REVITALISATION OF NATURAL DYES – RED SHADES OF TEXTILES DYED WITH *RUBIA TINCTORUM* UNDER DIFFERENT PROCESS PARAMETERS

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ABSTRACT: *The demands of modern life and industry tend toward environmentally sound and sustainable processes in all areas of human activity, including the textile industry. In response to this demand, natural dyes, which had fallen into oblivion at the end of the 19th century, gained popularity as an acceptable alternative to synthetic dyes. The natural dye obtained from the plant Rubia tinctorum belongs to the group of acid-mordant dyes. The chemical structure of the main pigment, alizarin, and the method of binding it to fiber are described in the paper. Basic botanical and agronomic data are presented, as well as the history of Rubia tinsctorum dyeing and the possibilities of its modern application. Dyeing of wool and silk fabrics was carried out at different pH values and with different mordants (without mordant and with aluminum, copper, and iron). After dyeing, spectrophotometric analysis of the aqueous solutions of Rubia tinctorum was performed, and the color parameters of the dyed samples were determined spectrophotometrically. A test of washing and sunlight fastness was performed and the color difference determined spectrophotometrically was revealed. Considering the obtained results, an optimal dyeing procedure with the Rubia tinctorum plant is recommended. By dyeing wool and silk material with different process parameters, a wide range of red tones with h values from 30° (red part of the spectrum) to 70° (yellow part of the spectrum) was obtained. In combination with different brightness and chromaticity, wool and silk textiles with orange, pink, red and burgundy tones of satisfactory fastness were obtained, ready for the challenges of the market.*

Keywords: *alizarin, mordant dyes, natural dyes, Rubia tinctorum.*

REVITALIZACIJA PRIRODNIH BOJA – CRVENE NIJANSE TEKSTILA BOJANOG SA *RUBIA TINCTORUM* U OVISNOSTI O PROCESNIM PARAMETRIMA

APSTRAKT: *Zahtevi savremenog života i industrije teže ekološki prihvatljivim i održivim procesima u svim oblastima ljudske delatnosti, uključujući i tekstilnu industriju. Kao odgovor na ovaj zahtev, prirodne boje, koje su pale u zaborav krajem 19. veka, stekle su popularnost kao prihvatljiva alternativa sintetičkim bojama. Prirodna boja dobijena iz biljke Rubia tinctorum pripada grupi kiselo-mordantnih boja. U radu je opisana hemijska struktura glavnog pigmenta alizarina i način njegovog vezivanja za vlakna. Prikazani su osnovni botanički i agronomski podaci, istorijat bojenja Rubia tinctorum i mogućnosti njegove savremene primene. Bojenje vunenih i svilenih tkanina vršeno je pri različitim pH vrednostima i različitim močilima (bez močila i sa aluminijumom, bakrom i gvožđem). Nakon bojenja, urađena je spektrofotometrijska analiza vodenih rastvora Rubia tinctorum, a parametri boje obojenih uzoraka su određeni spektrofotometrijski. Izvršen je test otpornosti na pranje i sunčevu svetlost i otkrivena je spektrofotometrijski određena razlika u boji. S obzirom na dobijene rezultate preporučuje se optimalan postupak bojenja biljkom Rubia tinctorum. Bojenjem vunenog i svilenog materijala sa različitim procesnim parametrima dobija se širok spektar crvenih tonova sa h vrednostima od 30° (crveni deo spektra) do 70° (žuti deo spektra). U kombinaciji različitog sjaja i hromatike, dobija se vuneni i svileni tekstili narandžastih, roze, crvenih i bordo tonova zadovoljavajuće postojanosti, spremni za izazove tržišta.*

Ključne reči: *alizarin, mordantne boje, prirodne boje, Rubia tinctorum.*

1. INTRODUCTION

In view of the fact that the synthetic dyes used for dyeing textiles generally pollute the environment and can cause health problems for people, there is an increasing revival in the use of natural dyes, in line with the global trend towards an "eco" lifestyle [1,2]. Many synthetic dyes are classified as hazardous on skin contact and customers are demanding safer products, especially for babies and children. Compared to synthetic dyes, natural dyes causes much less pollution in the dyeing process itself and in the subsequent disposal of textile waste due to its biodegradability and cleaner dyeing process. The applicability of natural dyes for dyeing cellulose materials is increasingly being researched, particularly because of current fashion trends [2,3]. Furthermore, scientific research in the field of natural dyes is extremely important for archaeology and the conservation and restoration of textiles [4].
Rubia tinctorum produces anthraquinone pigments in its root, the most important and common of which is alizarin, which has been used for dyeing textiles since 2000 BC. These pigments provide useful colours that have a pronounced light and heat fastness [5,6]. There are about 80 species of *Rubia tinctorum*, the most famous of which are the dyer's *Rubia*

tinctorum, the foreign or Mediterranean *Rubia peregrina* and the Indian *Rubia cordifolia*. *Rubia tinctorum* is a herbaceous, low-growing plant with lanceolate leaves and a stem [7-9]. *Rubia tinctorum* is native to southern Europe, western Asia and northern Africa, but is also cultivated elsewhere. Mature plants produce star-shaped, pale yellow flowers that bloom in June and round black seeds that look like pepper [6,8,10]. Only the root of the plant is used for dyeing. The root of *Rubia tinctorum* is used for dyeing cotton, silk and wool with premordanting it in aluminium salts (red tones), chromium salts (red-brown tones) or iron salts (purple tones). It is also used for the production of paints and inks and histological preparations [5,10-12]. In order for alizarin to be bound to the fibre, the material must be complexed with metal salts. One example of this is the formation of a complex with chromium. The chromium ion is bound to the alizarin by a covalent and coordinative bond via the hydroxyl groups of the alizarin. One chromium ion, which is trivalent, binds to three molecules of alizarin (Fig. 1) [6-8,11-13]. Protein fibres bind to alizarin by forming hydrogen bonds between the polypeptide chains and the dyes and simultaneously complexing alizarin with metal ions (e.g. chromium) (Fig. 2) [2,14].

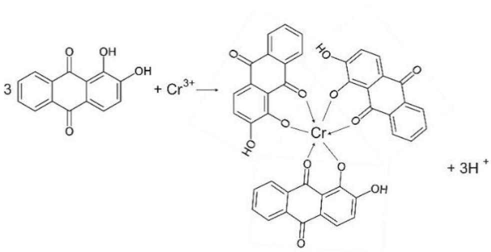


Figure 1: Formation of complex between alizarin and chromium [14]

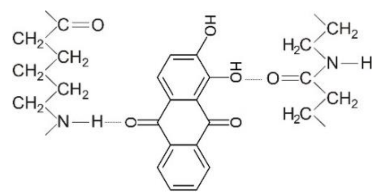


Figure 2: Binding of alizarin to protein textile material by hydrogen bonds [14]

Rubia tinctorum is not only used as a textile dye, but also has medicinal value. *Rubia tinctorum* has antioxidant, antimicrobial and antifungal properties as well as a blood pressure lowering effect and can be worn directly on the skin without any concerns. Root extracts are used to treat kidney and urinary stones. It is also used as a laxative mixture and mild sedative, as well as for menstrual and urinary problems [1,9,15]. Modern methods of dyeing textiles with *Rubia tinctorum* include research into replacing mordants with textile pre-treatments such as cationisation and plasma treatment, which achieve similar effects to pre-treatment with aluminium or tin salts, i.e. a brilliant shade and good fastens properties are achieved [16,17].

2. EXPERIMENTAL PART

2.1. Dye extraction

The dry root of *Rubia tinctorum* was used for dye extraction (Fig. 3). The plant was collected in the village of Petrovići in Montenegro at an altitude of about 700 metres above sea level, where it grows as a wild species.


(a) Dry root of Rubia tinctorum


(b) Chopped dry plant

Figure 3: Perpartion od dry *Rubia tinctorum* root for dye extraction

Dye extraction was performed in soft water containing 20 g/L *Rubia tinctorum* root. The extraction was performed in a 1:40 bath ratio (considering the mass of mass of the plant) at 100 °C for 60 min. The bath was then allowed to cool for 12 h and the extract was decanted.

2.2. Mordanting of the textile material with metal salts

Mordanting was performed as simultanion process with textile dyeing. For that reason were treated with 5% mordants (based on the mass of the material): potassium aluminium sulphate dodecahydrate $KAl(SO_4)_2{\cdot}12H_2O$, copper (II) sulphate pentahydrate $CuSO_4{\cdot}5H_2O$ and ferrous(II) sulphate heptahydrate $FeSO_4{\cdot}7H_2O$; (Kemika, Zagreb, Croatia).

2.3. Dyeing with *rubia tinctorum* root

Dyeing with *Rubia tinctorum* root was performed at 60 °C for 60 min with a bath ratio of 1:30 using the apparatus Polycolor (Mathis, Switzerland). Dyeing process was performed in acidic, neutral and alkaline conditions. pH of 4 was adjusted with 20% acetic acid (Kemika, Zagreb, Croatia) and pH of 8 was adjusted with Na_2CO_3 (Kemika, Zagreb, Croatia). After dyeing, the were rinsed with cold water.

2.4. Colour analysis

Colour characteristics were measured using a remission spectrophotometer, Datacolor 850, measuring geometry d/8°, D65, measuring aperture of 9 mm. The coordinates used to determine colour values are L* for lightness, a* for redness (positive value) and greenness (negative value), b* for yellowness (positive value) and blueness (negative value), C* for chroma and h° for hue angle in the range of 0° to 360° of undyed and dyed were determined according to ISO 105-J01:1997 Textiles—Tests for colour fastness—Part J01: General principles for measurement of surface colour.

2.5. Wash fastness analisys

Wash fastness of dyed materials were tested in a laboratory apparatus for wet processes Polycolor (Mathis, Switzerland). The test was performed according to standard ISO 105-

C06:2010 (A2S) Textiles—Tests for colour fastness—Part C06: Colour fastness to domestic and commercial laundering, using 2 g/L of standard detergent (James Heal ECE A, without optical brighteners and without phosphates), with a bath ratio of 1:20, temperature of 40 °C, time of 30 min. The results of wash fastness are given as numerical values of total colour difference (DE) calculated according to CIE76 equation (1), as well as in grey scale grades, obtained by comparing unwashed samples with samples that were washed after the 5th washing cycle.

$$DE = [(DL^*)^2 + (Da^*)^2 + (Db^*)^2]^{1/2} \quad (1)$$

Where are: DL* = (L* washed) – (L* unwashed); Da* = (a* washed) – (a* unwashed); Db* = (b* washed) – (b* unwashed).

2.6. Light fastness analisys

Lightfastness testing of the samples were performed on Xenotest 440 ((SDL Atlas, Rock Hill, SC, USA). Xenotest 440 is used for laboratory simulation of external weather influences on the stability and durability of textile and other materials. Analysis was evaluated according to the modified ISO 105-B02 and 13 B04 test methods using Xenotest 440. Test conditions simulated in this research were: Total light time: 41:10 h, Radiant exposure: 6226 kJ/m2, Irradiance control: 300–400 nm, Filter system: B04, E: 42 W/m^2 (± 2 W/m^2), CHT: 32 °C (± 3 °C), BST: 47 _C (± 8 °C), RH: 40% (± 8 %), no spray, fan speed: 2000 rpm. Using the same equation as for the wash fastness, the lightfastness properties was also evaluated by calculating total colour difference values (DE).

3. RESULTS AND DISCUSSION

3.1. Visual assessment of dyed textile samples

The visual assessment of the wool samples is shown in Tab. 1, while the silk samples are shown in Tab. 2. The visual assessment of the sample is extremely important when dyeing with natural dyes, as it often deviates considerably from objective spectrophotometric measurements, and it is extremely important in the real field of application of natural dyes, e.g. in the fashion industry or in textile restoration.

It can be observed that a wide range of red shades is achieved by changing both parameters, the pH conditions and the use of mordant. Without mordant and with aluminium, more brilliant shades are obtained and with copper and iron, duller shades.

Table 1: Visual assessment of dyed wool samples

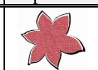
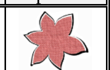
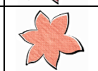
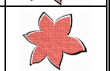
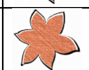
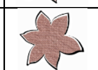
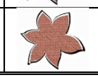
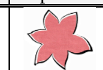
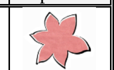
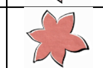
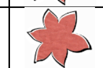
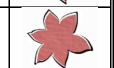
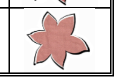
Mordant	pH 4	pH 7	pH 8
Without			
Al			
Cu			
Fe			

Table 2: Visual assessment of dyed silk samples

Mordant	pH 4	pH 7	pH 8
Without			
Al			
Cu			
Fe			

3.2. Spectrophotometric analysis of dyed textile samples

An objective spectrophotometric analysis monitored the influence of the pH solution for dyeing and the choice of mordant on the colour parameters lightness (L*), chromaticity (C*) and tone (h°). In this way, it is possible to determine the range of red shades that can be achieved with just one *Rubia tinctorum* plant, but with different parameters of the dyeing process. The results obtained for the wool samples are shown in Tab. 3 and Fig. 4 and for the silk samples in Tab. 4 and Fig. 5.

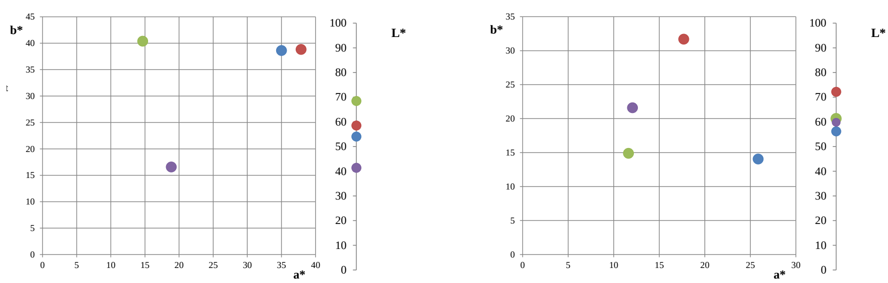
It can be see, all coloured samples belong to the yellow-red part of the spectrum between coordinates +a* (0 ° = red) and +b* (90 ° = yellow). Wool and silk samples dyed under acidic conditions show a higher chromaticity value than samples dyed under neutral and acidic conditions. Generally, silk samples showing a lower chromaticity than wool samples. For all samples, the highest chromaticity is achieved by mordanting with aluminium. In contrast to the neutral and acid-dyed wool samples, where the copper-treated samples have the lowest chromaticity, in acid, the iron-treated sample is the least saturated. Silk samples mordanted with iron have the lowest chromaticity, regardless of the pH value. The tone value of acidic wool samples dyed without mordant *and mordanted with aluminium they have a pronounced shift towards small values, i.e. A pure red hue.* The sample mordanted with copper has an angle closer to the yellow part of the spectrum. Under neutral conditions, the sample dyed without mordanting has the lowest tone value, tending towards the red part of the spectrum, in contrast to the samples mordanted with metals, whose angle is greater than 45° and which tend towards the yellow-orange colouration. Alkaline coloured wool samples have a tone value between yellow-orange and red-orange. In the case of silk samples, the colour tone value of acidic samples belongs to the red-orange part of the spectrum, with the exception of the sample mordanted with copper, which is approximately pure orange. The neutral silk samples dyed with iron has the yellowest tone, while the other three neutral samples tend towards red. The alkaline sample dyed with iron is most strongly attracted to the yellow-orange tone, but is difficult to detect due to its low chromaticity. The other alkaline samples are all below 45° and belong to the red-orange colour tone. The darkest samples are acidic, while the lightest wool samples are neutral. The copper-mordanted samples has the lowest brightness under alkaline conditions. In both neutral and alkaline, the lightest wool sample is treated with aluminium. The lightest silk sample in the alkaline conditions is dyed without mordanting, in the neutral, coming up the sample treated with aluminium and in the acidic conditions sample mordanted with copper. In all neutral and acidic samples, the darkest samples were treated with iron. As can be seen from the measurement results, all colour parameters obtained are largely dependent on the process parameters of the metal salt treatment (mordanting) and the pH value. The same metal salt used at different pH conditions does not produce the same colour. Even in the same pH range, the colour tone changes depending on the metal used. Apart from the dependence on the mordanting and the pH value, the colour shade also differs with regard to the chemical structure of the textile material used for dyeing. This results from the theoretical assumptions made in the introductory part of the article with regard to the formation of the dye-metal-fibre complex (Fig. 1 and 2).

Table 3: Spectrophotometric parameters of wool samples

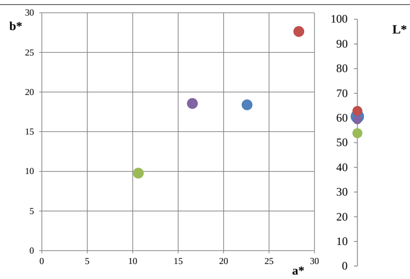
Sample	L*	C*	h°
wool_pH4_without	54.12	52.13	47.79
wool_pH4_Al	58.57	54.24	45.68
wool_pH4_Cu	68.52	42.95	70.00
wool_pH4_Fe	41.44	25.12	41.26
wool_pH7_without	56.16	29.43	28.52
wool_pH7_Al	72.18	36.29	60.83
wool_pH7_Cu	61.31	18.88	51.99
wool_pH7_Fe	59.80	24.74	60.79
wool_pH8_without	60.62	29.13	39.16
wool_pH8_Al	62.89	39.54	44.34
wool_pH8_Cu	53.85	14.43	42.61
wool_pH8_Fe	59.23	24.87	48.21

Table 4: Spectrophotometric parameters of silk samples

Sample	L*	C*	h°
wool_pH4_without	60.36	37.08	37.98
wool_pH4_Al	61.64	38.60	34.76
wool_pH4_Cu	65.43	26.42	47.48
wool_pH4_Fe	46.80	10.95	29.08
wool_pH7_without	66.24	29.23	30.87
wool_pH7_Al	68.54	35.75	43.78
wool_pH7_Cu	62.38	31.33	38.83
wool_pH7_Fe	57.69	23.83	54.19
wool_pH8_without	68.08	25.61	42.66
wool_pH8_Al	67.30	33.20	43.66
wool_pH8_Cu	61.59	25.76	33.20
wool_pH8_Fe	66.64	20.97	56.45



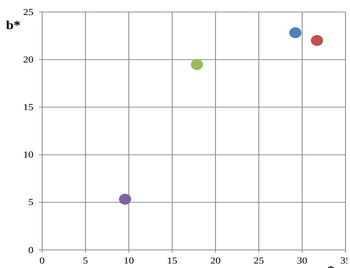
(a) pH 4 (b) pH 7



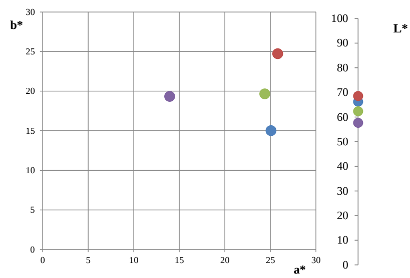
Legend: mordants ● wihout, ● Al, ● Cu, ● Fe

(c) pH 8

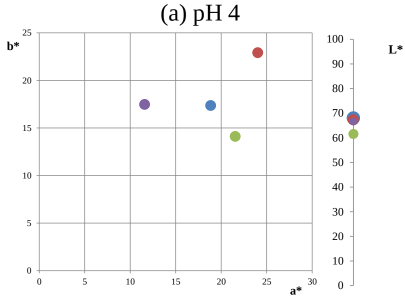
Figure 4: Colour analysis of wool samples in the a*/b* colour space



(a) pH 4



(b) pH 7



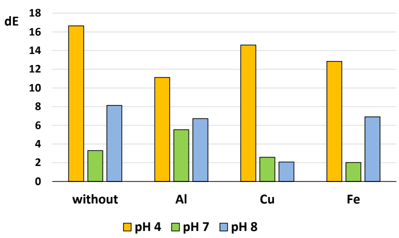
Legend: mordants ● wihout, ● Al, ● Cu, ● Fe

(c) pH 8

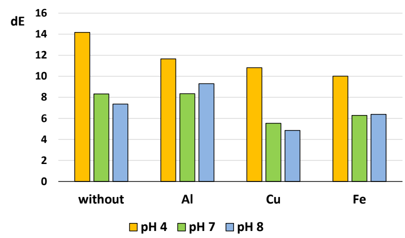
Figure 5: Colour analysis of silk samples in the a*/b* colour space

3.3. Fastnes Properties

Achieving good colour fastness is one of the most important properties of coloured textiles. This is especially true for textiles dyed with natural dyes, as poor colour fastness is often cited as one of their disadvantages. For this reason, research has carried out a test of colour fastness to washing (Fig. 6) and light fastness (Fig. 7). The diagrams show that the wool and silk samples have relatively poor fastness properties, especially after dyeing in a neutral medium. In terms of fastness to washing, the total colour difference (dE) is up to 16 for wool and 14 for silk, but these values are lower for light fastness, up to 7 for wool and 11 for silk. However, it is strongly noted that fastness is significantly increased by dyeing in an acidic medium and by using metal saalts as mordants, and dE decreases significantly for all samples. This is logical and to be expected considering that the main component of *Rubia tinctorum* root is alizarin. As shown in Fig. 2 and 3 in the introductory section, alizarin readily forms complexes with metal ions via a coordination bond and binds to textile protein materials via hydrogen bonds.

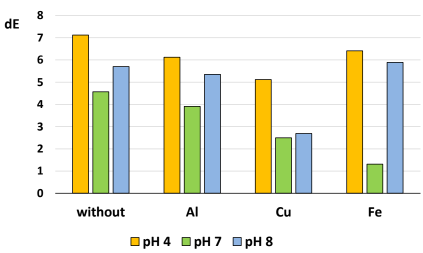


(a) wool

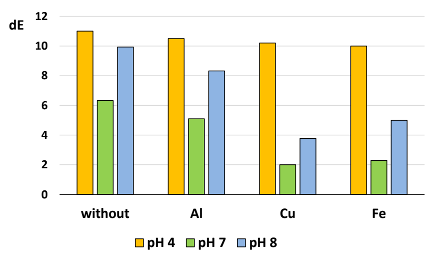


(b) silk

Figure 6: Wash fastness



(a) wool



(b) silk

Figure 7: Light Fastness

4. CONCLUSION

A root of *Rubia tinctorum* plant is rich in the chemical compound alizirine and can be used to successfully dye wool and silk in an extremely wide range of red shades. It has been confirmed that the red shades achieved are influenced by the pH value of the dye bath and the choice of mordants, the metal salts that form coloured red complexes with alizarin. When aluminium is used, brighter and more brilliant red shades are obtained, whereas with copper and iron the brightness and chromaticity decreases and red shades are obtained that belong to the darker, achromatic tones. As alizarin is an acidic mordant yes, the colour fastness of the textiles can be significantly improved by dyeing in an acidic medium and using mordants. This research can make an important contribution to revitalising the use of the *Rubia tinctorum* plant for dyeing modern textiles, whether for fashion purposes or for the restoration and preservation of traditional heritage textiles.

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