

Dyeing Wool Fiber with Natural Alizarin in a Vat System

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Abstract: Herein we report our study on wool dyeing with natural alizarin in a vat system using the Argan's pulp. Natural alizarin was extracted from the *Rubia tinctorum* plant using enzymatic hydrolysis and alkaline solution. In order to assess the role of the reducer in the dyeing process, we tested one dye bath without reducer containing just alizarin extract and sodium carbonate solution at pH 8. In the vat preparation using these components, we used Argan's pulp as the reducer. Under relatively soft dyeing conditions for wool (60°C and pH 8) dyeing in the vat system realized a higher degree of dye fixation and wash fastness.

Keywords: Argan's Pulp, Natural Alizarin, Rubia Tinctorum, Vat System, Wool

1. Introduction

Alizarin is the most well-known anthraquinone isolated from madder. In 1826 alizarin was first isolated from *Rubia tinctorum* by Colin and Robiquet [1]. After the first isolation of alizarin many other anthraquinones were isolated from *R. tinctorum*, for example purpurin, munjistin, rubiadin, pseudopurpurin, nordamnacanthal, lucidin, xanthopurpurin and anthragallol. Ruberythric acid was first isolated in a crystalline form by Rochleder in 1851 [2].

Ruberythric acid consists of the alizarin aglycone and a disaccharide (primeverose: glucose and xylose). The anthraquinone alizarin, the hydrolysis product of ruberythric acid, is known to be the main dye component of *R. tinctorum* [3].

In this study, we have used enzymatic hydrolysis (endogenous conversion) to convert the glucosidic anthraquinones, in particular, ruberythric acid to alizarin [4] (see paragraph: Preparation of dye baths A1 and B1).

A lot of different formulas for dyeing with *R. tinctorum* have been described in the literature. The recipes can be divided in two main classes according to the origin of the material to be dyed, the number of process steps and the necessary chemicals. The alizarin red procedure, which is used for dyeing animal derived fibers such as wool and the Turkish red procedure, which is used for dyeing plant derived fibers such as cotton. In the alizarin red procedure the main steps are: Pre-treatment, mordanting, dyeing and washing [5].

The aim of this work is to use another dyeing procedure with alizarin based on a reduction mechanism, which was applied in dyeing vat. The chemical classification of vat dyes is composed of three groups: indigoides, tioindigoides and anthraquinones [6, 7]. Since alizarin belongs to the anthraquinones group, it can be used as a vat dye.

The dyeing mechanism of vat dyes is based of a reduction reaction (Figure 1).

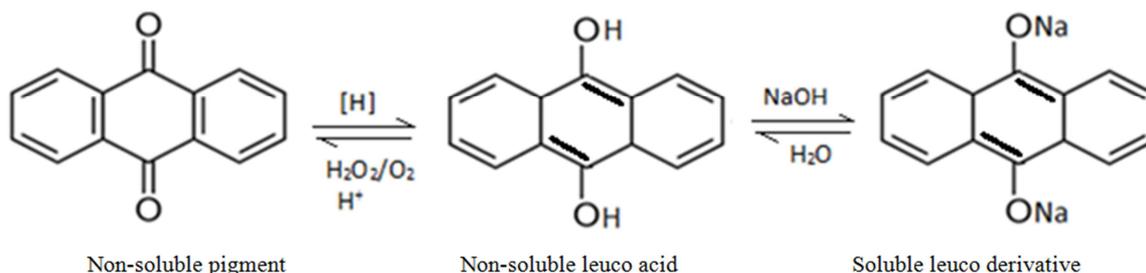


Figure 1. Reduction and Oxidation reactions of anthraquinonic dye.

At first, the dye is converted into its reduced form known as leuco acid, which is not soluble in water and has low substantivity to the fiber. After the addition of alkali, the leuco acid is converted to a water soluble leuco derivative, which has a higher substantivity to the fiber.

The reducer was chosen from Argan's pulp as a local plentiful product, which contains an important quantity of reducer sugar. The redox potential of the reducer sugar ranges from 245–700 mV dependent on the dyeing temperature [8].

2. Experimental

2.1. Materials

2.1.1. Features of Wool Fiber

The wool fiber used was obtained from the Boujaâd city region of Morocco. White fleece was compacted and homogenized into a medium weight fleece 1.5–3 kg and the fineness of the fiber was 50–60 using the Bradford scale [9].

2.1.2. Natural Dye

The dye used in the present study was from a natural source and extracted from the *R. tinctorium* plant, which grows in the South-East of Morocco [10]. The extraction method was based on 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) [9, 11, 12].

2.1.4. Alkali Agent

The alkali agent used, sodium carbonate (Na_2CO_3), was of analytical grade and obtained from Lobachemie company – Mumbai (India).

2.1.5. Common Salt

The common salt used, sodium chlorate (NaCl), was of technical grade and obtained from the customary magazine.

2.1.6. Spectrophotometer

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

2.1.7. pH Meter

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

2.1.8. Vat/Bath

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

2.1.9. Filter

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

2.2. Preparation of the Reducer

Two solutions were prepared at different concentrations: 6 g (dye bath A1) and 2 g (dye bath B1) of Argan's pulp were added separately in 500 mL of distilled water and heated at 95°C for 30 min. The extract was filtrated using the metallic sieve.

2.3. Dyeing Process

2.3.1. Preparation of Dye Baths A1 and B1

Two quantities of 2.5 g of the plant was stirred separately in 100 mL of water at 45°C. After 1 h, solutions of 0.1 g/L (dye bath A1) and 0.2 g/L (dye bath B1) of sodium carbonate (Na_2CO_3) were added to the two prepared solutions. The pH of the solution was adjusted to 8 (dye bath A1) and 9 (dye bath B1), respectively, which gave a color change from yellow to purple. Water was added to both of the prepared solutions to make them up to a volume of 500 mL, which were designated as the original solution of dye bath A1 and original solution of dye bath B1, respectively. Two fractions of 100 mL were extracted. 10 mL (dye bath A1) and 5 mL (dye bath B1) of Argan's pulp extract (described above) were be added to each one of these fractions solutions and stirred for 30 min at 45°C. The both fractions were be filtered through a Buchner funnel and designated dye bath A1 and dye bath B1, respectively.

2.3.2. Preparation of Dye Baths A2 and B2

Two fractions of 100 mL were extracted from both initial solutions of dye bath A1 and B1. The pH of these fractions were 8 (dye bath A1) and 9 (dye bath B1) as described above. The solutions were stirred for 30 min at 45°C. Then, both fractions were filtered through a Buchner funnel and designated dye bath A2 and dye bath B2.

2.3.3. Dyeing Conditions

i. Dye bath A1:

- Dye: 100 mL of extract prepared from 2.5 g of *R. tinctorium* 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 rato: 1/100.

ii. Dye bath A2:

- Dye: 100 mL of extract prepared from 2.5 g of *R. tinctorium* stirred 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.
- iii. Dye bath B1:
- Dye: 100 mL of extract prepared from 2.5 g of *R. tinctorum* stirred in 500 mL of water.
 - Reducer: 5 mL of Argan's pulp extract containing 2 g of Argan's pulp in 500 mL of water.
 - Sodium carbonate: 0.2 g/L (pH = 9).
 - Temperature: 45°C.
 - Time: 30 min.
 - Liquor ratio: 1/100.
- iv. Dye bath B2:
- Dye: 100 mL of extract prepared from 2.5 g of *R. tinctorum* stirred in 500 mL of water.
 - Sodium carbonate: 0.2 g/L (pH = 9).
 - Temperature: 45°C.
 - Time: 30 min.
 - Liquor ratio: 1/100.

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

v. Oxidation and rinsing

The oxidation was realized in the open air for 15 min for the both rinsing phases.

The rinse was realized (for the fourth samples) 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 baths for samples of dye baths A1 and A2 were

7.23.

- Neutralization with acetic acid to pH 6, only for samples of dye baths B1 and B2.
- Rinse in hot water (60°C) for 15 min, in order to delete the no fixed or weakly fixed dyes.

vi. Drying

Drying may be carried out open to air or in a sterile environment at a temperature between 60°C and 80°C.

vii. Spectral analysis

Calibration of the spectrophotometer

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

Measurement of the dye exhaustion and fixation rate

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 absorbances were measured at wavelength 500 nm.

The absorbance measurements are shown in Table 1 and 2.

3. Results and Discussion

3.1. Exhaustion of Alizarin Dye

The measurement of exhaustion dye rate is presented in Table 1.

Table 1. Exhaustion rate of alizarin dye.

	Absorbance of initial dye bath (Abs _i)	Absorbance of residual dye bath (Abs _f)	Exhaustion rate ((Abs _i -Abs _f)/Abs _i)*100
Dye bath A1	0.165	0.065	61%
Dye bath A2	0.145	0.054	63%
Dye bath B1	0.150	0.088	41%
Dye bath B2	0.100	0.068	32%

3.1.1. Comparison Between Dye Baths A1 and A2

The exhaustion rates for both samples were quite high when compared to classical dyeing methods. This can be due to the addition of salt (NaCl) that increases the dye substantivity to the fiber. Moreover, the difference between the exhaustion rates of dye baths A1 and A2 can be explained by the high solubility of alizarin dye in the dye bath using the reducer. The use of a reducer in the dye bath increases the solubility of alizarin dye (Abs A1 = 0.165 against Abs A2 = 0.145).

3.1.2. Comparison Between Dye Baths B1 and B2

The addition of a reducer in the dye bath increases the solubility of alizarin dye (Abs B1 = 0.150 against Abs B2 = 0.100). The difference between the exhaustion rates of dye baths B1 and B2 can be explained by the alkalinity of the dye bath (pH 9), which avoids the adsorption of dye into the fiber

via electrostatic repulsion (the dye and wool fiber are negatively charged). The reducer at this pH plays the role of an electrolyte to decrease the electrostatic repulsion between the dye and fiber.

3.1.3. Comparison Between Dye Baths A and B

The addition of common salt (NaCl) in dye bath A 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 bath A1 and A2 due to the effect of salt.

3.2. Fixation of Alizarin Dye

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

Table 2. Fixation rate of alizarin dye.

	Absorbance of residual rinse bath at 60°C (Absr)	Fixation rate ((Absi-Absf-Absr)/Absi)*100	Non-fixed dye rate (Absr/Absi)*100
Dye bath A1	0.014	52%	8.5%
Dye bath A2	0.021	48%	14.5%
Dye bath B1	0.004	39%	2.0%
Dye bath B2	0.008	28%	4.0%

3.2.1. Comparison Between Dye Baths A1 and A2

The fixation rate of alizarin dye shown in Table 2 was higher using the reducer process (vat system). Moreover, the non-fixed dye rate reveals a big difference in dye fastness using the two dyeing process. Dyeing without a reducer leads to the loss of a large amount of dye. In contrast, the reducer process results in less non-fixed dye. This was attributed to the good diffusion inside the fiber of the dye reducer form and due to the realization of more important physico-chemical interactions (hydrogen bonds) and physical interactions (Van der Waals interactions) with the fiber.

3.2.2. Comparison Between Dye Baths B1 and B2

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

3.2.3. Comparison Between Dye Baths A and B

The higher fixation rate of dye realized in dye bath A1 was attributed to the higher quantity of reducer (12 g/L in dye bath A1 against 4 g/L in dye bath B1). The non-fixed dyes depend closely on the pH of the rinse bath. In fact, the non-fixed dye rates for dye bath B1 and B2 were lower than dye baths A1 and A2 because the pH of rinse bath B was 6.0 when compared to the pH of rinse bath A at 7.3. This was due to the high solubility of phenols (like alizarin) in an alkaline solution.

4. Conclusions

The reducer process insures more fixation and wash fastness of alizarin dye even in slightly alkaline medium. Using Argan's pulp as a plentiful local product allowed a high degree of exhaustion and fixation when compared to other classical dyeing methods. This process can be recorded in a full ecological dyeing process. However, we have to note that the alizarin coloration does not have a good fastness in a high alkalinity medium.

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