

Mathematical modeling of absorption behavior of acid dye onto wool fibre using law of conservation of mass

Ali Shams Nateri^{1,2,a}, Hamid Fattahi Juybari³ & Ahmad Hivechi³

¹Textile Engineering Department, University of Guilan, Rasht, Iran

²Centre of Excellence for Colour Science and Technology, Tehran, Iran

³Textile Engineering Department, Amirkabir University of Technology, Tehran, Iran

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The absorption behavior of acid dye on wool fibre has been studied using isotherm, absorption kinetic and law of mass conservation equations. The Langmuir, Freundlich and Freundlich-Langmuir isotherm equations are used to represent the adsorption isotherm of acid dyes on wool. The findings show that the best fit to the adsorption isotherms for acid dyes by wool fibres is obtained by Freundlich-Langmuir model. The pseudo- first and second-order models of absorption kinetics are used to investigate the absorption behavior of acid dye on wool fibre. The obtained result shows good agreement between the practical data and the pseudo- second-order model of absorption kinetic. Also, the law of conservation of mass has been used for modeling the acid dye distribution during dyeing process and the rate of dye uptake by wool fibre. The performance of suggested mathematical model is acceptable.

Keywords: Absorption behavior, Acid dye, Dyeing, Law of mass conversion, Mathematical Modeling, Wool fibre

1 Introduction

Wool is a natural fibre which has different physical and chemical characteristics such as biodegradability, high water sorption, resiliency, and resistance to wrinkling, fire and fungi. All of these properties cannot be found in any other fibre¹. Acid, metal complex, chrome and reactive dyes can be used for wool coloration². Wool is a heterogeneous fibre which is made of cortex and cuticle. In fine wool, cuticle is normally one cell thick and usually constitutes about 10% by weight of total fibre. Cortex is main bulk which determines mechanical and chemical properties of fibre³.

Dyeing behavior at early stages of adsorption is determined by intercellular region of cuticle layer. Dye most readily enters the fibre by diffusion through the intercellular region between the scale cells of the wool fibre, penetrates fairly rapidly into the non-keratinous endocuticle region of the surface layer, and soon attains equilibrium with the dye in the outer solution. Within the cuticle cells, the endocuticle and then the exocuticle become colored, as the dye travels through the intercellular cement and penetrates into the cells from their undersides⁴. Outer layer (cuticle) of wool fibre is partially hydrophobic due to abundant disulfide bridges and fatty acids. This property makes

some difficulties during wool dyeing and printing. Thus, many researchers have presented solutions to overcome this problem and to increase hydrophilicity and dyeability of wool fibre².

Xue *et al.*⁵ pretreated wool fabric with microwave radiation to increase dye uptake. Apparent diffusion coefficient is used for comparing dyeing rate. Mendha *et al.*⁶ used low temperature plasma to enhance wool dyeability. They only studied dye exhaustion for comparing fabric dye adsorption. Sanislave *et al.*⁷ also used dye exhaustion as an indicator of treatment on dyeing behavior. Periolatto *et al.*⁸ used Ceggara Puente modified kinetic model for comparing dyeing rate of UV radiated wool fabric.

In earlier studies kinetic and dye exhaustion were used to evaluate dyeability of samples. In these above researches, dye adsorption was mostly investigated. During dyeing process, dye can be absorbed or desorbed from fibre. So, providing a way to measure these coefficients will be interesting. Therefore, in this research, the principles of mass conversion has been used to predict acid dye absorption behavior on wool.

2 Materials and Methods

2.1 Materials

Woolen fabric was provided from local companies. Acetic acid and sodium sulfate were purchased from Merck Co. Acid Yellow 137 was procured

^aCorresponding author.
E-mail: a_shams@guilan.ac.ir

from Dyestar Co., Cintra 10 UV-Visible transmittance spectrophotometer and X-rite color eye 7000A reflectance spectrophotometer were used to investigate wool fabric dyeing behavior.

2.2 Dyeing

Samples were dyed in bath containing 3% (v/v) acetic acid and 10% (w/v) sodium sulfate salt. Dyeing was processed at boiling temperature for 30 min with varied dye concentration from 0.2% to 3.5% (owf). Liquor ratio was kept constant (L:R 40:1) during process.

2.3 Model Evaluation

In order to study the proposed model, fabrics were separately dyed for 1, 5, 10, 20, 30, 40, 55, 70 and 90 min. Dye bath properties have already been mentioned in section 2.2. The amount of dye remained in bath was measured using calibration curve (absorbance versus dye concentration). Afterwards, the absorbed dye with fabric was calculated using the initial and final bath concentration⁹.

3 Results and Discussion

3.1 Dyeing Isotherm

In order to investigate dyeing isotherm, fabrics are dyed at different dye concentrations. Langmuir, Freundlich and Freundlich- Langmuir equations are used for modeling acid dye adsorption behavior on woolen fabric. Freundlich isotherm was first introduced in 1907, which the main equation was:

$$\frac{[c]_f}{[c]_s^{x_F}} = k_F \dots (1)$$

where $[c]_f$ and $[c]_s$ are respectively dye concentration adsorbed on to fibre and dye concentration remained in dye bath; k_F , the constant value, and x , the another constant value, related to dye and fibre system^{10,11}.

Langmuir isotherm equation is based on one-layer sorption. In other words, dye can't be absorbed to sites which are filled with other particles. Also each site is independent of its neighbor. The main equation for this isotherm is as followed:

$$[c]_f = \frac{k_L [c]_s [c]_{sat}}{1 + k_L [c]_s} \dots (2)$$

where $[c]_{sat}$ is the dye concentration adsorbed to fabric in saturation point and K_L is isotherm constant^{12, 13}.

Freundlich-Langmuir isotherm for dye adsorption and its linear format are mentioned in following equation¹⁴:

$$[c]_f = \frac{k_{FL} [c]_{sat} [c]_s^{x_{FL}}}{1 + k_{FL} [c]_s^{x_{FL}}} \dots (3)$$

Fabrics were dyed at different dye concentrations to investigate the best dyeing isotherm for wool fabric dyeing. Various isotherms are investigated for this system. Calculated values for Langmuir, Freundlich and Freundlich- Langmuir isotherm and correlation coefficient are reported in Table 1 and Fig. 1.

3.2 Dyeing Kinetic

Like any other chemical reaction, dyeing kinetic is the change of absorbed dye concentration against time. It can be generally shown as:

$$\frac{\partial c_t}{\partial t} = kf(c_t) \dots (4)$$

Table 1 — Parameters of isotherm and their correlation coefficient

Isotherm	Parameter	Value
Freundlich	k_F	6.183×10^{-1} mg/g
	x_F	0.729
	R^2	0.968
Langmuir	k_L	4.265×10^{-3} mg/g
	$[c]_{sat}$	61.96 g/mg
	R^2	0.981
Freundlich- Langmuir	k_{FL}	2.707×10^{-3} mg/g
	x_{FL}	1.221
	R^2	0.984

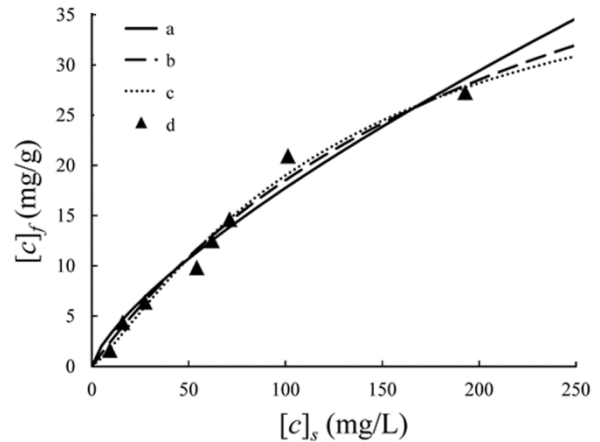


Fig. 1 — Experimental data and fitted isotherms (a) Freundlich isotherm, (b) Langmuir isotherm, (c) Freundlich-Langmuir isotherm, and (d) experimental data

where c_t is the dye concentration in fibre at appropriate time (t); and k , the kinetic constant. Order of dyeing kinetic is defined by the order of $f(c_t)$ function¹⁵. In this work, the first and second (Vicker-Staff) order equations are used to investigate dyeing kinetics, as shown in following equations¹⁶:

$$\frac{\partial c_t}{\partial t} = k_I (c_\infty - c_t) \quad \dots (5)$$

$$\frac{\partial c_t}{\partial t} = k_{II} (c_\infty - c_t)^2 \quad \dots (6)$$

Following equations are generated by integrating above-mentioned equations (boundary conditions $t=0-t, c_t=0-c_e$):

$$\ln(c_e - c_t) = -k_I \times t + \ln(q_e) \quad \dots (7)$$

$$\frac{t}{c_t} = \frac{1}{k_{II} \times c_e^2} + \frac{1}{c_e} \times t \quad \dots (8)$$

where c_t and c_e are the concentrations of absorbed dye at time t and at equilibrium; t , the time; and k , the values of coefficients for kinetic equations¹⁷. In this work the dyeing kinetics are studied for various concentrations of dye (1-3.5 %). First and second order kinetic equations are used to evaluate dyeing kinetics. Results for linear regression of data are shown in Table 2 and Figs 2 and 3.

Based on the obtained results from first and second order kinetics, the second order kinetic is found more fitting and suitable for this system due to higher R^2 (0.999) with respect to first order kinetic equation. Additionally, calculated dye concentration in equilibrium (c_e) from second order kinetic equation is closer to imperial values. So, the second order equation is a better simulator for kinetics of dye adsorption on wool.

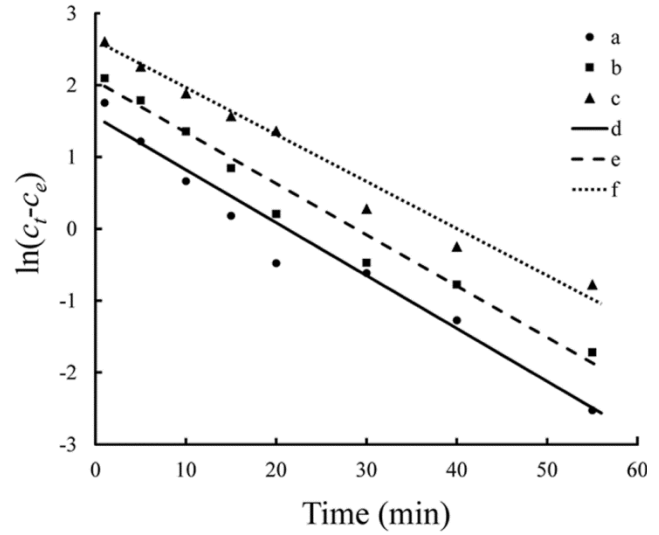


Fig. 2 — Dyeing kinetics for first order equations; experimental data for 1% (a), 2% (b) and 3.5% (c) dye concentrations; and linear regression for 1% (d), 2% (e) and 3.5% (f) dye concentration

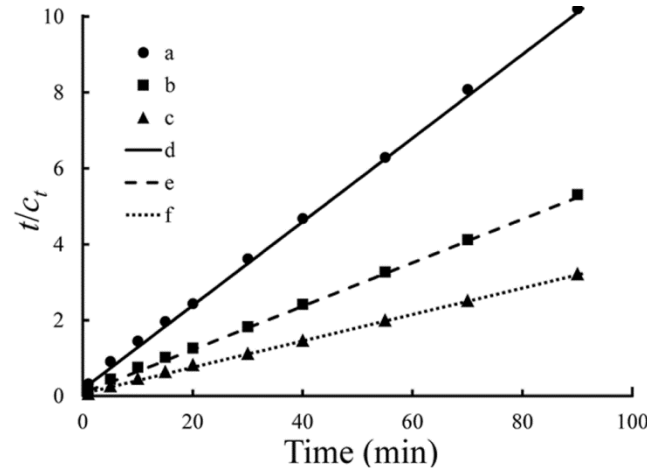


Fig. 3 — Dyeing kinetics for second order equations; experimental data for 1% (a), 2% (b) and 3.5% (c) dye concentrations; and second order dyeing kinetic for 1% (d), 2% (e) and 3.5% (f) dye concentrations

Table 2 — First and second order kinetic parameters for adsorption of acid dye on wool

Kinetic equation	Dye concentration, %	Parameter			
		Imperial (c_e), mg/g	Theoretical (c_e), mg/g	K_I/K_{II}^a	R^2
First order	1	8.82	4.42	7.36×10^{-2}	0.966
	2	16.96	7.27	7.13×10^{-2}	0.972
	3.5	27.84	12.88	6.54×10^{-2}	0.978
Second order	1	8.82	9.07	4.1×10^{-2}	0.999
	2	16.96	17.45	2.4×10^{-2}	0.999
	3.5	27.84	28.74	1.2×10^{-2}	0.999

^a K_I — First order equation, and K_{II} — Second order equation.

3.3 Modeling of Dyeing Behavior

The distribution of dye concentration in dye bath and the dye absorbed on to the fibres has been estimated based on the principles of mass conversion. Different models can be used to study the impact of system variables and their interactions, including the mathematical methods. Mathematical modeling is finding an equation which shows the effect of various parameters and variables on the behavior of the system. Like other chemical phenomenon, adsorption and penetration of dye to fibres is reversible. In the following model, it has been assumed that the mass transfer occurs in two ways:

- (i) Transfer of dye from dyeing bath to the fibre (adsorption coefficient= k)
- (ii) Transfer of dye from fibre to the dyeing bath (desorption coefficient= d)

Before the dyeing process, dye is present in dyeing bath. During the dyeing process, dye is defused and absorbed with fibres due to chemical affinity of the dye. Also, some of absorbed dyes can be returned to dyeing bath because of migration phenomena of dye during the process which continues until final dyeing

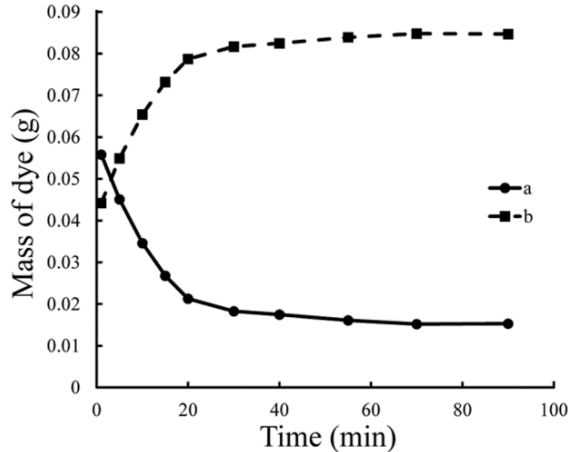


Fig. 4 — Mass of dye remained in bath and absorbed on to fibres (a) mass of dye in bath and (b) mass of dye in fibre

equilibrium. At the equilibrium, dye in bath and fibre will remain constant. Also, the finite element method is used for modeling the distribution of dye in fibre.

Considering the principles of mass conversion, the amount of dye in dyeing bath (m_s) can be calculated using the following equation:

Dye accumulation in bath = Transferred mass from fibre to bath – Transferred mass from bath to fibre

$$\Delta m_s = (d \times m_f \times \Delta t) - (k \times m_s \times \Delta t) \quad \dots (9)$$

$$\frac{d m_s}{dt} = (d \times m_f) - (k \times m_s) \quad \dots (10)$$

Similarly amount of dye absorbed with the fibres can be calculated using the following equation:

$$\frac{d m_f}{dt} = (k \times m_s) - (d \times m_f) \quad \dots (11)$$

Following equations are obtained from above differential equations (12) and (13) respectively:

$$m_f(t, k, d) = \frac{k \times m_0}{d + k} - \frac{k \times m_0}{d + k} e^{-t \times (k + d)} \quad \dots (12)$$

$$m_s(t, k, d) = \frac{d \times m_0}{d + k} + \frac{k \times m_0}{d + k} e^{-t \times (k + d)} \quad \dots (13)$$

Samples are dyed at different time periods from 1 min to 90 min to study the efficiency of proposed models. Mass of dye remained in bath and absorbed on to fibre has also been calculated using Beer-lambert law (Fig. 4). It is observed that the amount of dye in fibre increases with increasing time, however the mass of dye in dye bath decreases with increasing time of dyeing.

The calculated coefficients of absorption and desorption for 1% initial dye concentration are 0.12 and 0.026 respectively. The actual and predicted mass (concentration) of dye in dye bath and fibre are shown in Fig. 5 for 1-3.5% dye concentration. Also,

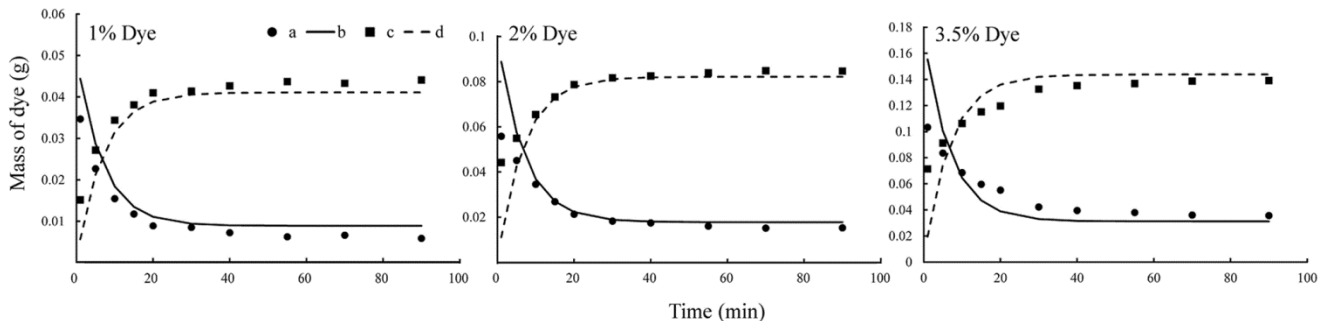


Fig. 5 — Actual and predicted mass of dye in bath and fibre (a) experimental mass of dye in bath, (b) predicted mass of dye in bath, (c) experimental mass of dye in fibre, and (d) predicted mass of dye in fibre

Table 3 — Relative error of mass prediction (%)

Initial dye concentration, %	Media	Average	Standard deviation	Min	Max
1.0	Bath	2.87	28	0.01	8.83
	Fibre	6.35	63.27	0	20
2.0	Bath	5.96	59.13	0	18.68
	Fibre	7.5	74.72	0	23.62
3.5	Bath	21.33	12	5.88	50.35
	Fibre	14.46	21.04	3.33	72.67

relative prediction error difference between actual and predicted values is shown in Table 3.

4 Conclusion

In this study, the Langmuir, Freundlich and Freundlich- Langmuir models are used to evaluate dyeing isotherm. Due to higher R^2 , wool dyeing with acid dye follows Freundlich-Langmuir isotherm. The kinetic studies show that this system obeys second order kinetic equation which is reasonable to describe the experimental data. In this study, for the first time, wool fibre dyeing factors were described using the law of conversion of mass. Fibres are dyed at different initial dye concentrations over time. Findings showed that the proposed models are well fitted on experimental data at 1% and 2% initial dye concentrations. However, the model deviates from experimental data at 3.5% initial dye concentration, which bring this idea into mind that our assumptions are not valid over a critical concentration and model needs to be modified. This error may be attributed to dye aggregates at higher concentrations which at this point need more studies.

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