Dyeing Mechanism of Wool and Silk with Extract of *Allium Cepa*

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Silk and wool fabrics were dyed with the colorant extracted from Allium cepa. Dyeing experiments were carried out varying temperature and pH. Colour uptake and colour fastness have been investigated. It was seen that pH of 3 and temperatures of 80 and 90 ºC are the ones that produced the best results in wool and silk, respectively. Such results have been used to investigate the dyeing kinetics and the dyeing process at equilibrium through adsorption isotherms. The kinetic study showed that the pseudo second order equation is the one that best represents the kinetic mechanism of dyeing both fabrics, which is related to the chemisorption process as the rate-controlling step. The equilibrium data for wool and silk fabrics were easily adjusted to the Langmuir-Freundlich model indicating the significant contribution of chemisorption process in a monolayer followed by a multilayer physisorption.

1. Introduction

Recently, the dyestuffs industry is increasingly forced to reduce toxic effluents and stop the production of dyes or pigments potentially hazardous (Mirjalili et al., 2011). Moreover, due to the increased perception of environmental and health risks associated with the synthesis, processing and use of synthetic dyes, interest in natural dyes has increased worldwide, growing a new market that values products produced from natural raw materials, which minimize damage to human health and the environment (Bechtold and Mussak, 2009). The growing global trend of conservation of environmental resources and quality of life is reflected in the textile industry as a whole, since the differentiation in products and processes have been seen as a means for consumer satisfaction. Thus, the use of the least toxic natural dyes for the dyeing textiles can be considered a very suitable alternative, since such compounds are already environmentally compatible, have biodegradability, low toxicity and absence of allergic effects (Ibrahim et al., 2010). Onions can be used as natural dyes. Their scientific name is *Allium cepa*. Quercetin, commonly presented in the onion skin is the natural colorant that provides different brown tones to natural fabrics such as silk and wool (Vankar et al., 2009). Wool and silk fibers are protein-based and both have a general chemical formula $NH_2.CHR.COOH$. There are various functional groups that can be found in proteins, which determine the polymer properties. The most important ones for the dyeing of wool and silk with acid dyes are COOH and NH_2 (Khan, 2011). In dyeing process, dyes in solution are adsorbed and diffused into the fiber, establishing with it physico-chemical interactions (Broadbent, 2001). However, the dyeing process with natural dyes is still quite empirical. The process is scarcely reported in literature, as well as investigations related to the sorption mechanism.Then, the present work aimed to investigate the best dyeing conditions, such as pH, temperature and initial dye concentration of silk and wool fabrics using onion skins as colorant. Kinetics and equilibrium data were investigated.

2. Experimental Section

2.1 Materials
Onion dry skins after being ground were used as the raw material. The dye solutions were prepared at

predetermined concentrations in the experimental design, as shown in Table 1. The samples were then heated with stirring at 90 °C, for 60 min and filtered. The filtrated solution was used in the dyeing process. Concentration of the dyeing solutions was analyzed through spectrophotometry. At first, the wavelength of maximum absorption (λ_{max}) of the filtrated solution was obtained through the Shimadzu 1601DC spectrophotometer. Once λ_{max} was determined, it was used to analyze the dyeing concentration in the Biospectro SP22 equipment. The amount of dye in solutions was monitored by spectrophotometric reading until the absorbance values remained constant. All concentrations were determined using a calibration curve of the standard solution of skin extract of onion Allium Cepa. The wool (140 g/m^2) and silk (70 g/m^2) fabrics used in all experiments were ready for dyeing. Before putting into contact with the dyeing solutions, all samples of wool (1.4 g) and silk (0.7 g) were submitted to a mordanting process. Then, the pre-mordanting procedure was carried out in the Kimak AT1-SW equipment.

2.2 Chemicals

The PA reagent hydrochloric acid was used for pH correction. Solutions of 5 g/L of potassium alum ($Al_2K_2(SO_4)_4$) was used as mordant (Vankar, 2007). The non-ionic detergent Nionlab CELM was applied in the fastness to washing procedure.

2.3 Mordanting Process

Fabric samples were immersed in aqueous solution of the mordant, using a liquor ratio of 1:100 for 45 min at 90 °C (Das et al., 2007). After treatment the samples were dried at room temperature.

2.4 Dyeing Process

All dyeing was conducted in the dyeing machine Kimak AT1-SW. They were divided into two steps: the first was related to obtain the best experimental conditions. The second step was devoted to investigate the dyeing mechanism through the kinetic and equilibrium data. In order to determine the optimum conditions of dyeing wool and silk fabrics it was necessary to study the influence of the dyeing parameters (temperature, pH and initial concentration of dye) in the dye uptake. It was adopted a 2^3 complete factorial design composed of eleven trials, with three trials for the central point. In the factorial design of dyeing the response variable was the amount of dye adsorbed in the fabrics. Table 1 lists the variables and levels for dyeing. It was used the Design-Expert software.

Table 1: Factorial design for dyeing of wool and silk fabrics

Numeric variables	Levels		Central Points
	-1	1	0
T (ºC)	80	90	85
pH	3.0	4.0	3.5
Initial dye concentration (g/L)	5	10	7.5

In dyeing wool and silk, firstly different pH of the solutions was adjusted with hydrochloric acid. Then, samples were dyed for 60 min using a liquor ratio of 1:100 in the pre-conditions set out in factorial design. After dyeing, the samples were submitted to one wash in order to remove unfixed dye during the process, using 2 g/L non-ionic detergent at 60 °C for 10 min, rinsed in cold water and dried at room temperature. The amount of dye adsorbed per gram of fabric (q) (mg/g fabric) was determined through a mass balance. To determine the adsorption kinetics of dyeing, the wool and silk fabrics were put in contact with the dye using also a liquor ratio 1:100 in the optimized conditions of dye concentration, temperature and pH, obtained. The fabrics were removed from the equipment AT1-SW at different dyeing times. For the interpretation of the kinetic batch experimental data two different kinetic models were used: the pseudo-first order model (Lagergren, 1898) and the pseudo-second order kinetic model. The pseudo-second-order rate expression is used to describe chemisorption involving valence forces through the sharing or exchange of electrons between the dye, mordant and the fabric as covalent forces (Ho, 2006).

The equilibrium data was carried out using dye solutions with different concentrations at 70, 80 and 90 ºC. pH was adjusted to 3.0 with hydrochloric acid and put into contact with the fabric sample up to the equilibrium times previously determined with the kinetic data. The Langmuir adsorption isotherm (Langmuir, 1918) has been successfully applied to many other real sorption processes, even in the dyeing process (Chairat et al., 2005; Kongkachuichay et al., 2010). The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available. It predicts the formation of multilayers (Freundlich, 1906). The experimental data may be also fitted to the three-parameter model of Langmuir-Freundlich when the two-parameter models of Langmuir and Freundlich do not provide reasonable results. The Langmuir-Freundlich model is able to describe both

the adsorptive behavior characteristic of the Langmuir type as the Freundlich. Normally this model fits better in cases where the adsorbent has heterogeneous surface, as it is the case of wool and silk (Kumar et al., 2010), and is commonly expressed by Eq(1).

$$q_e = \frac{q_m (K_{LF} C_e)^n}{1 + (K_{LF} C_e)^n} \tag{1}$$

where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_m is the maximum quantity adsorbed in the monolayer (mg/g), C_e is the dye concentration at equilibrium (mg/L), n is a constant of heterogeneity and K_{LF} is the Langmuir-Freundlich adsorption constant (L/mg) (Janoš et al., 2009).

2.5 Color Fastness to Washing
All samples were dyed in the optimal conditions of dyeing, given as the response of the factorial design (Table 1). The wash fastness test followed the procedures of Brazilian Association of Technical Standards, ABNT NBR ISO 105-C06: 2006 A1S cycle - Tests for color fastness: Part C-06: Color fastness to domestic and commercial laundering (Bechtold and Mussak, 2009). Evaluation of the transfer and change of color was performed using Datacolor 550 spectrophotometer.

3. Results and Discussion

The aqueous solution of the extract had a length of maximum absorption between 230-300 nm and a lower intensity peak was also observed at 430 nm which is in agreement with Vankar et al. (2009). This was used in all readings with significant sensivity.

According to the operational dyeing processes it was seen that all samples showed a yellowish-brown coloration. For wool this coloration was more intense in the sample dyed containing 10 g/L initial dye concentration at pH 3.0 and 80 °C, while for silk the coloration was more intense in the sample dyed with 10 g/L, pH 3.0 and 90 °C.

To confirm the optimum condition of wool and silk dyeing with extract of Allium cepa it was carried the full factorial design 2^3, in the response variable (q) in the process of dyeing. It is observed in Table 2 that the higher response values are found in tests 2 and 4 for the wool and silk fabrics, respectively. The initial concentration of 10 g/L, pH 3 and 80 ºC provided the higher adsorption value of 425 mg of dye/g of wool, while 10 g/L, pH 3 and 90 °C provided the higher adsorption value of 81 mg of dye/g of silk. These results are in total agreement with previous results and were already reported in Das et al. (2007).

Table 2: Results of the 2^3 factorial design for the wool and silk dyeing with extract of Allium cepa

Test	Concentration (mg/L)	Temperature (°C)	pH	q (mg/g wool)	q (mg/g silk)
1	-	-	-	216	32
2	+	-	-	425	67
3	-	+	-	113	54
4	+	+	-	377	81
5	-	-	+	110	21
6	+	-	+	326	56
7	-	+	+	82	32
8	+	+	+	280	64
9	0	0	0	249	47
10	0	0	0	255	52
11	0	0	0	244	51

Table 2 also shows that the amount of adsorbed dye was higher in the wool fabrics than the silk, possibly due to the larger amount of functional groups present in the structure of wool (Broadbent, 2001). It was also found that the adsorption capacity was dependent on concentration, once to 10 g/L there was a greater amount of dye adsorbed on wool and silk fabrics. This may be a result of an increase in the driving force of the concentration gradient with the increase in the initial dye concentration as already seen in Chairat et al. (2005). The best operational conditions were obtained in acidic pH. In these conditions amino groups ($-NH_2$) of protein fibers are protonated. Then, they are able to attract anionic dyestuffs. Protonation of the fibers often results in increased uptake of dye being greater for the dye solution at pH 3.0 (Das et al., 2007). Nevertheless, it was seen that an increase in temperature was favorable to the dye uptake in silk fabrics. This result may reflect an increase in the mobility of the large dye ions with temperature and

thus an increase in the number of molecules interacting with the active sites at the silk fabric (Chairat et al., 2005). For wool dyeing, the temperature increase decreased the amount of dye adsorbed. Possibly it is related the rupture of links in the structure of wool due to fragility of these bonds at higher temperatures, which makes the fibers weaker, less resistant and yellowish. Thus, it is possible to minimize any degradation of the wool performing the dyeing at a temperature of 80 °C (Broadbent, 2001).

The main effect of the variables on the response (q) and the percentage contribution of each variable showed that the initial concentration of the dye has the greatest contribution (81.38% and 69.40%) in increasing the response variable (q), followed by pH (11.53% and 15.45%) and the temperature (5.25% and 12.65%) for wool and silk dyeing respectively. Furthermore, it can be noted that the effects of temperature and pH on response variable are negative for the wool dyeing. For the silk dyeing only the effect of pH is negative. It means that an increase in these variables decreases the value of response variable (q). This is also in agreement with the experimental data.

Kinetic results showed that the equilibrium time was found in about 60 min for both fibers. The adsorption was very fast in the early stages of contact time and gradually decreased with time until it remained constant. The same behavior was observed in the work of Chairat et al., (2005). The linear fit of pseudo-second-order model for the dyeing of wool and silk is shown in Figure 1.

a)   b)
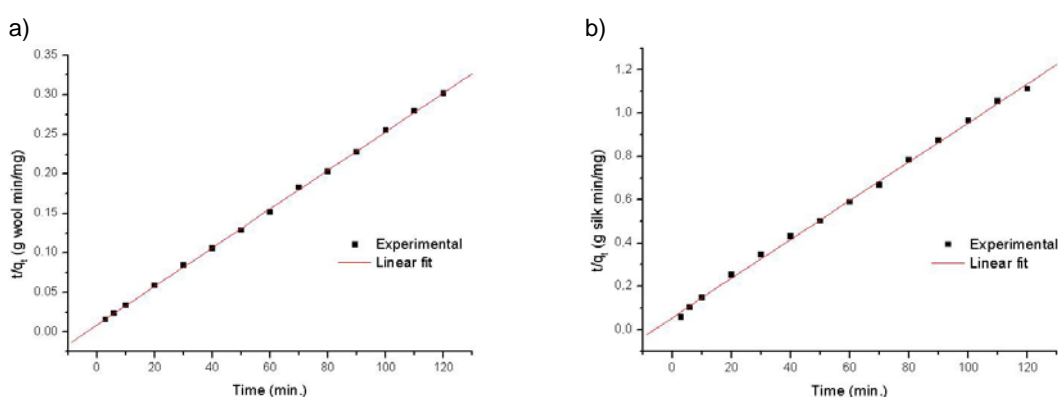

Figure 1: Graphic model of pseudo second-order (a) Wool. (b) Silk

It was observed that the kinetic model of pseudo second-order describes well the adsorption of *Allium cepa* dye on wool and silk. As it can be seen in Table 3, pseudo-first order did not provide good adjustments as the correlation factor R^2 is not close to 1. Moreover, the amount of dye experimentally retained in the equilibrium is quite similar to the value estimated through the pseudo-second order model for both fibers. These data suggest that the mechanism of adsorption of pseudo-second order is predominant and that the overall rate of adsorption of Allium cepa dye is more likely to be controlled by the chemisorption process (Chairat et al., 2005). In fact, it was already expected due to the chemical attraction earlier discussed and also reported in Das et al. (2007).

Table 3: Comparison of kinetic models pseudo-first and second-order

Fabric	$q_{e,exp}$ (mg/g)	Pseudo first-order model		
		k_1 (min^{-1})	$q_{e,cal}$ (mg/g silk)	R^2
Wool	397	0.01516	-5	0.67292
Silk	108	0.00359	-40	0.89585
Fabric	$q_{e,exp}$ (mg/g)	Pseudo second-order model		
		k_2 (g silk.mg dye^{-1}. min^{-1})	$q_{e,cal}$ (mg/g silk)	R^2
Wool	397	$1.05.10^{-7}$	408	0.99980
Silk	108	$9.17.10^{-6}$	111	0.99914

The isotherms of wool and silk dyeing are presented in Figure 2. The initial isotherms slope may be classified as type S2 according to Giles et al. (1960). In the very beginning of the isotherms it is seen a short plateau, which means that the dye molecules have nearly the same affinity for more dye molecules as the initial sites of the fabrics. This is the first evidence of the multilayer chemisorption process after the monolayer formation due to the strong electrostatic forces involving the fabrics, the mordant and the dye molecules. The second rise and the second and much more pronounced plateau are attributed to the

development of the monolayer as a new surface where chemisorption can also occur. Then, the second plateau represents the saturation of such new surface. This behavior is observed for both fibers.
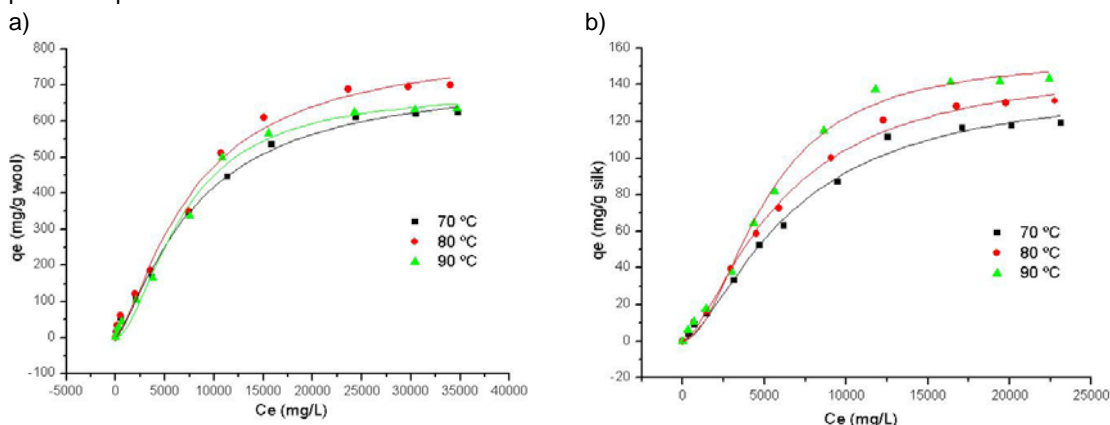
a)   b)

Figure 2: Nonlinear adsorption isotherm of Langmuir-Freundlich model. (a) Wool. (b) Silk.

Experimental data was better adjusted to the Langmuir-Freundlich model for both fibers. Adjustments of Langmuir and Freundlich models were poor and will not be shown. According to the Langmuir-Freundlich line of thinking, it is clear the contribution of the monolayer and the following layers. Possibly, the monolayer occurs with the interaction between the hydroxyl groups of the dye and the amino groups of the protein fibers (Vinod et al., 2011). The multilayer formed through chemisorption of other radicals that interact to the dye. Therefore, the Langmuir-Freundlich model that emphasizes the importance of both phenomena comes naturally as the model that may represent the equilibrium data of the dye from onion skins in the wool and silk fabrics. Parameters for the Langmuir-Freundlich for wool and silk dyeing are shown in Table 4. Nevertheless, equilibrium data were fitted to the Langmuir-Freundlich model, which is in total agreement with the isotherm shape for both fibers.

Table 4: Model parameters of Langmuir-Freundlich isotherm for silk and wool

Fabric	Parameters	70 ºC	80 ºC	90 ºC
Silk	$q_{max\ exp.}$ (mg/g fabric)	119	131	143
	$q_{max.}$ (mg/g fabric)	141.16 ± 9.08	152.88 ± 7.11	155.40 ± 6.08
	k_{LF}	0.00015 ± 0.00002	0.00017 ± 0.00001	0.0002 ± 0.00001
	n	1.53 ± 0.18	1.51 ± 0.13	1.93 ± 0.21
	R^2	0.9941	0.9964	0.99417
Wool	$q_{max\ exp.}$ (mg/g wool)	624	699	635
	$q_{max.}$ (mg/g silk)	729.76 ± 40.98	813.27 ± 56.10	688.13 ± 28.94
	k_{LF}	0.00012 ± 0.00001	0.00013 ± 0.00002	0.00014 ± 0.00001
	n	1.33 ± 0.14	1.39 ± 0.19	1.72 ± 0.20
	R^2	0.99553	0.99233	0.99384

The Langmuir-Freundlich model predicts q_{max} close to the experimental value $q_{max\ exp.}$. The heterogeneity parameter, n, assumes values close to one. Values close to the unity indicate an approximation to Langmuir isotherm, with the formation of a homogeneous monolayer, followed by the formation of multilayer, which may be expressed by values higher than one. The n value was greater for the isotherm of silk, which indicates that more multilayers than in the wool. It means that adsorption is stronger on wool fiber. Moreover, these results are in agreement with the good fastness ratio obtained, where the colour fastness index was higher in wool than silk, indicating, once more, that the chemical adsorption is predominant in the dyeing process.

The indices of wash fastness of dyed wool and silk fabrics in the optimized conditions with alum mordant were satisfactory being of 4-5 (very small change) for wool and 4 (slight change) for silk. The good fastness properties of dyed wool and silk fabric with *Allium cepa* with the addition of the mordant can be attributed to the fact that hydroxy and oxo groups present in the quercetin structure have ability to form complexes with the alum, thereby improving fastness to washing (Vankar et al., 2009). The index of greater fastness in the wool fiber than silk once again confirms that the adsorption is stronger for this fiber.

4. Conclusions

The best result of dyeing the silk was achieved using a temperature of 90 °C, pH 3.0 and 10 g/L initial dye concentration while the best result of dyeing the wool was achieved using a temperature of 80 °C, pH 3.0 and 10 g/L initial dye concentration. The pseudo-second order model may successfully represent the kinetic experimental data for wool and silk dyeing. The equilibrium data for both fibers can be represented by the Langmuir-Freundlich model. According to the kinetic and equilibrium results, it was concluded that chemisorption is quite important in the wool and silk dyeing. Tests of fastness to washing showed satisfactory results indicating that there was a good fixation of the dye on the fiber. Therefore, it was concluded that the wool and silk fabrics are easily dyed with extracts of *Allium cepa* providing a yellowish brown color. Considering that the dyeing process has a great contribution of chemisorption which promoted good color fastness to laundering, it is concluded that dyeing with *Allium cepa* has huge advantages as the textile wastewater is much more biodegradable than the textile wastewater generated with synthetic dyes.

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