Asian Journal of Chemistry Vol. 21, No. 1 (2009), 403-410

Thermodynamics of Adsorption of Iranian Weld Dye on Wool Fabric

K. FARIZADEH*, M.E. YAZDANSHENAS†, M. MONTAZER‡,
A. RASHIDI and R.M. A. MALEK‡
Deapertment of Textile, Islamic Azad University
Science and Research branch, Tehran, Iran
E-mail: k_farizad2005@yahoo.com

The adsorption properties of the colouing matter from Weld have studied on wool fabric. In this study, the rate of dyeing at different temperature as well as the values of adsorption isotherm, affinity, entropy and enthalpy were estimated. The results show that with increasing of temperature the values of partition ratio and affinity decrease. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir isotherm. The effect of alum was also studied on adsorption isotherm and resulted that the adsorption isotherm is similar to without alum.

Key Words: Weld, Wool fabric, Thermodynamics, Dyeing, Adsorption isotherm, Natural dyes.

INTRODUCTION

Natural dyes have become a part of human life since ancient time. Iran has a rich cultural heritage and the tradition of using dyes obtained from natural resources. People tried 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 due to increasing awareness of environment, ecology and pollution control. In the present context of eco preservation, natural dyes have got tremendous commercial potentialities as some of the synthetic dyes are associated with the release of enormous amount of hazardous chemicals in the environment. Though vegetable dyes cannot replace synthetic dyes, they have several advantages over synthetic dyes from the point of view of health, safety and ecology. Natural dyes exhibit better biodegradability and generally have a better compatibility with the environment. They produce various colours that are gentle, soft and subtle and create a restful effect[1-6]. Weld (*Reseda luteola* L., Family Resedaceae) is a

†Deapertment of Textile, Islamic Azad University, Yazd Branch, Yazd, Iran.
‡Deapertment of Textile, Amirkabir University of Technology, Tehran, Iran.

biennial or polycarpic perennial herbaceous plant, native of Euro-Asia and naturalized in the Mediterranean region where it could represent a source of yellow pigment for natural textiles productions[7,8]. Weld produces flavonoids in the aerial part of the plant, the most important being Luteolin (C.I. Natural yellow 2; C.I. 75590)[8,9], dye used mainly for dyeing wool and silk since ancient time. Chemical structure of Weld showed in Fig. 1. Recently, the thermodynamic and kinetic study of natural dyes on textile fibers is an important problem. It has been reported that the dyeing of wool fibers using natural dyes follows the same mechanism as that of disperse dyes, *i.e.*, *via* partition[10]. Also, according to previous studies about natural dyes on textile fibers, it indicated that adsorption isotherm of natural dyes on textile fibers fitted to the Langmuir and Freundlich isotherm[11-13]. In Iran, the dyers have used Weld for dyeing wool (carpet yarns) by trial and error.There are no scientific data (*i.e.* thermodynamic properties) of the process of Weld dyeing on wool. Thus, this research work aims to study the thermodynamic properties of adsorption of Weld dye (Fig. 1) on wool substrate and also the effect of mordant on this phenomenon.

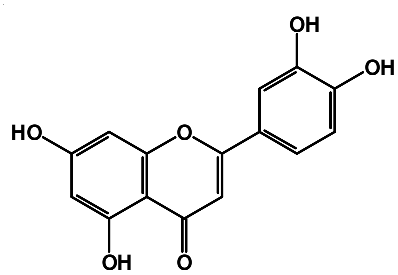

Fig. 1. Chemical structure of Weld dye

EXPERIMENTAL

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

Wool fabric: Woven wool fabric with the following characteristics was gifted from Iran Merino Co.: weight 205 g/m^2, 72 ends inch, 64 picks per inch. Before using, the fabric was treated with a solution containing 2 g/L non-ionic detergent, 1 g/L sodium carbonate at 70 °C for 0.5 h and L:G 50:1. Then, the fabric was thoroughly washed with water and air dried at room temperature.

Mordanting: One mordant, *viz.*, potassium aluminium sulphate (alum from Merck) was selected for the study. The mordanting bath was set for 20 % mordant, on weight of fabric at L:G 50:1. The scoured wool fabric samples were introduced at 40 °C. Temperature was raised to boil and mordanting was continued for 45 min. It was then squeezed and used for dyeing.

Preparation of dye solution: Weld dye was purchased from northeast Iran and it was finely powdered in a mill. The powdered material was soaked in deionized water for 0.5 h. The contents were then boiled for 1.5 h. The aqueous solution was filtered, diluted to the required quantity and used for dyeing purpose.

Methods

Batch kinetic experiments: 1 g of wool fabric (without mordant and with mordant) were dyed with Weld at 35, 60, 80, 100 °C and pH 3 in different time, keeping the L:G 100:1 and an initial dye concentration of 90 mg/L. The amount of dye in the residual bath ($[D_s]$) was measured by using the UV-Vis spectrophotometer and dye uptake by wool fabric ($[D_f]$) was calculated by subtraction. The graph of Weld concentrations of standard solution *vs.* absorbance at wavelength of 368 nm, at which 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 Weld in the residual bath and the dye uptake were calculated using the standard graph. Subsequently, rate of dyeing of Weld on wool, *i.e.* exhaustion *vs.* time, was plotted.

Batch equilibrium experiments: 1 g of wool fabric (without mordant and with mordant) were dyed with different dye concentration at 35, 60, 80, 100 °C, pH 3 for 1.5 h. The amount of dye in the residual bath ($[D_s]$) was measured by using the UV-Vis spectrophotometer and dye uptake by wool fabric ($[D_f]$) was calculated by subtraction. Subsequently, an adsorption isotherm of Weld on wool, *i.e.* $[D_f]$ *vs.* $[D_s]$, was plotted and classified.

Colour strength measurement: Colour strength (K/S) values of the dyed samples (without and with mordant) were measured and the K/S values were assessed using the Kubelka-Munk[14] eqn. 1:

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

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

RESULTS AND DISCUSSION

Effect of dye bath pH: The pH is an important factor that controls the adsorption of dyes from aqueous solution onto wool fabrics[12,15]. Therefore, the effect of pH on the adsorption of Weld dyes on wool fabric was studied in the pH range of 3-6. Studies carried out in this range due to the wool fibers were usually dyeing in this range of pH. Fig. 2 shows that the pH of dyeing bath has a considerable effect on the adsorption of Weld onto wool fabric. The results show that highest adsorption value of dye is in pH 3. The effect of pH can be attributed to the chemical structure of Weld dye, wool fiber and the correlation between dye and wool fiber. Since Weld dye used is soluble in water and it has OH groups, it would interact ionically with the protonated terminal amino groups of wool fibers at acidic pH *via* ion exchange reaction. Then decreased pH led to increasing adsorption of dye on wool. The effect of pH on K/S values also show that K/S values increased with pH decreases and highest K/S values obtained in pH 3. According above results, in this study pH of the dye bath in all experiments on the adsorption kinetics was fixed at 3.

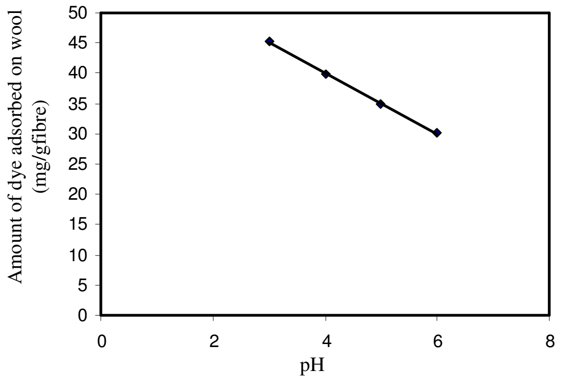

Fig. 2. Effect of dye bath pH on the adsorption of Weld dye on wool surface

Rate of dyeing: Determination of the equilibrium time is one of the most important characteristics which represents the adsorption of Weld dye on wool and therefore, determines their potential applications. According to Fig. 3, the adsorption of dye increase dramatically in the first 45 min and they reached equilibrium gradually at 1.5 h for different temperature. The results show that the temperature is a important factor to adsorption and it increased with decreasing temperature. Then, it is clear that the adsorption of Weld onto wool was controlled by an exothermic process. As shown in Fig. 4, K/S values obtained was increased as the time increases up to 1.5 h, then it will be constant, *i.e.*, dyeing for 1.5 h gave high K/S values. So in this search, time of dyeing in the adsorption experiments was set at 1.5 h.

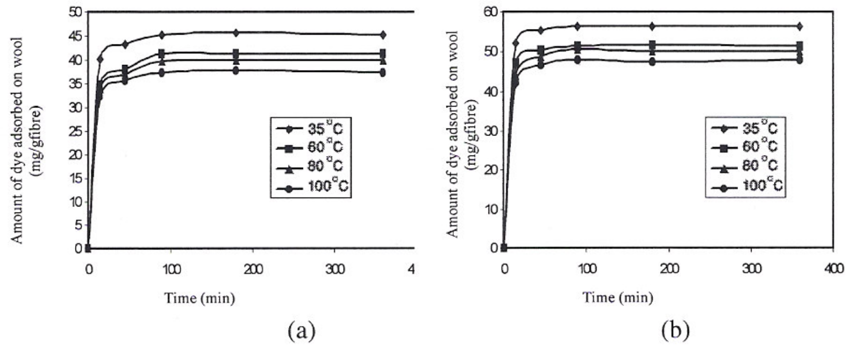

Fig. 3. Effect of contact time and temperature of Weld dyeing on wool. Dyeing conditions: initial dye concentration 90 mg/L, L:G 100:1and pH 3. (a) Without mordant (b) With mordant

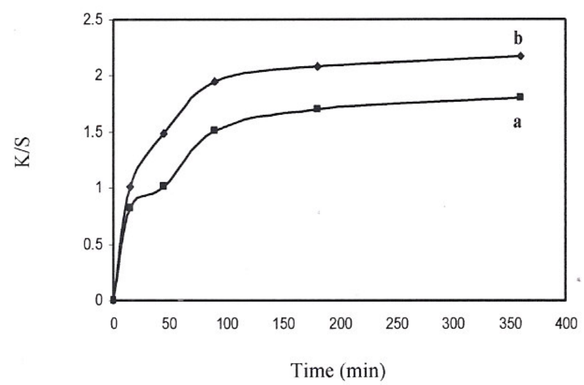

Fig. 4. Effect of contact time on K/S values of wool dyed with Weld dye. Dyeing conditions: initial dye concentration 90 mg/L, L:G 100:1, pH 3 at 35 °C. (a) Without mordant (b) With mordant

Adsorption isotherm: Fig. 5 shows the adsorption isotherm of Weld dye on wool at 35, 60, 80 and 100 °C. These data could be approximated by the Langmuir type. The results show that the equilibrium dye uptake continues to increase with increase of dye concentration until it reaches the saturation point. Prior reaching the saturation, the relations between $[D_f]$ and $[D_s]$ can be considered as a linear function. Therefore, partition ratio (K) is slope of this line and standard affinity ($-\Delta\mu°$) can be calculated using[11,16,17] eqn. 2

$$-\Delta\mu° = RT \ln K \quad (2)$$

where R is the gas constant, T is the absolute temperature. The values of partition ratio (K) and standard affinity ($-\Delta\mu°$) are presented in Table-1. From Table-1 it can be seen that standard affinity and partition ratio decreased with temperature increases. The effect of dye concentration on K/S values

TABLE-1
PARTITION RATIO AND STANDARD AFFINITY OF WELD DYEING ON WOOL

Temp. (°C)	Partition ratio		Standard affinity (Kcal/mol)	
	Without mordant	With mordant	Without mordant	With mordant
35	87.97	197.78	6.32	7.46
60	43.87	120.66	5.77	7.31
80	33.18	87.72	5.66	7.23
100	19.04	65.81	5.04	7.16

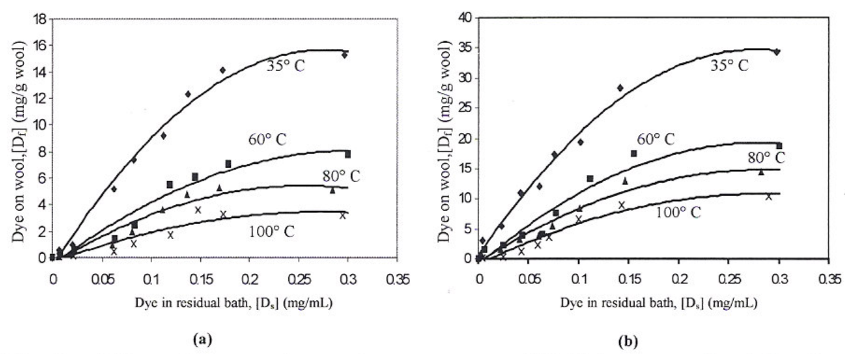

Fig. 5. Effect of contact time and temperature of Weld dyeing on wool. Dyeing conditions: G 100:1and pH 3 (a) Without mordant (b) With mordant

also show that K/S values increased with dye concentration increases until it reaches the saturation point. After this point K/S values will be constant while dye concentration increases (Fig. 6).

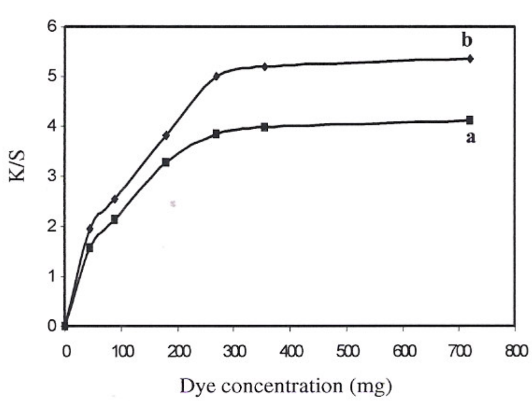

Fig. 6. K/S values of wool fabrics dyed with different dye concentration. Dyeing conditions: L:G 100:1, pH 3 at 35 °C, (a) Without mordant (b) With mordant

In order to determine of heat of dyeing ($\Delta H°$), a graph of ln K *vs.* 1/T was plotted (Fig. 7) and enthalpy was calculated from eqn. 3

$$\ln\frac{k_2}{k_1} = \frac{-\Delta H°}{R}\frac{1}{T_2} - \frac{1}{T_1} \quad (3)$$

Finally, entropy of dyeing ($\Delta S°$) was determined from a graph of $-\Delta\mu°$ *vs.* T (Fig. 8) and eqn. 4:

$$\Delta\mu° = \Delta H° - T\Delta S° \quad (4)$$

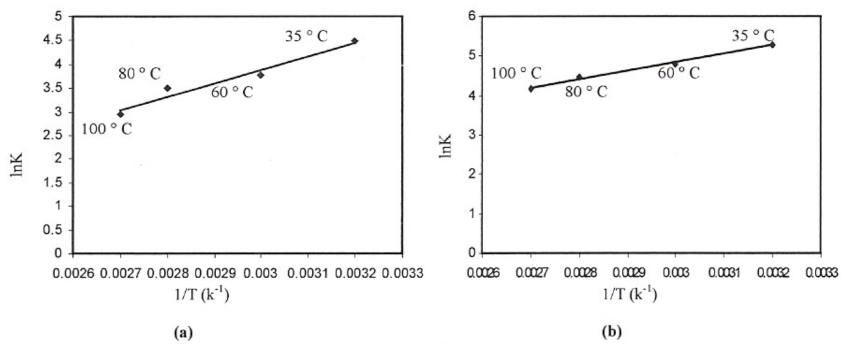

Fig. 7. Relations between ln K and 1/T from wool dyeing with Weld (a) Without mordant. (b) With mordant.

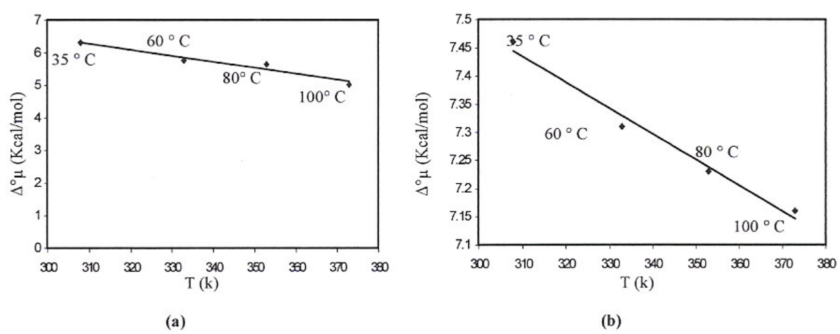

Fig. 8. Relations between $-\Delta\mu°$ and T from wool dyeing with Weld (a) Without mordant. (b) With mordant

The obtained values of $\Delta H°$ and $\Delta S°$ are -5.27, -0.02 Kcal/mol and Kcal/mol K, respectively. It means that adsorption of Weld on wool fabric is an exothermic process.

The effect of mordant on wool dyeing with Weld dye was investigated and the results are similar (Figs. 3b, 5b and Table-1) and the obtained isotherm is still a Langmuir type. The partition ratio and standard affinity are higher in comparing with dyeing without mordant at the same temperature.

The results reveal that using of mordant improves the adsorption of Weld dye on wool and increases the attraction between Weld and wool surface. From slopes of graphs in Figs. 7b, 8b, the heat of dyeing and the entropy of dyeing were calculated to be -3.86, -0.005 kcal/mol and kcal/mol K, respectively. It seems that the dyeing with mordant evolves less heat, compared to the dyeing without mordant.

Conclusion

The adsorption isotherm and kinetics of Weld dye on wool fabric were studied. The results show that adsorption dependent on the pH and temperature. Also adsorption isotherm of Weld on wool is a Langmuir type. The partition ratio (K), the standard affinity ($\Delta\mu°$), the heat of dyeing ($\Delta H°$) and entropy of dyeing ($\Delta S°$) were determined. It is noted that the adsorption of Weld on wool is an exothermic process.

The effect of alum used as a mordant on wool fabric dyeing with Weld dye was also studied. This reveals that using mordant promotes the adsorption of Weld on wool fabric and increases the attraction between Weld dye and wool surfaces.

REFERENCES

1. S. Paul, *J. Textile Assoc.*, **63**, 117 (2003).
2. H.T. Deo and R. Paul, *Alternative Colouration*, **November**, 49 (2003).
3. M.M. Kamel, R.M. El-Shishtawy, B.M. Youssef and H. Mashaly, *Dyes Pigments*, **73**, 279 (2007).
4. S. Paul, E. Grover and Anshu, *Alterative Colouration*, **November**, 55 (2003).
5. M.M. Kamel and R.M.EL. Shishtway, *Dyes Pigments*, **65**, 103 (2005).
6. R. Bhuyan, D.C. Saikia and C.N. Saikia, *Indian J. Fibre Textile Res.*, **27**, 429 (2002).
7. Daniela Cristea and Isabelle Bareau, *Dyes Pigments*, **57**, 267 (2003).
8. L.G. Angelini and A. Bertoli, *Ind. Crops Prod.*, **17**, 199 (2003).
9. T. Grygar, S. Kuckova, D. Hradil and D. Hradilova, *J. Solid State Electrochem.*, **7**, 706 (2003).
10. F.A. Nagia and R.S.R. EL-Mohamedy, *Dyes Pigments*, **75**, 550 (2006).
11. Paisan Kongkachuichay, Aroonsiri Shitangkoon and Nontalee Chinwongamorn, *Dyes Pigments*, **53**, 179 (2002).
12. M. Chairat, S. Rattanaphani, J.B. Bremner and V. Rattanaphanti, *Dyes Pigments*, **64**, 231 (2005).
13. S. Rattanaphani, M. Chairat, J.B. Bremner and V. Rattanaphanti, *Dyes Pigments*, **72**, 88 (2007).
14. D.B. Judd and G. Wyszecki, Color in Business, Science and Industry, John Wiley & Sons, New York (1975).
16. J. Alan, The Theory of Coloration of Textiles, West Yorkshire: Society of Dyers and Colourists, edn. 2 (1989).
17. Tae-Kyung Kim, Young-A. Son and Yong-Jin Lim, *Dyes Pigments*, **67**, 229 (2005).

(*Received*: 22 December 2007; *Accepted*: 23 August 2008) AJC-6783