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Kinetic Model and adsorption Isotherm studies on Natural Indigo and Madder Colorants for Dyeing Wool in One and Two Dye Baths

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Abstract

Herein, we report adsorption kinetic and adsorption isotherm studies on indigo (*Indigofera tinctoria*) and madder (*Rubia tinctorum*) colorants for dyeing wool in one and two dye baths. Two kinetic equations, pseudo-first-order and pseudo-second-order equations, were employed to investigate the adsorption rate. The pseudo-second-order model provided the best fit to the experimental data. This suggests that the pseudo-second-order kinetic model closely describes the sorption process of indigo and madder colorants for dyeing wool in one and two dye baths. The equilibrium adsorption data were fitted using the Nernst, Freundlich, Langmuir and Temkin isotherm models. The adsorption behavior was also in good agreement with the Temkin−Nernst model. However, the pseudo second rate constants obtained for both dyes [K(indigo)=1.543 $g.g^{-1}$ $.min^{-1}$ and K(madder)=0.078 $g.g^{-1}$ $.min^{-1}$] and their optimal dyeing conditions are significantly different. Moreover, the magnitude of the Temkin parameter (B_T) of indigo (B_T=-3.621) is lower than that obtained for madder (B_T=-0.122) for dyeing in two dye baths, which indicates the best coverage of wool fibres by indigo. These results suggest that indigo and madder are not compatible and cannot be mixed in a single dye bath. The complexity of the adsorption isotherms indicates the formation of stronger bonds between the dyes and wool fibres. This indicates that the both dyeing methods (mixed dyeing in one and two dye baths) achieve rigid fixation and an excellent degree of washing fastness.

Keywords:* *Adsorption Isotherms; Dyes, Indigo; Kinetics; Madder; Wool fibres

Introduction

The use of synthetic dyes in the textile industry, especially in the dyeing and finishing process, can generate toxic wastewater. The presence of these dyes in water gives rise to Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and high suspended solids (SS). Dye removal from colored effluent is difficult because of their complex structures, which are more stable and more difficult to biodegrade.

Recently, natural dyes have regained more and more interest in the textile industry, particularly in the area of traditional dyeing

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methods, in order to minimize the toxic effects of industrial effluent. Many studies, scientific research and conferences have promoted and improved the use of natural dyes [1-7]. Various studies have investigated the adsorption isotherms and kinetic models of natural dyes used to dye wool fibres. Somayeh Mirnezhad et al. investigated the dual mode adsorption of cochineal natural dye on wool fibres [8]. They found that the dual Langmuir-Nernst model was the most appropriate isotherm model to describe the adsorption behavior of cochineal dye onto wool fibres at pH 4. Elçin Gûnes et al. used nutshell from walnut rind as a natural dye for wool. They examined the adsorption equilibrium and kinetic sorption [9]. They established that the Langmuir model adequately described the adsorption isotherm of the nutshell colorant onto wool and cotton fibres. In addition, the kinetic data fitted the pseudo-second order kinetic model at low initial dye concentrations. However, there are very few research reports investigating the adsorption behavior of natural dyes in a mixed dye bath.

The aim of this work was to investigate the possibility of mixing two natural dyes, indigo and madder, in a one dye bath and examine the usability of dyeing wool fibres with both natural dyes in a two dye bath. We have studied various kinetic models and the adsorption isotherms obtained for indigo and madder colorants for dyeing wool in one and two dye baths. Therefore, we compare the kinetic and isotherms adsorption parameters obtained for both dyes separately and a mixed dye bath. Their fixation and washing fastness were tested according to ISO 105-C6:A1S [10].

Materials and Methods

Wool fiber features

Wool fibre was obtained from the Boujaâd city region in Morocco. White fleece was compacted and homogenized into a medium weight fleece (1.5-3 kg) and the fineness of the fibre was 50-60 using the Bradford scale [6,7].

Natural dyes

Alizarine and others anthraquinones dyes were extracted from R. tinctorum, which grows in South-East Morocco [11]. The extraction method was based on the enzymatic hydrolysis (endogenous conversion) of the dried and powdered root of the plant. Indigo dye was extracted from *Indigoferra tinctoria* and purchased from the Association Couleur Garance, Lauris-France.

Chemicals

The alkali reagents, sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and acidic reagent, acetic acid (CH_3COOH) were of analytical grade and obtained from Lobachemie Company (Mumbai, India) and VWR Prolabo Chemicals Company (Fontenay-Sous Bois, France), respectively. A Marseille-type soap prepared from vegetable oil was purchased from a mini supermarket. Sodium chloride (NaCl) was of analytical grade and obtained from Solvachim (Casablanca-Morocco).

Argan's pulp

The reducing agent, Argan's pulp, was collected from Argan trees located in the Essaouira city region of South Morocco. This natural product is composed of 20% reducer sugar, 13% cellulose, 6% protein, 2% fat and 4% latex (comprised of 86% of cis-polyisoprene:rubber) [6,7,12,13].

Spectrophotometry

An ultraviolet/visible spectrophotometer (Thermo, Helios Epsilon) was used to scan the range 325-1100 nm with a spectral bandwidth of 1 nm.

pH meter

The dyeing process was carried out in a stainless steel dye pot with a capacity of 500 mL housed in a basin laboratory-scale dyeing

apparatus (Castel-Tourtoy, France).

Bath

A 250-mL flask was used. Heating was by a thermostated hotplate (Scilogex MS-H280-Pro).

Filter

A metallic sieve (1-5 mm diameter) was used throughout this study.

Preparation of indigo vat

Indigo (0.1 g) was added to 100 mL of distilled water containing 1.2 g of sodium carbonate and 1.2 g of sodium bicarbonate at pH 10.86 and 45°C for 30 min with a liquor ratio of 1/100. Then, 4 g of fructose (100 mL of the extract prepared from 30 g of Argan's pulp) and 1 g of sodium chloride were added to the mixture.

Dyeing in the indigo vat

Wool yarn (1 g) was soaked and wrung before being placed in the indigo vat. The dyeing conditions were 100 mL of the dye mixture at 45°C for 30 min with a liquor ratio of 1/100.

Preparation of the madder dye bath

The dyeing conditions for the madder dye bath were 100 mL of the dye mixture (the extract prepared from 5 g of R. tinctorum in 100 mL water), 1.2 g of sodium carbonate and 1.2 g of sodium bicarbonate at pH 9.65 and 60°C for 30 min with a liquor ratio of 1/100.

Reduction of the madder dye bath

The reduction conditions used for the madder dye bath were 100 mL of the as-prepared madder dye mixture, 3 g of fructose (or 30 g of Argan's pulp extract) and 10 g/L of sodium chloride at 45°C for 30 min with a liquor ratio of 1/100.

Dyeing in the reduced madder dye bath

Wool yarn (1 g) dyed beforehand with indigo was being placed in the reduced madder dye bath at 45°C for 30 min with a liquor ratio of 1/100.

Spectral analysis

Spectrophotometer calibration: Spectrophotometer calibration was achieved using a standard solution prepared according to the mass of wool yarn and the concentration of reducer (fructose or Argan's pulp), sodium chloride and alkali (sodium hydroxide, sodium carbonate and sodium bicarbonate) added in the dye bath.

Measurement of the dye exhaustion and fixation rate: A volume of 1 mL of the solution from each dye bath was removed for measurement. Each sample was diluted to 10 mL using the prepared standard solutions. The absorbance measurements are shown in TABLES 1 and 2. The absorbances were measured at 380 nm.

Dyeing process with indigo and madder in a one dye bath

Preparation of the indigo vat: Indigo (0.05 g) was stirred in 50 mL of distilled water at 45°C for 10 min in order to reduce the grain size of the indigo dye particles.

Preparation of the madder dye bath: Madder plant (5 g) was macerated in 100 mL of distilled water at 40°C for 2 h and then filtered using a metallic sieve. A volume of 50 mL of the as-prepared extract was used in the mixed dye bath with indigo.

Preparation of the reduced mixed dye bath: The reduction conditions of the mixed dye bath were 100 mL of the as-prepared indigo (50 mL) and madder (50 mL) colorants, 3 g of fructose (or 30 g of Argan's pulp extract), 1 g of sodium chloride, 1.2 g of sodium carbonate and 1.2 g of sodium bicarbonate at pH 10.73 and 45°C for 30 min with a liquor ratio of 1/100.

Dyeing in the mixed dye bath

Wool yarn (1 g) was soaked and wrung before being placed in the mixed dye bath. The dyeing conditions were 100 mL of the dye mixture at 45°C for 30 min with a liquor ratio of 1/100.

Cold rinse

Rinsing the samples from the mixed dyeing process using one and two dye baths was conducted at the end of the process to remove dyes from the fibre and inter-fibre surfaces and to neutralize the alkaline medium

Oxidation and rinse

Oxidation was achieved for the samples in the open air for 15 min during the rinsing phase. At the end of the dyeing process, two successive rinses were conducted in cold water.

Acidification (neutralization)

The samples were treated with an acidic solution at pH 6.5 containing CH3COOH (30% v/v).

Drying and soaping

The samples were dried in a sterile environment at 60°C and 80°C, then soaped with 0.6 g/L Marseille-type soap at 60°C for 15 min with a liquor ratio of 1/100. The soaping step was used to test the washing fastness of the samples dyed in the mixed dye bath.

Washing fastness

The washing fastness was determined at 40°C according to ISO 105-C6:A1S [10].

Adsorption kinetics

The adsorbed quantity of dye on the wool fibres was calculated as follows:

$$\mathbf{Q=(C_0-C_i)\ (V/m)\ (1)}$$

Where, C_0 and C_i are the initial dye concentration and the dye concentration at time t in the reduction phase, respectively; V is the volume of the reduction bath; and m is the weight of the wool yarn used.

Kinetic models

Pseudo first-order and pseudo second-order kinetic models were used to predict the dye adsorption behavior of the wool fibers. The pseudo-first-order equation is generally suitable for the initial stage of the adsorption process, but the pseudo-second-order equation predicts the adsorption behavior during the whole process. The kinetics of adsorption were determined by analyzing the dye adsorbed from an aqueous solution at various time intervals and then fitting the data to the two models. The pseudo first-order rate equation is given as follows [14-18]:

$$\ln(Q_{e1}-Q_t)=\ln Q_{e1}-K_1 t \quad (2)$$

Where, Q_t is the quantity of dye adsorbed at equilibrium and time t, (g/g); Qe_1 is the theoretical equilibrium adsorption (g/g), and K_1 is the pseudo first-order adsorption rate constant (min^{-1}).

The pseudo second-order kinetic model is given below [14,15,17,19]

$$t/Q_t=1/K_2(Q_{e2})^2+t/Q_{e2} \quad (3)$$

Where Q_t is the quantity of dye adsorbed at the time t, (g/g); Qe_2 is the theoretical equilibrium adsorption (g/g); and K_2 is the pseudo second-order adsorption rate constant (min^{-1}).

Adsorption isotherms

Adsorption isotherms are important to describe how the molecules of an adsorbate distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [20]. The Langmuir and Freundlich isotherms are widely applied to describe the equilibrium adsorption isotherm data. The Nernst and Temkin isotherms are relatively less applied. The Langmuir isotherm is based on the hypothesis that uptake occurs on a homogeneous surface via monolayer adsorption without any interaction between the adsorbent and adsorbate [20,21]. In this model, once a site is filled, no further sorption can take place at that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved [22-24]. The simplest isotherm method is presented by the Nernst equation. This indicates that dye repartition is constant between the dye bath and wool fibres until an equilibrium state is reached. The equation can be expressed as follows:

$$C_e=K_n Q_e+A_n \quad (4)$$

where C_e is the equilibrium concentration of dye (g/L); Q_e is the amount of dye adsorbed per gram of wool fibres at equilibrium (g/g); K_n is Nernst isotherm constant (L/g); and An is the concentration of dye (g/L) when $Q_e=0$.

The Kn and An values were computed from the slope and intercept of the Nernst plot of C_e versus Q_e [8]

The linear equation of the Langmuir isotherm can be expressed as follows:

$$C_e/Q_e=1/KQ_m+C_e/Q_m \quad (5)$$

Where C_e is the equilibrium concentration of dye (g/L); Q_e is the amount of dye adsorbed per gram of wool fibres at equilibrium (g/g); Q_m is the maximum monolayer coverage capacity (g/g); and K is the Langmuir isotherm constant (L/g).

The Q_m and K values were computed from the slope and intercept of the Langmuir plot of C_e/Q_e versus C_e The Freundlich isotherm is generally used to describe non-ideal adsorption on heterogeneous surfaces, suggesting multilayer adsorption on the adsorbent surface. The application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centres of the adsorbent [25]. The linear form of the Freundlich isotherm [26] is given by the following equation:

$$\log Q_e=\log K_f+1/n \log C_e \quad (6)$$

where Q_e is the amount of dye adsorbed per gram of the dye at equilibrium g/g; C_e is the equilibrium concentration of dye g/L; K_f is the Freundlich isotherm constant (L/g), which is an approximate indicator of the adsorption capacity; n is a constant related to the adsorption intensity; and while 1/n is a function of the strength of adsorption.

The K_f and n values were calculated from the intercept and slope of the plot of log Q_e versus log C_e. The values indicate the degree

of non-linearity between the solution concentration and adsorption as follows: If n=1, then the adsorption is linear; if n<1, then the adsorption is a chemical process; if n>1, then the adsorption is a physical process [25, 26]. The Temkin isotherm model [27-29] suggests an equal distribution of binding energies over a number of exchange sites on the surface. The Temkin isotherm in its linear form is given as follows:

$$\mathbf{Q_e=B_T LogK_T+B_T LogC_e} \quad \mathbf{(7)}$$

Where B_T is the magnitude of the Temkin parameter, which is related to the heat of adsorption; and K_T is the equilibrium binding constant.

Results and Discussion

Kinetic models

The pseudo first-order model and pseudo second order model for the indigo and madder colorants using one and two dye baths were investigated. The $\ln(Q_{e1}-Q_t)$ and t/Q_t values were calculated using the equations described in the experimental section. Linear plots of $\ln(Q_{e1}-Q_t)$ against t were constructed and used to calculate the kinetic parameters. The calculated kinetic parameters are shown in TABLE 1, FIG. 1 shows that the pseudo-second-order kinetic model for the indigo and madder colorants in the two dye baths gave the best fitting of the kinetic data. Equally, FIG. 2 shows that the pseudo-second order kinetic model of indigo and madder colorants in one dye bath gave the best fitting of the kinetic data. Using the calculated kinetic models parameters for dyeing in the two dye bath (TABLE 1), the equilibrium adsorption amount ($Q_{e2}-Q_t$) and t/Q_t predicted by the pseudo-second-order kinetic model for the indigo and madder colorants (Q_{e2}, calc=0.056 g/g and Q_{e2},calc=1.326 g/g) was relatively close to the measured values (Q_{exp}=0.041 g/g and Q_{exp}=2.04 g/g) and the correlation coefficient R^2 was >0.990. These results suggest that the pseudo-second-order kinetic model closely describes the sorption process of indigo and madder colorants for dyeing in the two-dye bath. The similar results were found by M. S. Kiakhani and al [30] investigating the sorption process of natural carminic acid (an anthraquinonic colorant like madder colorants, extracted from cochineal) on polyamide fiber.

In the case of dyeing in the one dye bath, the equilibrium adsorption amount ($Q_{e2}-Q_t$) and t/Q_t predicted using the pseudo-second-order kinetic model for the indigo and madder colorants (Q_e,calc=0.378 g/g) is relatively close to the measured value (Q_{exp}=0.186 g/g) and the correlation coefficient R^2 was >0.990. This implies the adsorption process is probably a chemical process and chemisorption may be the rate limiting step in the sorption process involving ion exchange between the dyes and wool fibres [30,31]. The correlation coefficients (R^2=0.915) for the pseudo first-order kinetic model for both dyes are lowest when compared to the values obtained for the pseudo-second-order kinetic model. Moreover, a large difference between the Q_e,calc value for indigo (Q_e,calc=1.016 g/g) and Q_{exp} (Q_{exp}=0.041 g/g) for dyeing in the two dye bath and between the Q_e,calc value for both dyes (indigo and madder: Q_e,calc=1.032 g/g) and Q_{exp} (Q_{exp}=0.186 g/g) in the one dye bath were observed, indicating a poor pseudo-first-order fit to the experimental data.

TABLE 1 shows a comparison of the adsorption pseudo-second rate constants obtained for indigo (1.543 $g.g^{-1}.min^{-1}$) and madder (0.078 $g.g^{-1}.min^{-1}$) colorants for dyeing in the two dye bath indicate the higher speed of indigo dye adsorption. The pseudo second rate constant obtained for the indigo and madder (0.081 $g.g^{-1}.min^{-1}$) colorants for dyeing in the one dye bath is lower. This can be explained by the difference in the optimal dyeing conditions between the indigo and madder colorants. Therefore, indigo required a highly alkaline medium to achieve complete solubility in the dye bath, whereas madder has a lower substantivity towards wool fibres in this highly alkaline medium. We conclude that both dyes, which were described by the adsorption kinetic model, were not compatible and could not be

mixed in the one dye bath.

TABLE 1. The adsorption kinetic parameters obtained for the indigo and madder colorants for dyeing in one and two dye baths.

Sample	Pseudo-first order			Pseudo-second order			Q_{exp} (g/g)
	K_1 (min^{-1})	Q_{e1} (g/g)	R^2	K_2 ($g.g^{-1}.min^{-1}$)	Q_{e2} (g/g)	R^2	
Indigo dye	–0.001	1.016	0.915	1.543	0.056	0.990	0.041
Madder colorants	–0.021	1.537	0.919	0.078	1.326	0.997	2.04
Indigo and madder colorants	0.245	0.976	0.914	0.081	0.378	0.928	0.186

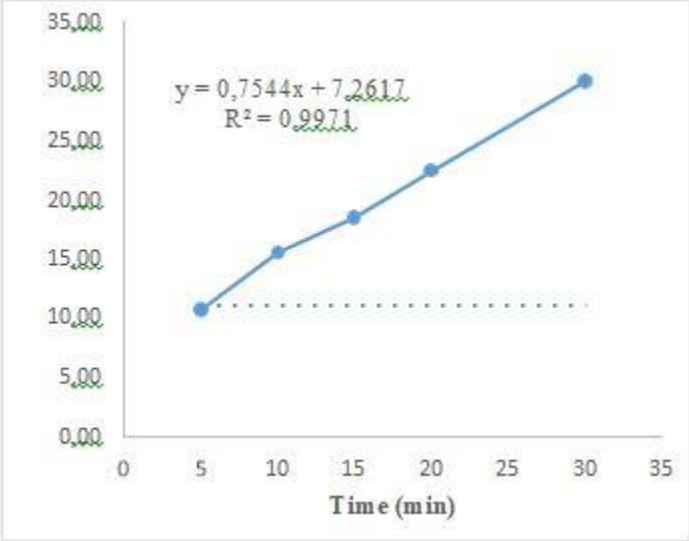


FIG. 1. **Adsorption kinetic of indigo for dyeing in two baths according to pseudo second order model**

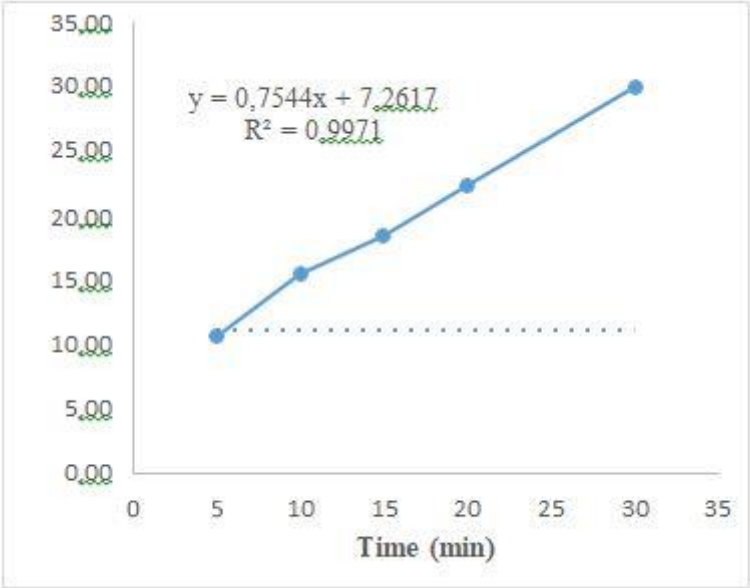


FIG. 2. **Adsorption kinetic of madder colorants for dyeing in two baths according to pseudo second order model.**

Adsorption isotherms

Adsorption isotherms for dyeing in a two-dye bath: The isotherm studies obtained for the indigo and madder colorants for dyeing in a two dye bath (FIG. 3-5) showed that the Nernst and Temkin models were followed unlike the Langmuir and Freundlich models according to their R^2 values. The experimental data for the effect of the initial indigo concentration on dye adsorption were fitted to the Nernst and Temkin models, which were obtained by plotting C_e versus Q_e and Q_e versus LogCe, respectively. All the isotherm model parameters are presented in TABLE 2. It can be seen that the correlation coefficients (R^2) obtained for the Nernst and Temkin isotherms of the indigo and madder colorants a two dye baths were 1 and 0.9843, and 1 and 0.999, respectively. This result suggests an equal distribution of binding energies over a number of exchange sites on the surface (Temkin model) and that dye repartition is constant between the dye bath and wool fibres until it reaches an equilibrium state (Nernst model). The linearity of the models shows that the number of free sites is constant during the adsorption process. The comparable results were found by M. S. Kiakhani and al [31], also by Mirnezhad, S and al.[32] investigating the behaviour adsorption of natural carminic acid colorant on wool fibers at pH6. However, the R^2 value (0.984) obtained using the Freundlich isotherm for the madder colorants are higher. Therefore, the adsorption isotherm obtained for the madder colorants may be described by the Freundlich isotherm. This suggests that the binding of the dye molecules also occurs on the heterogeneous surface of the wool fibres via a multi-layer adsorption process. The n value for the madder colorants was >1 indicating a favourable adsorption process (chemical process). This complex mechanism can contribute to the formation of relatively stronger bonds between the dyes and wool fibres.

Adsorption isotherms for dyeing in a one dye bath: The isotherm studies for dyeing in a one dye bath (Fig. 3-5) show that the Nernst, Temkin and Freundlich models were followed unlike the Langmuir model according to their correlation R_2 values. The experimental data for the effect of the initial concentrations of the indigo and madder colorants on dye adsorption were fitted with the Nernst, Temkin and Freundlich models, and were obtained by plotting C_e versus Q_e, Q_e versus $LogC_e$ and $logQ_e$ versus log C_e, respectively. All the isotherm model parameters are presented in TABLE 2. It can be seen that the correlation coefficients (R^2) obtained for the Nernst and Temkin isotherms for the indigo and madder colorants are 1 and 0.999, respectively. However, the R^2 value (0.956) for the Freundlich isotherm is less than those of the Nernst and Temkin isotherms. The differences in the correlation coefficients indicate that the adsorption of indigo during the dyeing process followed the Nernst and Temkin models more closely

than the Freundlich model.

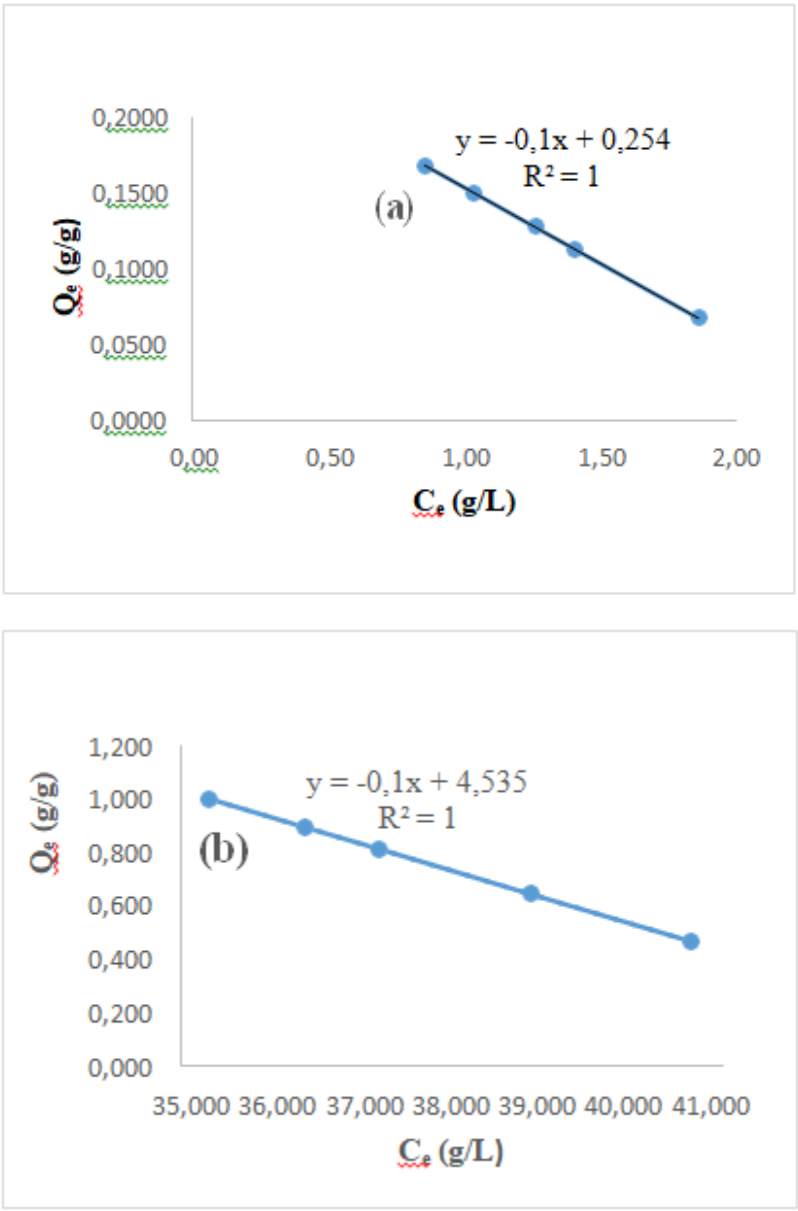
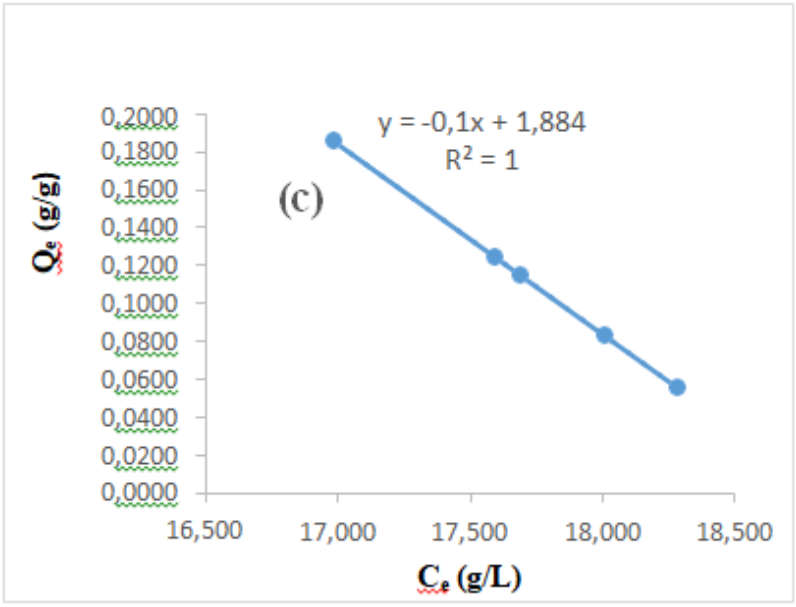


FIG. 3. **Linear Nernst isotherm plots for the adsorption of indigo (a), madder colorants (b) and mixed dyes (c) on the wool fiber**



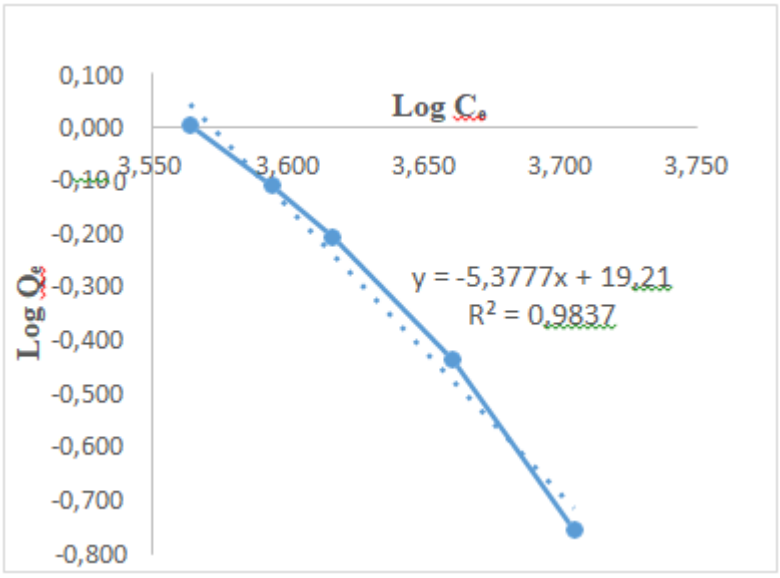
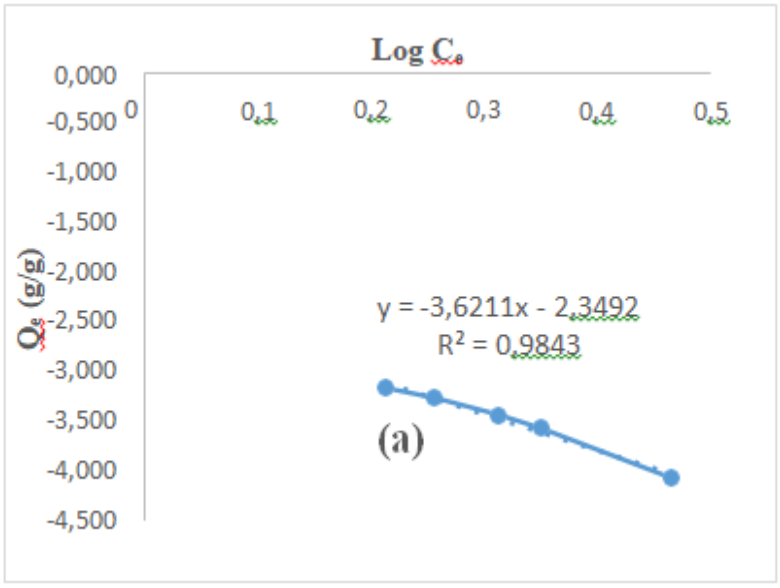
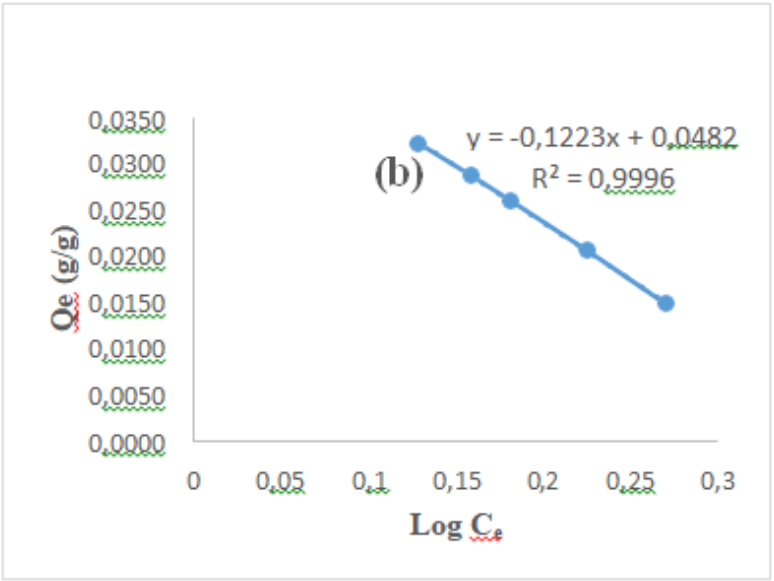


FIG. 4 **Linear Freundlich isotherm plots for the adsorption of madder colorants on the wool fiber.**





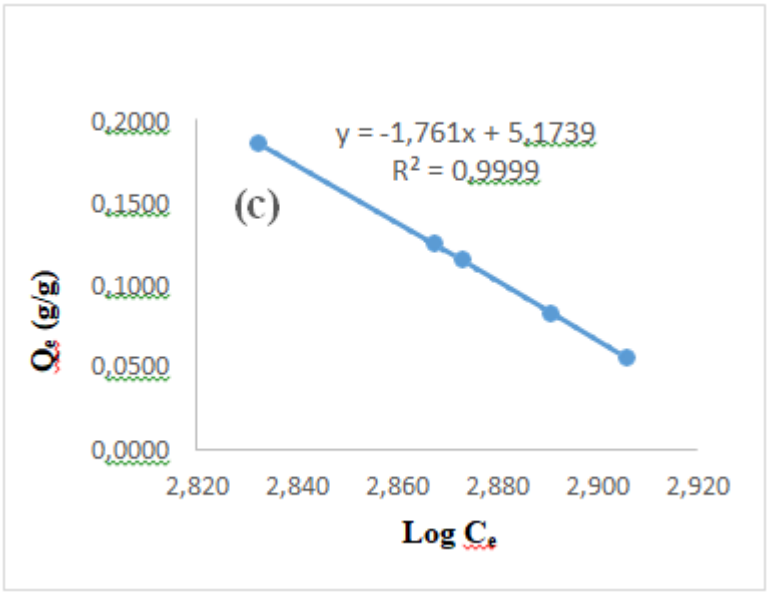


FIG. 5. **Linear Temkin isotherm plots for the adsorption of indigo (a), madder colorants (b) and mixed dyes (c) on the wool fiber**.

A comparison study of the adsorption isotherms: Notably, the Nernst constant (K=0.1) is similar for all dyes using the one and two dye baths, which indicates the similar adsorption isotherms obtained for these dyes. The magnitude of the Temkin parameter (B_T) for indigo (B_T=-3.621) is lower than that obtained for the madder colorants (B_T=-0.122) for dyeing in a two dye bath, which indicates the best coverage of wool fibre by indigo (since the heat of adsorption decreases linearly with increasing coverage). Equally, examination of the data obtained for dyeing in a one dye bath showed that the Temkin parameter for the two mixed dyes (B_T=-1.761) was lower than the madder colorants and higher than indigo for dyeing in the two dye bath, indicating that mixed dyeing increases the coverage of wool fibres. The calculated Freundlich constants as presented in TABLE 2 and show that the n value for the mixed dyes was >1 indicating a favourable adsorption process (chemical process). These results confirm that the adsorption isotherms obtained for the indigo and madder colorants in a one dye bath are similar to those in the two dye bath (as described above). The complexity of the adsorption isotherms indicates that the formation of stronger bonds between the dyes and wool fibres.

TABLE 2. **Adsorption isotherm parameters of indigo and madder colorants for dyeing in one and two baths.**

Sample	Nernst			Temkin			Freundlich			Langmuir		
	K_n	R^2	A_n	B_T	K_T	R^2	K_f	n	R^2	R^2	K_L	Q_m
Indigo	-0.1	1	0.2	-3.621	1.913	0.984	0.008	0.871	0.939	0.937	478.52	90.91
Madder colorants	-0.1	1	4.5	-0.122	0.703	0.999	—	-0.186	0.984	0.956	0.309	10.00
Indigo and madder colorants	-0.1	1	1.9	-1.761	0.053	0.999	43.45	-0.063	0.956	0.859	—	—

Washing fastness

The measurements obtained for the two soaping samples are presented in TABLE 3. The values from these experiments confirm the hard fixation. An excellent washing fastness was achieved for both dyeing methods. In fact, the reduction method (vat system) for the indigo and madder colorants in both methods, which improve the diffusion and fixation on the wool fibres, convert the dye molecules onto non-soluble molecules inside the wool fibres. This increases the fastness properties in the dyeing process. We can conclude that both methods achieved similar fastness. This can be explained by the seam fixation mechanism (reduction and oxidation reactions).

TABLE 3. **Washing fastness of indigo and madder colorants for dyeing in one bath and two baths.**

Samples	Washing fastness (assessing staining)						Washing
	WO	PAC	PES	PA	CO	CA	fastness (assessing color change)
Dyeing in two Baths	5	5	5	5	5	5	4-5
Dyeing in one bath	5	5	5	5	5	5	4-5

Conclusion

This study demonstrates the complexity of the adsorption kinetics and adsorption isotherms obtained for indigo and madder colorants in one and two dye baths. The pseudo-second-order model provides the best fit to the experimental data and closely describes the sorption process for indigo and madder colorants in one and two dye baths. The isotherm studies for dyeing in one and two baths show that the Nernst and Temkin models are obeyed unlike the Langmuir and Freundlich models according to their

correlation coefficients.

However, the pseudo second order rate constant obtained for indigo are significantly greater than those of the madder colorants and the optimal dyeing conditions for both dyes are different. Moreover, the magnitude of the Temkin parameter for indigo (B_T=-3.621) is lower than that obtained for the madder colorants (B_T=-0.122) in the two dye bath, which indicates the best coverage of wool fibre by indigo. We can conclude that both dyes were not compatible and could not be mixed in a one dye bath. The complexity of the adsorption isotherms indicates the formation of stronger bonds between the dyes and wool fibres. This indicates that both dyeing methods (mixed dyeing in one and two dye baths) achieved hard fixation and an excellent degree of washing fastness. This was confirmed by experimental data obtained in the fastnestest.

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