)$ against t for dyed wool samples were achieved and the k_1 and q_e values calculated from slope and intercept of these lines were summarized in Table IV.

Pseudo-second-order

The pseudo-second-order kinetic model is another important model to investigate kinetic of adsorption of dye on textile materials and it is based on adsorption equilibrium capacity and can be expressed as¹⁵

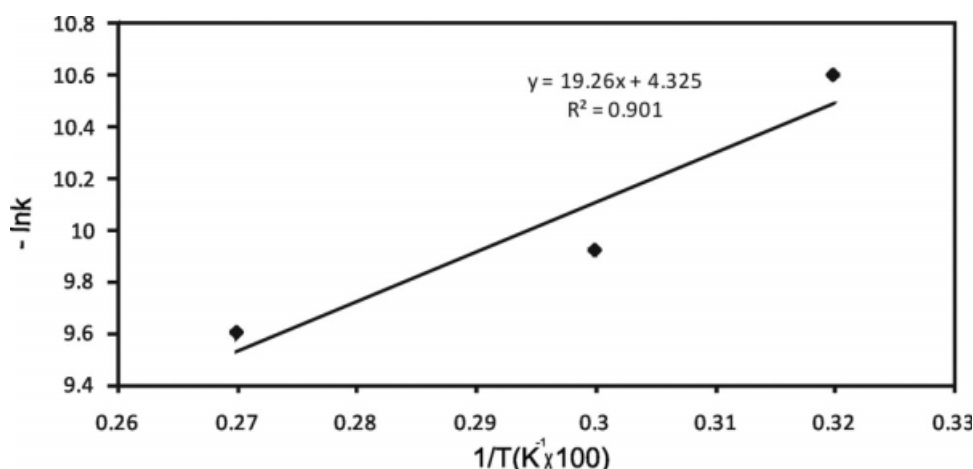


Figure 7 Relation between $\ln k$ and $1/T$ for dyeing of wool with madder.

TABLE V
Thermodynamic Parameters ($\Delta\mu^\circ$, ΔH° , and ΔS°) for the Adsorption of Madder by Wool

Temperature	K	$\Delta\mu^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	R^2
40	3.30	-3.11			
60	2.56	-2.60	-8.55	-17.62	0.991
100	1.96	-2.09			

eq. (11):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (11)$$

where, k_2 is the rate constant of pseudo-first-order adsorption (g wool/mg min). Integrating eq. (11) and applying the initial conditions, we have

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (12)$$

The pseudo-second-order rate constant k_2 and q_e calculated from slope and intercept of plotted t/q_t against t . The values of k_2 and q_e are listed in Table IV. The correlation coefficient (R^2) for both of kinetics models are shown in Table IV. The correlation coefficient of pseudo-first-order and pseudo-second-order both close to 1, however the q_e , adsorption capacity, is in accord with experimental results and pseudo-second-order model. Therefore, it can be concluded that the adsorption kinetic of madder on wool fitted by pseudo-second-order.

Activation parameters

The amount of dye adsorbed at equilibrium at different temperatures, are 40, 60, and 100°C, have been utilized to evaluate the thermodynamic param-

eters for the dyeing wool samples with madder. The pseudo-second-order rate constant of dye adsorption is expressed as a function of temperature by the following Arrhenius-type relationship eq. (13)²²:

$$\ln k_2 = \ln A - \frac{E_a}{RT}, \quad (13)$$

where, E_a is the Arrhenius activation energy of adsorption, A is the Arrhenius factor, R is gas constant, and T is temperature (K). When $\ln k$ is plotted against $1/T$ (Fig. 7), a straight line with slope E_a/R is obtained. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. The physisorption processes usually have energies in the range of 5–40 kJ/mol, whereas higher activation energies (40–800 kJ/mol) suggest chemisorptions.²² The result obtained is 16.01 kJ/mol for dyeing of wool samples with madder at different temperatures (40, 60, and 100°C). Considering that this values is in the typical activation energy for physisorption.

Standard affinity

The data for dyeing equilibrium is generally reported as the standard affinity of dyeing, $-\Delta\mu^\circ$.^{5,23} It has been reported that the dyeing of wool fibers with natural dyes follows the same mechanism as that of disperse dyes. Therefore, the standard affinity ($-\Delta\mu^\circ$) were determined by using following eq. (14)⁵:

$$-\Delta\mu^\circ = RT \ln K, \quad (14)$$

where, R is the gas constant, T is the absolute temperature (K), and K is the partition ratio. The values of partition ratio (K) and standard affinity ($-\Delta\mu^\circ$) are presented in Table V. It can be observed from

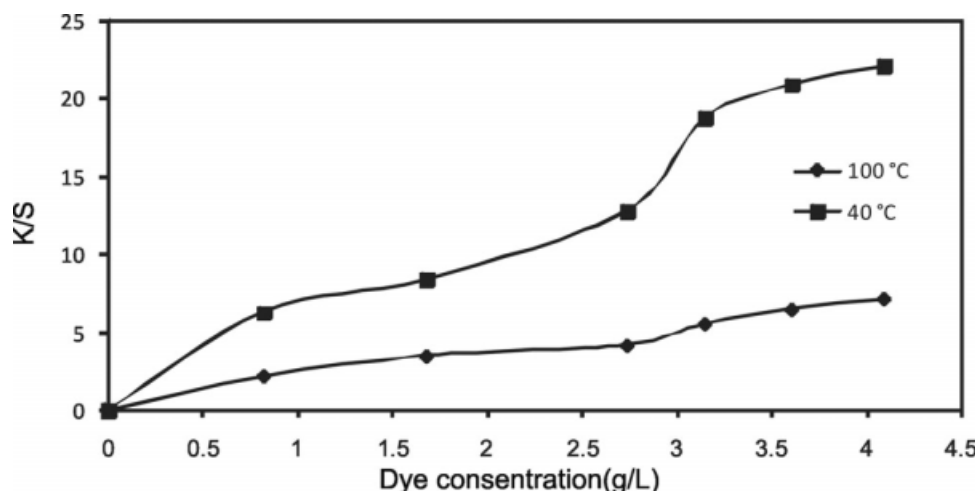


Figure 8 Effect of dye concentration on K/S values. Dyeing conditions: initial dye concentrations 1174–4160 mg/L, L : G 100 : 1, dyeing time 120 min, and pH 3. L : G 100 : 1 and pH 3.

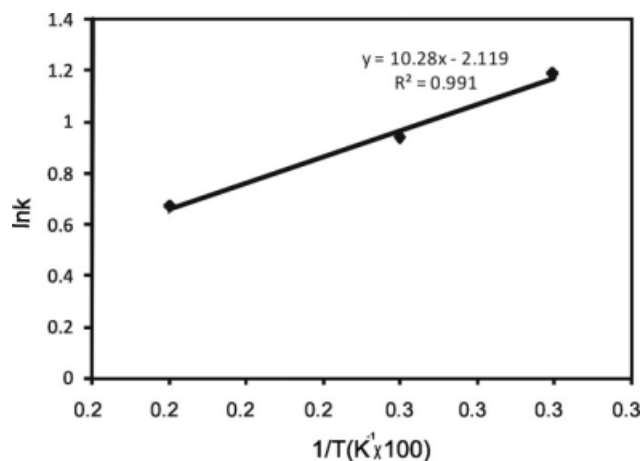


Figure 9 Relation between $\ln K$ and $1/T$ for dyeing of wool with madder.

Table V that the standard affinity and partition ratio decrease as temperature increase. Also, the effect of dye concentration on K/S values shows that K/S values increase with increasing of dye concentration until the saturation point is reached. It can be conclude from Figure 8 that after saturation point K/S values will be constant with increasing of dye concentration.

In Figure 9, to determine the heat of dyeing (ΔH°) and entropy of dyeing (ΔS°), $\ln K$ against $1/T$ was plotted and enthalpy and entropy were calculated by eq. (15)¹⁵:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (15)$$

The values of ΔH° and ΔS° are -8.55 and -17.62 kJ/mol and J/mol K, respectively. This means that the adsorption of madder on wool sample is an exothermic process.

CONCLUSIONS

In initial experimental, the extraction parameters such as time, temperature, pH, and dye concentrations on absorbance, K/S , and yield of dye extracted solution from madder powder were determined. The results showed that increase of each mentioned parameters on extraction leads to increasing of absorbance, K/S , and yield. The main compounds in madder (alizarin, purpurin, and 1,4-dihydroxyan-

thraquinone) were identified by TLC and HPLC. The adsorption isotherm, thermodynamics, and kinetic study of adsorption of madder on wool fiber were studied. The results show that adsorption dependent on the pH and temperature and the adsorption isotherm of madder on wool is a Langmuir type. The partition ratio (K), the standard affinity ($\Delta\mu^\circ$), the heat of dyeing (ΔH°), and entropy of dyeing (ΔS°) were determined. It is noted that the adsorption of madder on wool is an exothermic process.

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