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Improvement in the Washing Fastness of Wool Dyed with Natural Alizarine Dye

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Abstract: Herein we report our study on the improvement of the Washing fastness of wool dyed with natural alizarin using an alkaline dyeing process. Natural alizarin was extracted from the *Rubia tinctorum* plant using enzymatic hydrolysis and alkaline solution. The dyeing alkaline process was realized at pH 10 without any mordant. The fastness was clearly higher using a post treatment acidification step. The exhausted dye was completely fixed after this post treatment. In contrast, the non-treated dyed sample lost nearly three quarters of coloration after a single hot rinse process. The alizarine dyeing process using the argan's pulp reducer insure higher fastness proprieties when compared to the alkaline dyeing process without acidification post treatment step.

Keywords: Wool, Natural Alizarin, Enzymatic Hydrolysis, Rubia Tinctorum, Argan's Pulp

1. Introduction

Many different formulas for dyeing with *Rubia tinctorum* have been described in the literature. Dyeing recipes using *Rubia* root particles can be divided into two main classes according to the origin of the material to be dyed, the number of process steps and the chemicals used: 1) The dyeing procedure with *Rubia* root particles used for dyeing animal derived fibers such as wool and 2) the Turkish red procedure used for dyeing plant derived fibers such as cotton. In the dyeing procedure using *Rubia* root particles the main steps are: pre-treatment, mordanting, dyeing and washing [1-4].

*D. De Santis et al. report*ed that the dyed wool and cotton fibers using an ethanolic or methanolic extract of alizarin obtained from *R. tinctorum* had a lighter color intensity and a more pinkish shade than those dyed with *Rubia* root particles. However, the manual washing fastness at 40°C and acid or basic perspiration tests was found to be sufficiently high [5].

Most of the anthraquinones in *R. tinctorum* are phenols. In general phenols dissolve well in basic solutions [6, 7]. *Masawaki et al*. used this property for the simultaneous extraction of both the aglycones and glycosides. When an aqueous KOH solution (50 mmol/m^3) or aqueous solution of NaOH [8] was used as the extraction solvent, both ruberythric acid and lucidin primeveroside were extracted.

Another possibility is the hydrolysis of the glycosides using hydrolases. *Masawaki et al.* claimed that ruberythric acid, in a two phase chloroform–water solution, could be selectively and completely converted to alizarin within six hours via enzymatic hydrolysis using 6-glucosidase at 50°C and pH = 5 [9].

In our study, we have used enzymatic hydrolysis (endogenous conversion) to convert glucosidic anthraquinones, in particular, ruberythric acid to alizarin [10, 11] (see paragraph: Preparation of dyebaths 1 and 2).

The aim of this work was to use a non-classical dyeing process with alizarin based on alkaline solubilization with the purpose of improving the washing and rubbing fastness. After dye diffusion into the wool fiber in a dyebath at pH 10, the fiber was treated with acetic acid (CH_3COOH) at pH 3.5 in order to convert the alizarin dye into a non-soluble molecule but this time inside the fiber. This process involved designing an alkaline dyeing process with a post treatment acidification step (dyebath 2). Also we have tested and compared the washing fastness of the present dyeing procedure with different dyeing process using reducer treatment.

2. Experimental

2.1. Materials

2.1.1. Features of Wool Fiber

The wool fiber used was provided from the Boujaâd city region of Morocco. White fleece was compacted and homogenized to a medium weight of fleece 1.5–3 kg and the fineness of fiber was 50–60 using the Bradford scale [12].

2.1.2. Natural Dye

The dye used in the present study was obtained from a natural source and extracted from the *R. tinctorum* plant, which grows in the South-East of Morocco [13]. The extraction method was based on the enzymatic hydrolysis (endogenous conversion) of the dried and powdered root of the plant.

2.1.3. Argan's Pulp

The reducer agent, Argan's pulp, was collected from around the Argan tree from the Essaouira city region of South Morocco. This natural source was composed of 20% reducer sugar, 13% cellulose, 6% protein, 2% fat and 4% latex (comprised of 86% of *cis*-polyisoprene: rubber) [12, 14, 15].

2.1.4. Chemical Products

The alkali agent, NaOH, and acid agent, CH_3COOH, were of analytical grade and obtained from Lobachemie company –Mumbai (India), and VWR Prolabo Chemicals company, Fontenay-Sous Bois (France), respectively. The soap used was a Marseille soap type which prepared from vegetables oil, and obtained from customary magazine. The common salt, NaCl, was of technical grade and obtained from customary magazine.

2.1.5. Spectrophotometer

The ultraviolet–visible (UV–vis) spectrophotometer used in this study was a Thermo, model Helios Epsilon. The wavelength range was 325–1100 nm with a spectral bandwidth of 1 nm.

2.1.6. pH Meter

The pH meter used was a Henne, model AD1000. It is a multimeter with professional banc for pH, redox (oxido-reduction potential) and temperature measurements.

2.1.7. Bath

The bath used was a 250 mL flask. Heating was provided using a thermostat hotplate, Scilogex MS-H280-Pro.

2.1.8. Filter

Two types of filter were used in this study, the metallic sieve (diameter 1-5 mm) and Buchner funnel with water trumped.

2.2. Dyeing Process

2.2.1. Preparation of Dyebaths 1 and 2

Two quantities of 2.5 g of the *R. tinctorum* plant were stirred separately in 100 mL of water at 45°C. After 1 hour, a solution of 0.1 g/L NaOH was added to the prepared solutions of plant material. The pH of the solutions was adjusted to 12.6, which gave a color change from yellow to purple. Water was added to make up the prepared solutions to 500 mL, which was designated as the original solution of dyebath and was stirred for 30 min at room temperature. Two fractions of 100 mL were extracted from there. The pH of both fraction solutions was adjusted to pH 10 using acetic acid. Both fractions were filtered through a Buchner funnel and designated dyebath 1 and dyebath 2, respectively.

2.2.2. Preparation of the Reducer

6 g of Argan's pulp was added in 500 mL of distilled water and heated at 95°C for 30 min. The extract was filtrated using the metallic sieve.

2.2.3. Preparation of Dye Bath 3

2.5 g of the *R. tinctorum* plant was stirred in 100 mL of water at 45°C. After 1 h, solution of 0.1 g/L of sodium carbonate (Na_2CO_3) was added to the prepared solution. The pH of the solution was adjusted to 8, which gave a color change from yellow to purple. Water was added to the prepared solution to make it up to a volume of 500 mL, which was designated as the original solution of dye bath 3. One fraction of 100 mL was extracted. 10 mL of Argan's pulp extract (described above) was be added to this fraction solution and stirred for 30 min at 45°C. The present fraction was be filtered through a Buchner funnel and designated dye bath 3.

2.2.4. Dyeing Conditions

i. Dyebaths 1 and 2

- Dye: 100 mL of prepared extract from 2.5 g of *R. tinctorum* stirred in 500 mL of water with NaOH.
- NaOH and CH_3COOH: pH = 10
- Temperature: 60°C
- Time: 30 min
- Liquor ratio: 1/100

The both samples of yarn of wool (1 g) were soaked and wrung before being involved in the dyeing baths.

ii. Dye Bath 3

- Dye: 100 mL of extract prepared from 2.5 g of *R. tinctorum* stirred in 500 mL of water.
- Reducer: 10 mL of Argan's pulp extract containing 6 g of Argan's pulp in 500 mL of water.
- Sodium carbonate: 0.1 g/L (pH = 8).
- Sodium chlorate: 5 g/L.
- Temperature: 45°C.
- Time: 30 min.
- Liquor ratio: 1/100.

The sample of yarn of wool (1 g) was soaked and wrung before being involved in the dyeing bath.

iii. Cold Rinse

The rinse was realized (for samples of dye baths 1 and 2) at the end of the dyeing process in order to delete the dyes on surface of the fibers and interfibers, also for neutralization of

the alkaline medium.

iv. Oxidation and Rinse

The oxidation was realized for the sample of dye bath 3, in the open air for 15 min for the both rinsing phases.

The rinse was realized at the end of the dyeing process as presented below:

- 1st rinse in cold water.
- 2nd rinse in cold water, the pH measured in the residual rinse bath for this sample was 7.2

v. Acidification

The dyed sample of dye bath 2 was treated in an acidic solution at pH 3.5. Therefore, acetic acid (0.1 mL in 100 mL) was added to this sample.

vi. Drying

The acidified sample was dried in a sterile environment at a temperature between 60°C and 80°C.

vii. Hot Rinse

The three samples were treated with distilled water at 60°C for 15 min at pH 7, with liquor ratio of 1/100. This rinse was used to delete the non-fixed and weakly fixed dye inside the fibers.

viii. Soaping

The three samples, were treated with 0.6g/L of Marseille soap at 60°C for 15 min, with liquor ratio of 1/100. This soaping was used to test the washing fastness of the three dyeing procedures.

ix. Spectral Analysis

Calibration of the spectrophotometer

Calibration of the spectrophotometer was realized using a standard solution prepared according to the weight of wool yarn, the concentration of argan's pulp, NaOH and CH_3COOH used in each dye bath.

Equally, for the measurement of the soaping baths, the standard solutions were prepared according to the concentration of Marseille soap used in each soaping bath.

Measurement of the dye exhaustion and fixation rates

We removed 2 mL of the solution from each dye bath to be measured. Each sample was diluted to 10 mL using the prepared standard solutions. The absorbance measurements are shown in Table 1 and 2. The absorbances were measured at wavelength of 500 nm.

Measurement of the soaping baths absorbances

We removed 2 mL of the solution from each residual soaping bath to be measured. Each sample was diluted to 10 mL using the prepared standard solutions. The absorbance measurements are shown in Table 3. The absorbances were measured at wavelength of 500 nm.

3. Results and Discussion

3.1. Exhaustion of Alizarin Dye

The measurements obtained for the exhaustion rates are presented in Table 1.

Table 1. *The exhaustion dye rates for the alkaline dyeing process with and without post treatment acidification step.*

	Absorbance of initial dye bath (Absi)	Absorbance of final dye bath (Absf)	Exhaustion dye rate ((Absi-Absf)/Absi)*100
Dye bath 1 without post treatment acidification step	0.072	0.046	36.1%
Dye bath 2 with post treatment acidification step	0.072	0.047	35.0%
Dye bath 3 with reducer	0.165	0.65	61.0%

Comparison between exhaustion rates of dye baths 1 and 2

The exhaustion rates for both dyebaths are nearly equal because they have the same dyeing conditions and recipe composition. This confirmed the possibility of reproducing the current dyeing procedure.

Comparison between exhaustion rates of dye baths 3 and 2

The addition of common salt (NaCl) in dye baths 3 and 4 increased the substantivity of alizarin dye towards the fiber. The weak alkalinity of the medium (pH 8) increased the substantivity of dye towards the fiber. This can be used to explain the higher exhaustion value for dye baths 3 and 4 due to the effect of salt and the weak alkalinity.

3.2. Fixation of Alizarin Dye

The measurements obtained for the fixed and non-fixed dye rates are presented in Table 2.

Table 2. *The fixation dye rates for the alkaline dyeing process with and without post treatment acidification step.*

	Absorbance of hot rinse bath (Absr)	Fixation dye rate ((Absi-Absf-Absr)/Absi)*100	Non-fixed dye rate (Absr/Absi)*100
Dye bath 1 without post treatment acidification step	0.020	8.3%	28.0%
Dye bath 2 with post treatment acidification step	0.000	35.0%	0.0%
Dye bath 3 with reducer	0.014	52.1%	8.5%

Comparison between dye baths 1 and 2

The fixation dye rate obtained for acidified dyeing process was clearly higher. The totality of exhausted dye was fixed in the wool fibers. In contrast, the non-acidified dyeing process lost nearly three quarters of its coloration from the dyed fiber. This can be explained by the weak fastness of anthraquinonic

dyes in an alkaline medium. The acidification treatment step converts the dye into a non-soluble molecule inside the fiber. Moreover, the dye establishes different bonds (hydrogen bonding and Van der Waals interactions) with the different amino acids in the wool fiber. These interactions give the dyed fiber an important washing and rubbing fastness.

Comparison between dye baths 3 and 2

The exhausted dye obtained for the dye bath 3 was not completely fixed on the wool fiber when compared to the dye bath 2, which had realized the entire fixation of exhausted dye. This was attributed to the non-soluble dye form established after the post treatment acidification step.

3.3. Washing Fastness

The measurements obtained for the three soaping samples are presented in Table 3.

Table 3. *The removed dye rates obtained for the three soaping samples.*

	Absorbance of Soaping bath (Abss)	Removed dye rate ((Abss)/Absi)*100
Dye bath 1 without post treatment acidification step	0.020	27.3%
Dye bath 2 with post treatment acidification step	0.011	15.5%
Dye bath 3 with reducer	0.035	21.2%

The values mentioned in this experience confirm all the conclusions described beforehand.

The higher washing fastness was realized in the dye bath 2. The removed dye in the washing step depend closely on the dyeing process. In fact, the acidification treatment step which converts the dye into a non-soluble molecule inside the fiber gives more fastness proprieties to the coloration when compared to the dyeing process using reducer (dye bath 3).

4. Conclusions

Whole fixation and higher washing fastness were observed using an alkaline dyeing process with a post treatment acidification step. This was confirmed by the weak fastness obtained using the alkaline dyeing process without the post treatment acidification step. The reducer dyeing process insures more exhaustion dye rate in the slightly alkaline medium using the common salt, This was attributed to the high solubility of alizarin dye in a highly alkaline medium. Because of this solubility, the substantivity becomes lower towards wool fiber.

However, the fastness of dyeing using the alkaline process with a post treatment acidification step was also weak in a highly alkaline medium.

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