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Barvanje volne z rastlinskimi barvili in vrednotenje vzorcev z uporabo barvnega sistema CIE

Izvirni znanstveni članek

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Dyeing of Wool with Plant Dyes and Sample Evaluation with CIE Colour System

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Abstract

*The aim of the research was to study the possibility of using plant dyes for the dyeing of wool yarn, which would later be used for unique knitted and embroidered products. In order to achieve this goal, the extraction of dyes was performed using various plants that are widely present in our area, using mainly yellow, red, brown and green shades. These plants are birch tree, lady's bedstraw root, nut tree and big nettle. To attain a wider palette of colour shades, and superior dye exhaustion and fixation (for better colour fastness), different mordants (i.e. Al, Cu and Fe) were used during the extraction, the dyeing process or after the dyeing (i.e. aftertreatment). The liquor ratio of the extraction (different initial dye concentrations) and pH of the extract varied as well. Wool samples were washed after the dyeing and tested for colour fastness during washing at temperature 40 °C. The dyed samples were colourimetrically evaluated using the CIE colour system and graphically presented in the CIE a*b* colour diagram.*

Keywords: plant dyes, dye extraction, wool dyeing, mordants, colourimetry, CIE colour system.

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Izvleček

V raziskavi smo proučili možnost uporabe rastlinskih barvil za barvanje volnene preje, ki se bo uporabljala za izdelavo unikatnih pletenih in vezenih izdelkov. V ta namen je bila izvedena ekstrakcija barvil iz različnih delov štirih izbranih rastlin, ki so v naravi razširjene in dostopne ter dajejo v osnovi rumene, rdeče, rjave in zelene barvne tone. To so navadna breza, navadna lakota, navadni oreh in velika kopriva. Za doseganje obsežnejše palete barvnih tonov ter boljše izčrpanje in fiksiranje barvil (večje obstojnosti) smo uporabili različne kovinske soli (Al, Cu in Fe) pri postopku ekstrakcije, pri barvanju in po barvanju (naknadna obdelava). Prav tako smo spreminjali kopelno razmerje ekstrakcije (različna začetna koncentracija barvil) in pH ekstrakta. Po barvanju smo vzorce oprali in izvedli preskus barvne obstojnosti na pranje pri temperaturi 40 °C. Obarvane vzorce volnene preje smo barvnometrično ovrednotili z uporabo barvnega sistema CIE in jih grafično prikazali v CIE a*b* barvnem diagramu.

Ključne besede: rastlinska barvila, ekstrakcija barvil, barvanje volne, kovinske soli, barvna metrika, barvni sistem CIE.

1 Uvod

Pred vpeljavo sintetičnih barvil v devetnajstem stoletju so bili vsi uporabni in umetniški izdelki obarvani izključno z naravnimi barvili in anorganskimi pigmenti, ki so jih našli v naravi [1]. Ohranjeni stari izdelki so večinoma v rumenih, rdečih in rjavih odtenkih v kombinaciji z ognjeno črno. Barvanje z modro je omogočilo šele

1 Introduction

Prior to the introduction of synthetic dyes in the nineteenth century, all utilitarian and art products were painted exclusively with natural and inorganic pigments found in the nature [1]. The preserved antique products are mainly

odkritje indiga. Zelene tone so v umetnosti zelo redko uporabljali, saj barvilo klorofil ni dovolj obstojno.

Naravna barvila so snovi, ki nastajajo v celicah živega organizma in so lahko živalskega ali rastlinskega izvora. Anorganskih pigmentov po tej definiciji ne prištevamo mednje. Po kemijski zgradbi so naravna barvila zelo različna. Ena od razvrstitev glavnih skupin organskih barvil je predstavljena na sliki 1 [2]. Številčno so najbolj

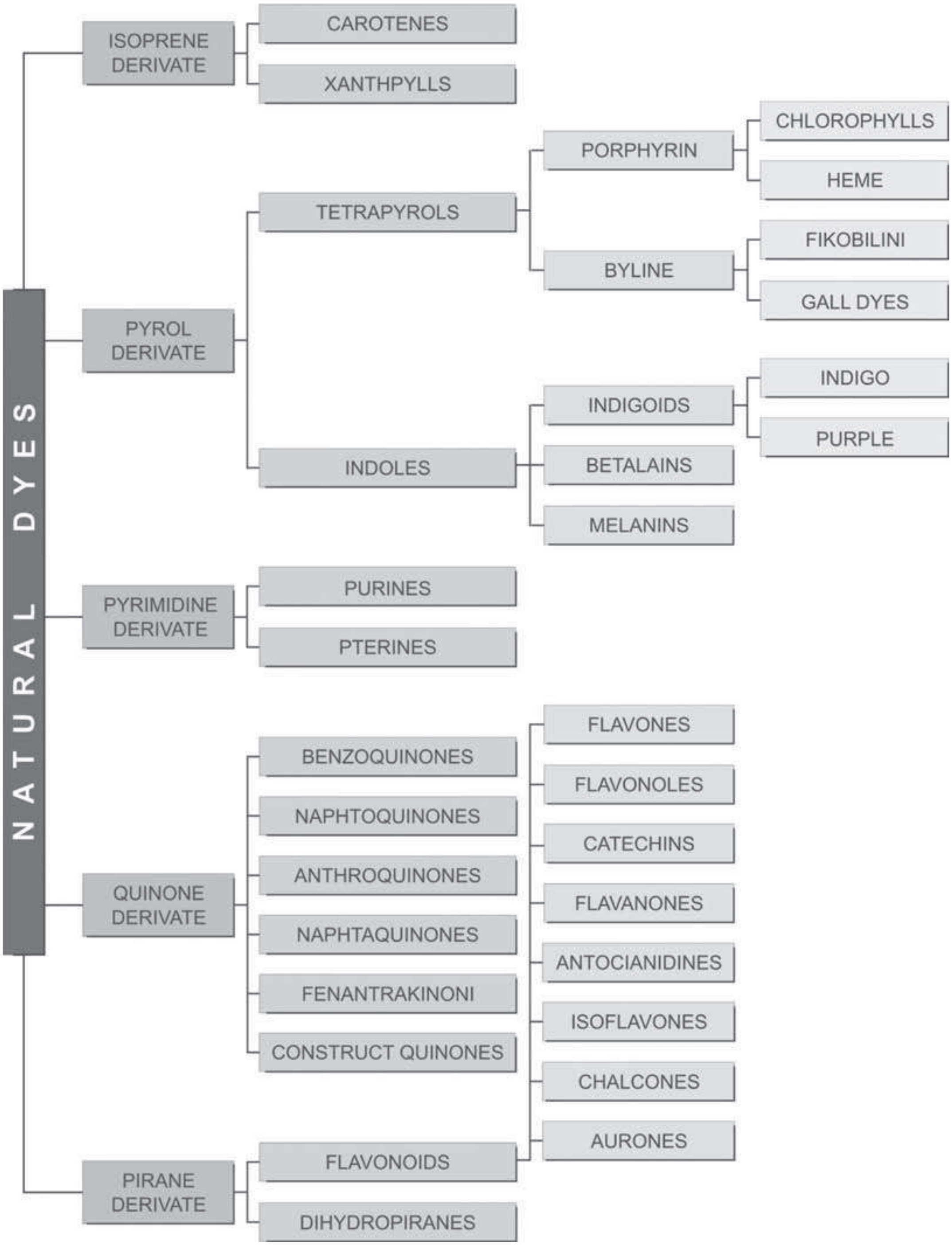


Figure 1: Classification of natural dyes

in yellow, red and brown shades in a combination with fiery black. After the discovery of indigo, blue dyeing was enabled as well. Due to the chlorophyll poor stability, green shades were very rarely used in art.

Natural dyes are substances produced in the cells of living organisms and can be of animal or plant origin. Accordingly, inorganic pigments are not included among the latter. Based on their chemical structure, natural dyes are very different. One possible classification of major organic dye groups is presented in Figure 1 [2]. Despite the yellow natural dyes being most common, they have disadvantageous technological and applicable properties if compared with the blue and black natural pigments.

The dyeing with natural dyes is a complex process. Merely to extract the pigments from individual plant parts is time consuming and requires extensive knowledge and experience, while the dyeing alone with old recipes can take several weeks [3, 4].

Natural plant dyes can be obtained from different parts of plants, e.g. flowers, leaves, barks, roots and fruits [3, 4, 5]. Fresh plant parts containing dyes are usually covered with water and boiled until the whole pigment is extracted. The bath is then cooled down and the plant residues are removed. The extraction may take several days, depending on the plant or plant parts. The dyeing takes place in an extraction bath as the second phase of the process. The simplest procedure of dyeing is processing the textile material in the dye extraction bath at the boiling point. The dyeing time depends on the type of pigment and can take up to several days. As the levelling agent and to increase the exhaustion level, Glauber's salt ($Na_2SO_4 \cdot 10\,H_2O$) can be added into the dyeing bath. Many natural dyes are sensitive to the change in the pH value, which leads to colour shade variations with the addition of base or acid. Ammonia and soda are used to achieve alkaline pH, while for acidic pH, oxalic, formic and acetic acids are used.

Only a few natural dyes are substantive, while all other require inorganic oxides or salts – metal salts, which together with the dye form a differently coloured complex to bind to fibres. Metal salts are various compounds with different metal ions, e.g. ferric sulphate, alumini-

zastopana rumena naravna barvila, vendar imajo slabše tehnološke in uporabne lastnosti kot rdeča, modra in črna naravna barvila.

Barvanje z naravnimi barvili je precej zapleten proces. Že pridobivanje barvil iz posameznih delov rastlin je dolgotrajno ter zahteva veliko znanja in izkušenj, medtem ko barvanje po starih recepturah lahko traja tudi več tednov [3, 4].

Naravna rastlinska barvila pridobivamo iz različnih delov rastlin: cvetov, listov, skorje, korenike in plodov [3, 4, 5]. Sveže rastlinske dele, ki vsebujejo barvila, ponavadi prelijemo z vodo in jih prekuhavamo tako dolgo, da se vse barvilo ekstrahira. Kopel nato ohladimo in odstranimo rastlinske ostanke. Ekstrakcija lahko traja več dni, to je odvisno od rastline oz. rastlinskega dela. V ekstrakcijski kopeli potem poteka barvanje kot druga faza postopka. Najpreprostejši postopek barvanja je obdelava tekstilije v ekstrakcijski kopeli barvila pri temperaturi vrenja. Čas barvanja je odvisen od vrste barvila in barvanje lahko traja tudi več dni. V barvalno kopel lahko dodamo tudi Glauberjevo sol ($Na_2SO_4 \times 10\,H_2O$), ki deluje kot egalizirno sredstvo in hkrati povečuje stopnjo izčrpanja. Z dodatki baz ali kislin lahko spreminjamo barvni ton, saj so številna naravna barvila občutljiva na spremembo vrednosti pH. Za doseganje alkalnega pH se največ uporabljata amoniak in soda, za kisel pH pa oksalna, mravljična in ocetna kislina.

Le nekaj naravnih barvil je substantivnih, preostala je potrebno na vlakna vezati s pomočjo anorganskih oksidov ali soli – čimž, ki z barvilom tvorijo drugače obarvan kompleks. Čimže so različne spojine, v katerih nastopajo kovinski ioni, npr. železov sulfat, aluminijev sulfat, kalijev dikromat, kositrov klorid, bakrov sulfat itd. Nekoč so kot čimže uporabljali: urin, pepel, rastlinske šiške, sok divjega jabolka itd. Izbira kombinacije barvilo–čimža odločilno vpliva na barvo in obstojnost obarvanj. Vlakna pa lahko obdelamo s čimžami pred barvanjem, med njim ali po njem. Najpogosteje se uporablja obdelava pred barvanjem [5].

Danes smo naravna barvila skoraj popolnoma zamenjali s sintetičnimi, ki so v primerjavi z naravnimi dostopna v velikih količinah ter široki paleti barvnih tonov; so cenejša in dobro obstojna. Vendar pa imajo sintetična barvila tudi nezaželene lastnosti: nekatera so strupena in kancerogena, njihova proizvodnja in uporaba obremenjuje okolje, čedalje več je alergičnih reakcij itd. [6]. Naravna barvila so v primerjavi s sintetičnimi dražja, praviloma manj obstojna, vendar imajo bistveno manj negativnih učinkov na organizem. Zakonodaja na področju prehrane postaja čedalje strožja in v številnih državah uporaba sintetičnih barvil v hrani za dojenčke in otroke ni več dovoljena. Tako se vračajo naravna barvila, zlasti v živilsko industrijo, farmacevtske izdelke, dražjo kozmetiko in umetniško barvane tekstilije [4, 5].

Za ekstrakcijo barvil in barvanje je primernih več rastlin iz naravnega okolja. V predstavljeni raziskavi smo uporabili naslednje štiri: navadno brezo, navadno lakoto, navadni oreh in veliko koprivo, katerih osnovne značilnosti so opisane v nadaljevanju [7].

um sulphate, potassium dichromate, stannous chloride, copper sulphate etc. In the past, people used urine, ash, plant galls, wild apple juice etc as metal salts. The combination dye-metal salt has a strong influence on the colour and colour fastness properties. Fibres can be treated with metal salt before, during or after the dyeing. The most frequently used procedure is the treatment before the dyeing [5].

Natural dyes are today almost completely replaced with synthetic ones, which are in comparison with natural dyes available in larger quantities and wider range of colour shades, they are cheaper and with good fastness properties. Nevertheless, synthetic dyes also possess undesirable properties, e.g. some are toxic and carcinogenic, their production and application burden the environment, there is an increasing number of allergic reactions etc [6]. On the other hand, natural dyes are more expensive than synthetic dyes, generally less stable, while they do have significantly fewer negative effects on organisms. Food legislation becoming stricter, many countries no longer allow the use of synthetic dyes in baby and children food. Therefore, natural dyes are again on an increase, particularly in the food industry, pharmaceuticals, quality cosmetics and art painted textiles [4, 5].

Numerous plants from the natural environment are suitable for the dye extraction and dyeing. In the present study, birch tree, lady's bedstraw root, nut tree and big nettle were used. Their main characteristics are described below [7].

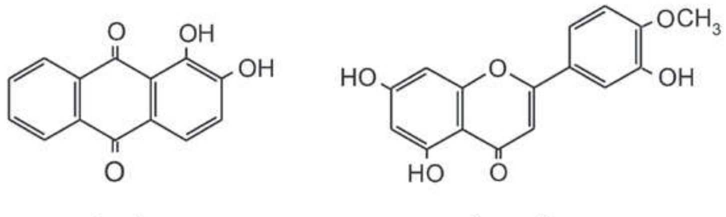
Birch tree (Betula pendula) grows primarily in sandy soils and humid climates as the front forest shrubbery on the clearing. It blooms from April to May and grows up to 25 m in height. Fresh or dried leaves are the most suitable parts for dyeing.

Lady's bedstraw root (Galium mollugo) grows in pastures, wooded hillsides and it is widespread throughout Europe. It blooms from May to September and reaches the height 12–80 cm. Mainly roots are suitable for dyeing. With the plant extraction, alizarine and diosmetin dyes are obtained (cf. Figure 2).

Nut tree (Junglans regia) can be found in the Sub-Mediterranean regions of Eastern Europe, as well as elsewhere in Europe as a cultivated plant. It blooms in May and grows up to the

Navadna breza (*Betula pendula*) uspeva predvsem na peščenih tleh v vlažnem podnebju kot predgozdno grmičevje na posekah. Cveti od aprila do maja in zraste do 25 metrov visoko. Za barvanje so najprimernejši sveži ali posušeni listi.

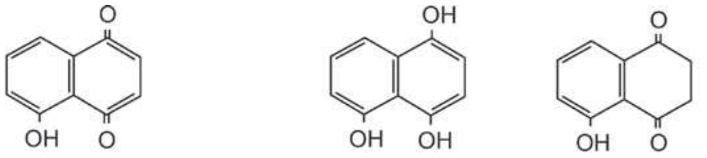
Navadna lakota *(Galium mollugo)* raste na pašnikih, gozdnih obronkih in je razširjena po vsej Evropi. Cveti od maja do septembra in doseže višino med 12 in 80 centimetrov. Za barvanje so primerne predvsem korenine. Z ekstrakcijo rastline dobimo barvili alizarin in diosmetin (slika 2).



alizarine diosmetine

Figure 2: Natural dyes extracted from lady's bedstraw

Navadni oreh *(Junglans regia)* najdemo v submediteranskih predelih vzhodne Evrope, kot kulturno rastlino pa so ga ponesli daleč po Evropi. Cveti v maju in zraste do 25 metrov visoko. Za barvanje se lahko uporabljajo listi in lubje. Vsebuje barvili juglon in hidrojuglon (slika 3).



juglon hydro juglon (α- and β- configuration)

Figure 3: Natural dyes extracted from nut tree

Velika kopriva (*Urtica dioica*) je razširjena po vsem svetu, prvotno pa je uspevala samo v severnih in osrednjih delih Evrazije. Cveti od junija do oktobra, je dvodomna rastlina, raste v bližini naselij, ob gozdnih obronkih, ugajajo ji z dušikom bogata in vlažna tla ter zraste do višine 2,4 metra. Vsebuje fotosintezna barvila, klorofil a in b ter karotenoide.

2 Eksperimentalni del

2.1 Uporabljene kemikalije

Pri raziskavi so bile uporabljene naslednje kemikalije in pomožna sredstva:

- aluminijev sulfat – $Al_2(SO_4)_3 \times 18H_2O$ (Al-sol)
- kalijev hidrogen tartrat – $KOOC(CHOH)_2COOH$ (tar)
- bakrov sulfat – $CuSO_4 \times 5H_2O$ (Cu-sol ali modra galica)

height of 25 m. For dyeing, leaves and bark are used. It contains juglon and hydro-juglon dyes (cf. Figure 3).

Big nettle (Urtica dioica) is worldwide spread, while it initially grew only in the northern and central parts of Eurasia. It blooms in the period from June to October and it is a two-area plant, which means that it grows close to settlements and in forest hillsides. It prefers moist soil rich in nitrogen and can grow up to 2.4 m in height. It contains photosynthetic dyes, chlorophyll a and b and carotenoids.

2 Experimental

2.1 Used chemicals

The following chemicals and auxiliaries were used during the research:

- *aluminium sulphate – $Al_2(SO_4)_3 \cdot 18H_2O$ (Al-salt),*
- *potassium hydrogentartrate – $KOOC(CHOH)_2COOH$ (tar),*
- *copper sulphate – $CuSO_4 \cdot 5H_2O$ (Cu-salt or blue vitriol),*
- *ferric sulphate – $FeSO_4 \cdot 7H_2O$ (Fe-salt),*
- *acetic acid – CH_3COOH,*
- *sodium carbonate – Na_2CO_3 (soda), and*
- *sodium chloride – NaCl (table salt).*

As apparent from the article continuation, only certain metallic salts and additives were used for individual natural dyes. Selected metal salts were chosen on the basis of previous research, where all types of metallic salts were used with each natural dye in different concentrations. It was found that Al-salt treatments gave the most lively colour tones. While copper salt treatments emphasized blue-green shades, Fe-salt treatments highlighted brown tones with enabled darker colourations. Based on the findings, metal salts, which enabled a wide range of colour tones of individual dyes, were selected.

2.2 Wool yarn

In the study, wool yarn (82 × 2 tex) made from Slovenian sheep wool for hand knitting, a product by Soven d. o. o., a company from Selnica ob Dravi, was used. Yarn was rough, yellowish-coloured, with the tow length of 73.6 mm and fat content of 1%.

- železov sulfat – $FeSO_4 \times 7H_2O$ (Fe-sol)
- ocetna kislina – CH_3COOH
- natrijev karbonat – Na_2CO_3 (soda)
- natrijev klorid – NaCl (kuhinjska sol)

Kot izhaja iz nadaljevanja članka, smo pri posameznih naravnih barvilih izbrali samo določene kovinske soli in dodatke. Za izbrane kovinske soli smo se odločili na podlagi predhodnih raziskav, pri katerih smo na vsakem naravnem barvilu uporabili vse vrste kovinskih soli v različnih koncentracijah in ugotovili, da nam obdelave z Al-solmi dajejo najživahnejše barvne tone, obdelave z bakrovimi solmi poudarjajo modro-zelene odtenke in obdelave z železovimi solmi poudarjajo rjave tone in omogočajo doseganje temnejših obarvanj. Na podlagi teh ugotovitev smo pri posameznih barvilih izbrali tiste kovinske soli, ki so nam omogočale doseganje široke palete različnih barvnih tonov.

2.2 Volnena preja

V raziskavi smo uporabili volneno prejo za ročno pletenje s finostjo 82 × 2 tex, ki je izdelek podjetja Soven, d. o. o., v Selnici ob Dravi in je izdelana iz slovenske ovčje volne. Preja je groba, rumenkasto obarvana, dolžina prediva je 73,6 mm in vsebnost maščobe do enoodstotna.

2.3 Izbor rastlin in njihova ekstrakcija

Na podlagi predhodnih raziskav smo se odločili, da bomo za ekstrakcijo naravnih barvil uporabili štiri rastline: navadno brezo, navadno lakoto, navadni oreh in veliko koprivo, ki dajejo intenzivna obarvanja, so lahko dostopne, imajo dolgo vegetacijo in jih je mogoče nabrati v večjih količinah. Uporabili smo sveže liste posameznih rastlin, razen pri navadni lakoti, kjer smo ekstrahirali sveže korenine. Navadno lakoto smo izbrali zato, ker je to edina poznana rastlina pri nas, ki vsebuje naravna barvila, s katerimi lahko dosežemo rdeče barvne tone. Izbrali smo rastline in drevesa, ki niso bila škropljena, gnojena ali kako drugače agrotehnično oskrbovana in na njih ni bilo sledi bolezni ali škodljivcev.

Nabrane rastline smo pripravili za ekstrakcijo tako, da smo liste ločili od pecljev in jih narezali. Koreninice navadne lakote smo oprali, posušili in drobno zmleli v mlinčku. Pri ekstrakciji barvil iz rastlin smo uporabili različna kopelna razmerja (KR_E je 1 g rastline: x mL deionizirane vode); 1 : 10 in 1 : 30. Pokrito čašo z deli rastlin v določenem KR_E smo segreli do vrelišča in nato ekstrahirali eno uro. Ekstrakcijsko zmes smo pustili stati približno 18 ur in nato prefiltrirali (dele rastlin smo ločili od ekstrakta).

Pri določenih poskusih (pri ekstrakciji navadne breze – štirje poskusi in pri ekstrakciji navadne lakote – dva poskusa) smo v ekstrakcijsko kopel dodali kombinacijo aluminijevega sulfata – $Al_2(SO_4)_3 \times 18H_2O$ in kalijevega hidrogentartrata – $KOOC(CHOH)_2COOH$ v različnih koncentracijah.

Po končani ekstrakciji smo ekstrakcijskim kopelim izmerili pH (pH_E) in ga za posamezne preskuse barvanja uravnali na pH 5 (s

2.3 Selection of plants and their extraction

Based on previous research, four plants were chosen for the natural dye extraction, i.e. birch tree, lady's bedstraw root, nut tree and big nettle. These plants enable intense colourations, are easily accessible, have long vegetation and can be collected in large quantities. Fresh leaves of individual plants were used, except in the case of lady's bedstraw, where a fresh root extract was used. Lady's bedstraw was chosen, for it is the only plant known in Slovenia that contains natural dyes with red colour shades.

The chosen plants were not pesticide-sprayed or fertilized, or treated agriculturally in any way. Moreover, no signs of diseases or pests were detected.

The harvested plants were prepared for extraction. The leaves were separated from the stalks and cut. Lady's bedstraw roots were washed, dried and finely ground in the mill. Different bath ratios, i.e. 1 : 10 and 1 : 30 (1 g of plant : x mL deionized water) were used when the dyes were extracted from plants. A covered tumbler with plant parts with a particular bath ratio was heated to the boiling point and extracted for one hour. The extraction mixture was left to stand for approx. 18 hours and then filtered (plant parts separation from the extract).

In the experiments (birch tree extraction – four experiments, and lady's bedstraw root – two experiments), different concentrations of aluminium sulphate combination – $Al_2(SO_4)_3 \cdot 18H_2O$ *and potassium hydrogentartrate –* $KOOC(CHOH)_2COOH$ *were added before the extraction into the extraction bath.*

After the extraction, the pH value of extraction baths (pH_E*) was measured and adjusted to pH 5 (using* CH_3COOH*) or to pH 8 (using* Na_2CO_3*) for individual experiments.*

The pH measurements were performed using a pH-meter MA 235 (Mettler Toledo) in accordance with the ISO 10523 standard.

2.4 Wool dyeing and after-treatment

The dyeing was performed with the Turby (Mathis) dyeing machine using 10 g of wool yarn and 1 : 20 bath ratio. The dyeing bath (extraction bath) was warming for 45 minutes to 98 °C and was dyed at that temperature for 15 min-

CH_3COOH) oz. na pH 8 (z Na_2CO_3). Meritve pH smo izvedli s pomočjo pH-metra MA 235 (Mettler Toledo) skladno s standardom ISO 10523.

2.4 Barvanje volnene preje in poobdelava

Barvanje je potekalo z 10 g volnene preje v barvalnem aparatu Turby (Mathis) pri kopelnem razmerju $KR_B = 1 : 20$. V 45 minutah smo barvalno kopel (ekstrakcijsko kopel) segreli na 98 °C in pri tej temperaturi barvali 15 minut. Po končanem barvanju smo volneno prejo dobro izprali s toplo (40 °C) in hladno destilirano vodo.

Barvanje je potekalo v ekstrakcijski kopeli brez dodanih kemikalij ali v ekstrakcijski kopeli, ki smo ji že na začetku ekstrakcije dodali kemikalije. Pri določenih poskusih pa smo različne kemikalije v različnih koncentracijah dodali med samim barvanjem. Pri barvanju z ekstraktom iz listov navadnega oreha (trije poskusi) smo dodali železov sulfat – $FeSO_4 \times 7\,H_2O$ in pri barvanju z ekstraktom iz listov velike koprive NaCl (trije poskusi) ali ocetno kislino – CH_3COOH (en poskus).

Določene vzorce, ki smo jih barvali v ekstrakcijski kopeli brez dodanih kemikalij, smo pozneje obdelali z različno kombinacijo kemikalij v različnih koncentracijah.

Tako so bili vzorci barvani v ekstraktu iz listov navadne breze v dveh primerih pozneje obdelani s kombinacijo $Al_2(SO_4)_3 \times 18\,H_2O$ in $KOOC(CHOH)_2COOH$ ter v dveh primerih s kombinacijo bakrovega sulfata – $CuSO_4 \times 5\,H_2O$ in CH_3COOH.

Vzorci, barvani v ekstraktu iz korenin navadne lakote, so bili v dveh primerih pozneje obdelani s kombinacijo $Al_2(SO_4)_3 \times 18\,H_2O$ in $KOOC(CHOH)_2COOH$ ter v dveh primerih z natrijevim karbonatom (soda) – Na_2CO_3.

Vzorci, barvani v ekstraktu iz listov navadnega oreha, so bili v šestih primerih pozneje obdelani s $FeSO_4 \times 7\,H_2O$ ter v dveh primerih s kombinacijo $CuSO_4 \times 5\,H_2O$ in ocetne kisline.

Vzorci, barvani v ekstraktu iz listov navadnega oreha, so bili v šestih primerih pozneje obdelani s kombinacijo $CuSO_4 \times 5\,H_2O$ in CH_3COOH.

2.5 Vrednotenje obarvanih vzorcev z uporabo barvnega sistema CIE

Obarvane vzorce volnene preje smo barvnometrično ovrednotili s pomočjo sistema za merjenje barv CIE, v spektralnem območju z valovno dolžino 400–700 nm, na spektrofotometru SF 600+, (Datacolor), ki je dvožarkovni spektrofotometer z Ulbrichtovo kroglo in geometrijo merjenja d/8°. Kot vir svetlobe smo uporabili halogensko žarnico in ksenonsko bliskavico, ki v kombinaciji s filtrom dajeta standardizirano dnevno svetlobo D65. Meritve so potekale na vzorcih preje, večplastno navite na kartonski nastavek, z izključenim leskom pri merilni odprtini 6,6 mm. Za vsak obarvani vzorec smo izvedli tri meritve. Povprečne vrednosti meritev CIE L^*C^*h barvnih vrednosti pobarvanih vzorcev so podane v preglednicah od 2 do 5.

utes. Afterwards, the dyeing wool yarn was washed several times with warm (40 °C) and cold distilled water.

The dyeing was conducted in the extraction bath without any added chemicals or in the extraction bath where chemicals were added at the beginning of the extraction. In the experiments, different chemicals in different concentrations were added during the dyeing process. When dyeing with the nut tree extract (three experiments), ferric sulphate – $FeSO_4 \cdot 7H_2O$ was added and in the case of dyeing with leaves of big nettle, NaCl (three experiments) or acetic acid – CH_3COOH (one experiment) was added.

Certain samples which were dyed in the extraction bath without any added chemicals were additionally treated with a different combination of chemicals at different concentrations.

Thus, the birch tree dyed samples were in two cases subsequently treated with a combination of $Al_2(SO_4)_3 \cdot 18\,H_2O$ and $KOOC(CHOH)_2COOH$, and in two cases with a combination of copper sulphate – $CuSO_4 \cdot 5H_2O$ and CH_3COOH.

The lady's bedstraw root dyed samples were in the two cases subsequently treated with a combination of $Al_2(SO_4)_3 \cdot 18\,H_2O$ and $KOOC(CHOH)_2COOH$, and in two cases with sodium carbonate (soda) – Na_2CO_3.

The nut tree dyed samples were in six examples additionally treated with $FeSO_4 \cdot 7\,H_2O$, and in two examples with a combination of $CuSO_4 \cdot 5\,H_2O$ and acetic acid.

Finally, the big nettle dyed samples were in six examples additionally treated with a combination of $CuSO_4 \cdot 5\,H_2O$ and CH_3COOH.

2.5 Evaluation of dyed samples using CIE colour system

Dyed wool yarn samples were colourimetrically evaluated with the CIE colour system using the two-ray SF 600+ spectrophotometer (Datacolor) with Ulbricht sphere and geometry d/8° in the spectral range of 400–700 nm wavelength. As the source of light, halogen lamp and xenon flash in a combination with a filter, giving the standard daylight D65, were used. The measurements were conducted on yarn samples, which were rolled up in multilayers onto the cardboard accessory without the sheen at

Barvni prostor v CIE $L^*a^*b^*$ barvnem sistemu je definiran z L* osjo in barvnima koordinatama a*in b* [8].

$$L^* = 116\,(Y / Y_n)^{1/3} - 16 \qquad L^* \text{ – svetlost (0–100),} \tag{1}$$

$$a^* = 500\,[(X / X_n)^{1/3} - (Y/Y_n)^{1/3}] \qquad a^* \text{ – rdeče/zelena os,} \tag{2}$$

$$b^* = 200\,[(Y / Y_n)^{1/3} - (Z/Z_n)^{1/3}] \qquad b^* \text{ – rumeno/modra os,} \tag{3}$$

kjer so:

X, Y, Z – standardizirane barvne vrednosti,

X_n, Y_n, Z_n – standardizirane barvne vrednosti belega standarda $BaSO_4$, ki znašajo za 10°/D65: X_n = 94,81, Y_n = 100,00 in Z_n = 107,34.

Barvni sistem CIE L^*C^*h uporablja polarne koordinate namesto pravokotnih. Vrednost L^* je enaka kot pri barvnem sistemu CIE $L^*a^*b^*$, vrednosti krome (C^*) in barvnega tona (h) pa določimo iz naslednjih enačb:

$$C^* = (a^{*2} + b^{*2})^{1/2} \tag{4}$$

$$h = \arctan\,(b^* / a^*) \tag{5}$$

(0° – rdeča, 90° – rumena, 180° – zelena, 270° – modra)

2.6 Barvne obstojnosti

Preskus barvnih obstojnosti posameznih vzorcev na pranje smo izvedli po standardu SIST EN ISO 20105-C01: Test 1 – pranje pri temperaturi 40 °C. Spremembo barve obarvanih vzorcev in obarvanje spremljevalnih tkanin smo ocenili vizualno s pomočjo sive lestvice. Ocene so podane v preglednicah od 2 do 5.

3 Rezultati z razpravo

3.1 Merjenje pH ekstrakcijskih kopeli

V preglednici 1 so prikazani rezultati meritev vrednosti pH ekstrakcijskih kopeli (pH_E), ki smo jih uporabili za barvanje, glede na vrsto rastline in kopelno razmerje ekstrakcije, ki pomeni tudi različno začetno koncentracijo (ekstrahiranega) barvila pri barvanju.

Table 1: pH values of extraction baths

Plant	KR_E	pH_E
Birch tree (fresh leaves)	1:10	5.3
	1:30	5.2
	1:50	4.7
Lady's bedstraw (fresh roots)	1:10	5.5
	1:30	5.2
	1:50	5.1

6.6 mm measuring aperture. For each dyed sample, three measurements were performed. The average CIE L*C*h colour values of dyed samples are given in Tables 2–5.

The colour space in the CIE L*a*b* colour system is defined by the L* axis and colour coordinates a* and b* [8] (Equations 1–3).

Where:

X, Y, Z – standard colour values,

_X_n, Y_n, Z_n – standard colour values of $BaSO_4$ white standard, accounting for 10°/D65: X_n = 94.81, Y_n = 100.00 and Z_n = 107.34._

The CIE L*C*h colour system has polar coordinates instead of rectangular ones. The L* value is the same as in the CIE L*a*b* colour system, while the chroma value (C*) and colour tone (h) are determined with the following equations 4–5. Where:

(0° – red, 90° – yellow, 180° – green, 270° – blue).

2.6 Colour fastness

The colour fastness of individual samples to washing was determined according to the standard SIST EN ISO 20105-C01: Test 1 – washing at 40 °C. The change in colour of the dyed samples and the staining of adjacent fabrics were visually evaluated with the grey-scale. The estimates are given in Tables 2–5.

3 Results and discussion

3.1 pH values of extraction baths

The pH values of extraction baths (pH_E) used for dyeing are shown in Table 1. The baths differ in the plant type and bath extraction ratio, which leads to different initial dye concentrations (extracted) at dyeing.

The results showed that the pH of most plant or plant part extraction baths at the bath ratio 1 : 10 were slightly acidic with pH 5.1–5.5. An exception was the big nettle extract, which was alkaline with pH 8.1 (cf. Table 1). With an increased bath ratio (a smaller amount of plant parts), the pH of all extraction baths lowered, which was probably due to the plant extraction using deionized water with a slightly acidic pH (4.8–5.2).

Plant	KR_E	pH_E
Nut tree (fresh leaves)	1:10	5.1
	1:30	4.7
	1:50	4.6
Big nettle (fresh leaves)	1:10	8.1
	1:30	7.1
	1:50	6.4

Iz rezultatov je razvidno, da so ekstrakcijske kopeli večine rastlin oz. rastlinskih delov pri KR_E 1 : 10 rahlo kisle s *pH* med 5,1 in 5,5, z izjemo ekstrakta velike koprive, ki je alkalen s *pH* 8,1. Pri večjem kopelnem razmerju (manjša količina rastlinskih delov) se je *pH* v vseh ekstrakcijskih kopelih znižal, verjetno zato, ker smo rastline ekstrahirali v deionizirani vodi z rahlo kislim *pH* (4,8 do 5,2).

3.2 Barvne vrednosti in barvne obstojnosti CIE

V preglednicah od 2 do 5 so prikazane CIE L*C*h barvne vrednosti in barvne obstojnosti na pranje pri temperaturi 40 °C 49 vzorcev volnene preje, ki smo jih barvali z naravnimi barvili, ekstrahiranimi iz štirih rastlin. Čeprav je celotna raziskava zajemala barvanje več kot 300 različnih vzorcev, so v prispevku prikazani samo najpomembnejši. Pri ekstrakciji smo uporabili dve kopelni razmerji, 1 : 10 in 1 : 30, ter tako dobili dve različni začetni koncentraciji barvil. Ker smo želeli ugotoviti, kako *pH* kopeli vpliva na barvo, smo barvanje izvedli pri treh različnih vrednostih *pH*: pri pH_E, *pH* 5 in *pH* 8. Da bi dobili večjo paleto barvnih tonov, večje izčrpanje in boljše obstojnosti na pranje, smo v različnih fazah obdelave dodali različne kovinske soli. Njihova osnovna naloga je, da omogočijo tvorbo vezi vlakno–barvilo ter hkrati vplivajo tudi na končni barvni ton. Vzorce smo obdelali na štiri različne načine:

- ekstrakcija in barvanje brez dodanih kemikalij (E, B);
- dodajanje kemikalij pri ekstrakciji (E + K, B);
- dodajanje kemikalij pri barvanju (E, B + K);
- poznejša obdelava obarvanih vzorcev (E, B, PoK).

Na slikah od 4 do 7 so prikazani položaji obarvanih vzorcev v barvnem diagramu CIE a*b*, ki kaže hkrati barvni ton in čistost barve [8].

Iz preglednice 2 in slike 4 je razvidno, da z barvilom, ekstrahiranim iz svežih listov navadne breze, dosežemo svetlo rjava obarvanja, pri čemer alkalni *pH* (vzorec 3) in večje kopelno razmerje (vzorec 4) vplivata na večjo svetlost vzorcev. Barvanje v ekstraktu z dodanim aluminijevim sulfatom in soljo vinske kisline – kalijevim hidrogentartratom (vzorci od 5 do 8) daje svetlejša obarvanja, poveča se nasičenost (kroma), vzorci so bolj rumeni (barvni ton je med 81 in 90°, kar je odvisno od količine aluminijeve soli in

Table 2: CIE L*C*h colour values of samples dyed according to different procedures (various chemicals, liquor ratio (KR_E) and pH) using dyes extracted from fresh leaves of birch tree

Sample number	Procedure	Chemicals	KR_E	pH	L*	C*	h	Colour fastness *W/S/C
1	E, B		1:10	pH_E	62.61	22.63	78.37	5/1/5
2	E, B			5	59.39	23.03	75.69	5/1/5
3	E, B			8	65.03	27.96	75.37	5/1/5
4	E, B		1:30	pH_E	64.50	19.98	78.39	5/1/5
5	E+K, B	9 g Al + 3 g tar.	1:10	pH_E	68.80	45.76	90.22	5/1-2/5
6	E+K, B	9 g Al + 3 g tar.		5	68.99	43.23	88.08	5/2/5
7	E+K, B	6 g Al + 6 g tar.		pH_E	68.84	31.84	81.42	5/2/5
8	E+K, B	6 g Al + 6 g tar.	1:30	5	70.59	31.04	88.92	5/2/5
9	E, B, PoK	7 g Al + 5 g tar.	1:10	8	52.63	29.51	73.21	5/2-3/5
10	E, B, PoK	2 g Cu + 2 mL acetic acid		8	36.92	27.90	75.49	5/2-3/5
11	E, B, PoK	7 g Al + 5 g tar.	1:30	8	63.87	27.80	75.66	5/2-3/5
12	E, B, PoK	2 g Cu + 2 mL acetic acid		8	45.83	29.22	82.53	5/2-3/5

*W/S/C – staining on wool/ change in colour of sample/ staining on cotton

3.2 CIE colour values and colour fastness

Tables 2–5 present the CIE L*C*h colour and colour fastness values (washed at 40 °C) of 49 woollen yarn samples, which were dyed with natural dyes extracted from four plants. Although the entire research consisted of dyeing of over 300 different samples, only the most important ones are presented here. At extraction, two bath ratios were used, i.e. 1 : 10 and 1 : 30, and thus two different initial dye concentrations were obtained. Due to the importance of knowing the pH influence on the colouration, the dyeing was performed at three different pH values, i.e. pH_E, pH 5 and pH 8. In order to attain a wider range of colour shades, higher exhaustion and better wash fastness, various metallic salts were added at different stages of the process. Their primary role was to enable the fibre-dye bond formation and at the same time, affect the final colour shade. The sample treatments were conducted in four different methods, namely:

- extraction and dyeing without the addition of chemicals (E, D),

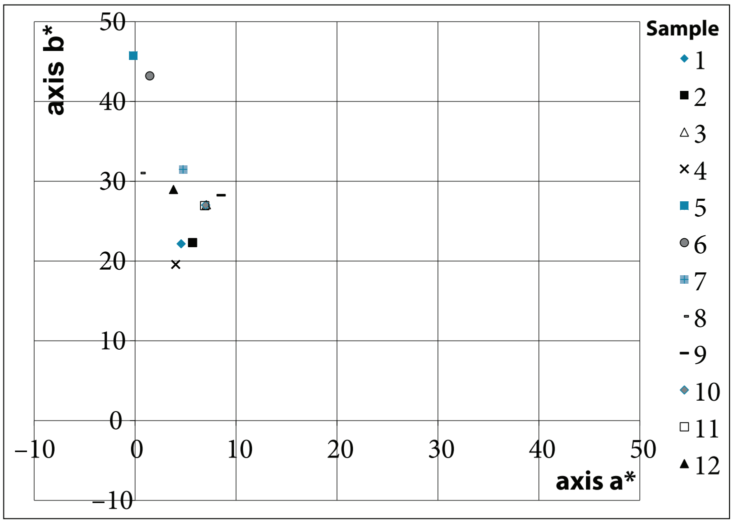


Figure 4: Position of dyed samples (leaves of birch tree) in a*b* colour diagram

soli vinske kisline, pH in koncentracije ekstrahiranega barvila). Pri vzorcih 9 in 11, ki smo jih pozneje obdelali z aluminijevim sulfatom in kalijevim hidrogentartatom v alkalnem mediju, pa se barvni ton bistveno ne spreminja. Vzorci so nekoliko bolj rumeni oz. manj modri glede na vzorec 3, ki smo ga barvali v alkalni ekstrak-

- *addition of chemicals during extraction (E+C, D),*
- *addition of chemicals during dyeing (E, D+C),*
- *after-treatment of dyed samples (E, D, After C).*

*Figures 4–7 show the positions of dyed samples in the CIE a*b* colour graph, showing both the colour shade and colour purity [8].*

Table 2 and Figure 4 demonstrate light brown colouration of the samples dyed with the dye extracted from fresh leaves of birch tree, where the alkaline pH (Sample 3) and increased bath ratio (Sample 4) induced higher lightness. Brighter colourations, increased saturation (chroma), increased yellow shade (colour tone is 81–90°, depending on the amount of aluminium salt and tartaric acid salt, pH and extracted dye concentration) were achieved (Samples 5–8) when dyeing in the extract with the added aluminium sulphate and tartaric acid – potassium hydrogentartrate. There was no significant change in the colour shade when Samples 9 and 11 were subsequently treated with aluminium sulphate and potassium hydrogentartrate in an alkaline medium. However, in comparison with

cijski kopeli brez kovinskih soli. Poobdelava z bakrovim sulfatom vpliva na pomik barve v rjavo območje, kar opazimo pri meritvah le na podlagi nižje svetlosti. V primerjavi s postopki barvanja brez dodatka kovinskih soli vpliva poobdelava s kovinskimi solmi predvsem na boljšo barvno obstojnost na pranje pri temperaturi 40 °C; vizualna ocena po sivi lestvici je med 2 in 3.

Iz preglednice 2 je razvidno tudi, da dosežemo najslabše barvne obstojnosti na pranje (sprememba barve obarvanega vzorca je bila ocenjena z 1) pri barvanju v ekstrakcijski kopeli brez dodanih kovinskih soli, kar je skladno z literaturnimi viri [4, 6]. Spremljevalni tkanini (volnena in bombažna) se ne obarvata pri nobeni obdelavi.

Iz preglednice 3 in slike 5 je razvidno, da barvanje z ekstraktom svežih korenin navadne lakote daje rdeče barvne tone, ki postanejo še bolj intenzivni oz. bolj nasičeni, vendar svetlejši, z dodajanjem kombinacije aluminijevega sulfata in kalijevega hidrogentartata v ekstrakcijsko kopel (vzorca 17 in 18). Pri naknadni obdelavi s kombinacijo aluminijeve soli in soli vinske kisline (vzorca 19 in 21) se prav tako poveča nasičenost, vzorca sta temnejša ter bolj rdeča in bolj rumena v primerjavi z vzorcema 13 in 15, ki sta bila barvana v ekstrakcijski kopeli brez dodanih kovinskih soli. Barvanje v alkalni ekstrakcijski kopeli brez dodanih kovinskih soli (vzorca 14 in 16) vpliva na večjo nasičenost in barvni ton; vzorca sta svetlejša ter bolj rdeča in bolj rumena kot vzorca 13 in 15, ki smo ju barvali v kisli ekstrakcijski kopeli. Dodatek sode pri poobdelavi (vzorca 20 in 22) pa daje manj intenzivne rdeče tone, svetlost je

*Table 3: CIE L*C*h colour values of samples dyed according to different procedures (various chemicals, liquor ratio (KR_E) and pH) using dyes extracted from fresh roots of lady's bedstraw*

Sample number	Procedure	Chemicals	KR_E	*pH*	*L**	*C**	*h*	Colour fastness *W/S/C
13	E, B		1:10	pH_E	53.64	23.76	55.87	5/1-2/5
14	E, B			8	47.01	29.38	45.35	4-5/1/4-5
15	E, B		1:30	pH_E	57.71	19.04	52.61	5/2/5
16	E, B			8	55.12	27.94	44.57	5/1/5
17	E+K, B	9 g Al + 3 g tar.	1:10	pH_E	64.88	33.86	53.94	5/2-3/5
18	E+K, B	9 g Al + 3 g tar.	1:30	pH_E	67.61	32.82	53.51	5/2-3/5
19	E, B, PoK	9 g Al + 3 g tar.	1:10	5	50.96	33.11	45.42	5/2/5
20	E, B, PoK	2 g soda		8	48.68	23.70	41.84	5/1/5
21	E, B, PoK	9 g Al + 3 g tar.	1:30	5	54.33	32.58	45.09	5/2-3/5
22	E, B, PoK	2 g soda		8	59.19	23.11	46.70	5/2/5

*W/S/C – staining on wool/ change in colour of sample/ staining on cotton

Sample 3, which was dyed in the alkaline extraction bath without the added metal salts, the samples were slightly yellower or less blue. The copper sulphate after-treatment caused the colour shift into the brown region, which was observed only at lower lightness. Compared with the processes of dyeing without metallic salts, the after-treatment with metallic salt improves particularly the wash colour fastness at 40 °C. The visual assessment on the grey-scale was 2–3. When dyeing in the extraction bath without metal salts, poor colour fastness to washing (colour change of the dyed sample was evaluated with 1) were achieved (cf. Table 2), which is consistent with the literature sources [4, 6]. The adjacent fabrics (wool and cotton) were not stained in any of the treatments.

The red colour shades that became more intense or saturated, but brighter (cf. Table 3 and Figure 5) when aluminium sulphate and potassium hydrogentartrate combinations were added into the extraction bath were achieved with the dyeing with the lady's bedstraw fresh roots extract (Samples 17 and 18). The aluminium and tartaric acid salt after-treatment combinations also increased saturation, the samples were darker, redder and yellower (Samples 19 and 21) if compared with Samples 13 and 15, which were dyed in the extraction bath without the added metal salt. The dyeing in the alkaline extraction bath without the added metal salt (Samples 14 and 16) increased the saturation and colour shade. The samples were brighter, redder and yellower than Samples 13 and 15, which were dyed in the acid extraction bath. The soda after-treatment (Samples 20 and 22) gave less intensive red tones, reduced brightness, and had a lower saturation angle compared with Samples 17 and 18. The best fastness properties were achieved when dyeing with birch tree leaves (cf. Table 2) and lady's bedstraw roots (cf. Table 3) with an additional metal salt treatment. The wash colour fastness was not affected by the soda after-treatment.

The dyeing in the nut tree fresh leaves extract gave a range of brown tones (cf. Table 4 and Figure 6). Unlike in the previous dyeing (cf. Tables 2 and 3), the ferric sulphate was added instead of the aluminium sulphate – in three cases into the fresh leaves nut tree dyeing

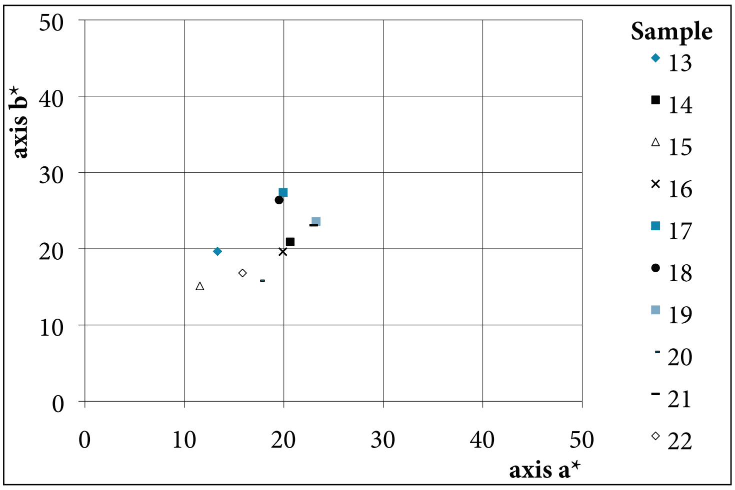


Figure 5: Position of dyed samples (roots of lady's bedstraw) in CIE a^*b^**colour diagram*

nižja, manjši pa je tudi kot pestrosti kot pri vzorcih 17 in 18. Enako kot pri barvanju z listi navadne breze (preglednica 2) dosežemo tudi pri barvanju s korenino navadne lakote (preglednica 3) najboljše obstojnosti na pranje s poznejšo obdelavo s kovinsko soljo. Poobdelava s sodo ne vpliva na barvno obstojnost pri pranju.

Barvanje v ekstraktu iz svežih listov navadnega oreha daje paleto rjavih barvnih tonov (preglednica 4 in slika 6). V nasprotju s prednodnimi obarvanji (preglednici 2 in 3), smo pri barvanju s svežimi listi navadnega oreha dodajali namesto aluminijevega sulfata železov sulfat, v treh primerih v barvalno kopel (vzorci od 25 do 27) in v šestih primerih pri poobdelavi (vzorci od 28 do 30 in vzorci od 32 do 34). To je bil tudi razlog za največjo spremembo barvnega tona. Pri vzorcih 23 in 24, ki sta bila barvana v ekstrakcijski kopeli pri pH_E brez dodanih kovinskih soli, je bila vrednost a^* 12,07 oz. 10,86 in vrednost b^* 22,66 oz. 19,63 ter pri vzorcih 31 in 34, ki sta bila pozneje obdelana s kombinacijo bakrovega sulfata in ocetne kisline, je bila vrednost a^* 12,06 oz. 5,96 in vrednost b^* 17,33 oz. 12,87. Pri vseh drugih vzorcih so vrednosti CIE a^*b^* bolj skupaj (vrednosti a^* med 0,37 in 3 ter vrednost b^* med 5,13 in 12). Vzorci 23, 24, 31 in 35 so tudi veliko svetlejši in bolj nasičeni kot drugi vzorci. Količina dodanega železovega sulfata pomembno vpliva na svetlost vzorcev in barvno obstojnost pri pranju. S povečevanjem koncentracije se svetlost vzorcev zmanjšuje, barvne obstojnosti na pranje pa se povečujejo. Pri poobdelavi s 5 g železovega sulfata pri KR_E 1:10 (vzorec 28) in 2,5 g pri KR_E 1:30 (vzorec 32) smo dosegli zelo temno rjavo-zelena obarvanja z dobrimi barvnimi obstojnostmi na pranje (ocena 3). Najslabše barvne obstojnosti smo dosegli v primerih ekstrakcije in barvanja brez dodanih kovinskih soli, enako, kot pri barvanju z drugimi rastlinami. Iz preglednice 4 je razvidno tudi, da pride pri vseh vzorcih, obdelanih na različne načine, do rahlega obarvanja oz. umazanja obeh spremljevalnih tkanin pri preskusu barvnih obstojnosti na pranje (ocena 4 in 4–5).

*Table 4: CIE L*C*h colour values of samples dyed according to different procedures (various chemicals, liquor ratio (KR_E) and pH) using dyes extracted from fresh leaves of nut tree*

Sample number	Procedure	Chemicals	KR_E	pH	L*	C*	h	Colour fastness *W/S/C
23	E, B		1:10	pH_E	47.26	25.68	61.95	4/1-2/4
24	E, B		1:30	pH_E	48.29	22.43	61.06	4/1-2/4
25	E, B+K	2.5 g Fe	1:10	pH_E	21.25	6.39	81.48	4/1-2/4
26	E, B+K	5 g Fe		pH_E	25.37	7.34	83.95	4/1-2/4
27	E, B+K	15 g Fe		pH_E	18.72	5.14	85.93	4/1-2/4
28	E, B, PoK	5 g Fe	1:10	pH_E	18.97	6.14	81.93	4-5/3/4-5
29	E, B, PoK	1 g Fe		pH_E	26.70	9.77	77.11	4-5/3/4-5
30	E, B, PoK	0.5 g Fe		pH_E	30.55	12.03	75.25	4-5/2-3/ 4-5
31	E, B, PoK	2 g Cu + 2 mL acetic acid		8	24.01	21.12	55.17	4-5/3/4-5
32	E, B, PoK	2.5 g Fe	1:30	5	19.83	7.91	78.25	4-5/3/4
33	E, B, PoK	1.5 g Fe		5	22.50	8.78	77.12	4-5/2/4-5
34	E, B, PoK	0.5 g Fe		5	26.60	11.05	74.61	4-5/1-2/ 4-5
35	E, B, PoK	2 g Cu + 2 mL acetic acid		8	33.48	14.18	65.15	4-5/2/4-5

*W/S/C – staining on wool/ change in colour of sample/ staining on cotton

bath (Samples 25–27) and in six cases after the treatment (Samples 28–30 and 32–34). This was also the reason for a substantial change in colour shades. At Samples 23 and 24, which were dyed in the extraction bath pH_E without any added metal salts, the value a was 12.07 and 10.86, and value b* 22.66 and 19.63, respectively. At Samples 31 and 34, which were subsequently treated with a combination of copper sulphate and acetic acid, the value a* was 12.06 and 5.96, and value b* 17.33 and 12.87. All other samples had similar CIE a*b* values (a* value 0.37–3, and b*value 5.13–12). Samples 23, 24, 31 and 34 were also brighter with a higher saturation if compared with other samples. The added ferric sulphate amount had a significant influence on the sample lightness and colour fastness to wash. With the increased concentration, the sample lightness reduced, while the colour fastness increased. The after-treatment with 5 g of ferric sulphate in the bath ratio 1 : 10 (Sample 28) and 2.5 g in*

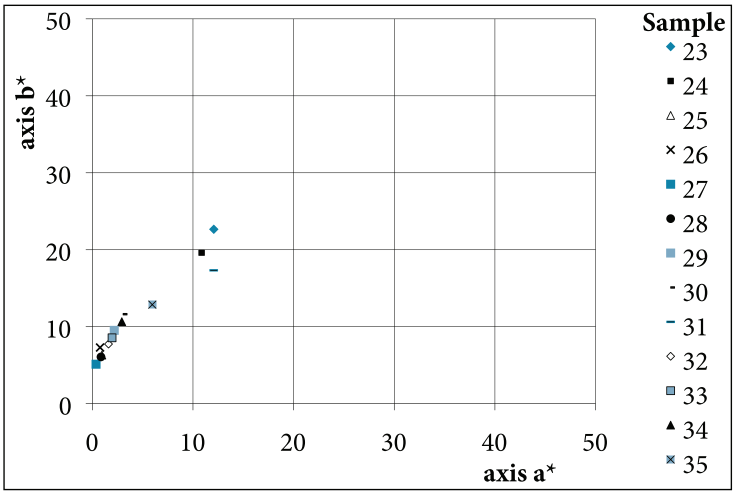


*Figure 6: Position of dyed samples (leaves of nut tree) in CIE a*b*colour diagram*

Pri barvanju z barvili, ekstrahiranimi iz listov sveže koprive, dobimo paleto zelenih barvnih tonov (preglednica 5). Večjo globino in temnejša obarvanja ter najboljše barvne obstojnosti smo dosegli pri poznejši obdelavi z bakrovim sulfatom (vzorci od 44 do 49).

*Table 5: CIE L*C*h colour values of samples dyed according to different procedures (various chemicals, liquor ratio (KR_E) and pH) using dyes extracted from fresh leaves of big nettle*

Sample number	Procedure	Chemicals	KR_E	pH	L*	C*	h	Colour fastness *W/S/C
36	E, B		1:10	pH_E	53.34	17.81	81.34	5/1-2/4-5
37	E, B			5	56.51	16.05	81.95	5/1-2/5
38	E, B			8	53.71	20.78	80.77	4-5/1/4-5
39	E, B		1:30	pH_E	67.81	15.62	85.36	5/1-2/5
40	E, B+K	5 g NaCl	1:10	pH_E	56.90	18.16	81.25	5/1-2/5
41	E, B+K	5 g NaCl		5	62.11	19.15	81.74	4-5/2/4-5
42	E, B+K	5 g NaCl		8	54.05	18.73	81.71	5/1/4-5
43	E, B+K	2 mL acetic acid	1:30	pH_E	58.30	12.84	83.24	5/2/5
44	E, B, PoK	2 g Cu + 2 mL acetic acid	1:10	pH_E	46.03	25.01	85.88	4-5/3/5
45	E, B, PoK	2 g Cu + 2 mL acetic acid		5	38.60	21.08	86.19	4-5/2-3/ 4-5
46	E, B, PoK	2 g Cu + 2 mL acetic acid		8	38.76	20.34	86.87	4-5/2/5
47	E, B, PoK	2 g Cu + 2 mL acetic acid	1:30	pH_E	56.39	20.11	87.97	5/3/5
48	E, B, PoK	2 g Cu + 2 mL acetic acid		5	55.18	20.92	87.61	5/3-4/5
49	E, B, PoK	2 g Cu + 2 mL acetic acid		8	48.27	20.75	90.76	5/2/5

*W/S/C - staining on wool/ change in colour of sample/ staining on cotton

the bath ration 1 : 30 (Sample 32) produced dark brown-green colourations with good colour fastness (grade 3). Poor colour fastness properties were achieved when the extraction and dyeing were performed without any added metal salts. When dyeing with other plants, the situation was the same. Table 4 also shows that with all samples treated in different ways, it came to slight staining or dirtiness of adjacent fabrics when testing the colour fastness properties (grade 4 and 4–5).

*Dyeing in the nettle fresh leaves extract gave a range of green colour shades (cf. Table 5). Greater depth, darker colourations and good colour fastness were achieved with an additional copper sulphate treatment (Samples 44–49). These samples had also similar CIE a*b* in the diagram (cf. Figure 7), which indicates a resembling colour shade. In comparison with all other samples (Samples 36–43), they were also*

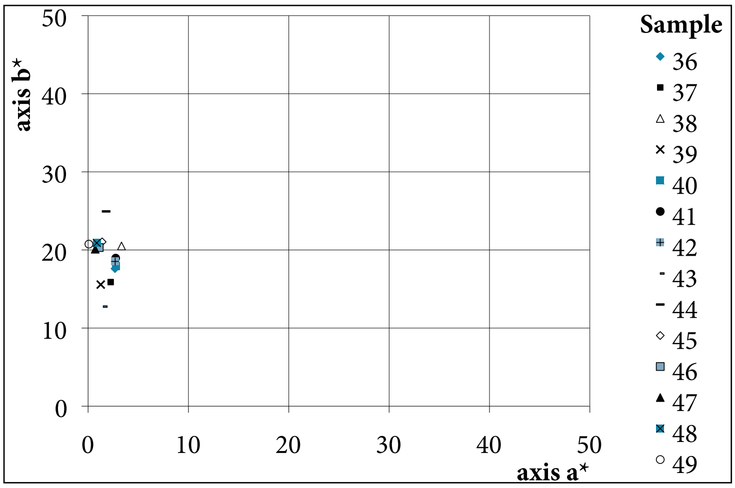


*Figure 7: Position of dyed samples (leaves of big nettle) in CIE a*b*colour diagram*

Ti vzorci so tudi v diagramu CIE *a*b** najbolj skupaj (slika 7), kar pomeni zelo podoben barvni ton. V primerjavi z vsemi drugimi *less red. The NaCl addition into the dyeing bath (Samples 40–42) increased the saturation and reduced the lightness. The colour shade remained the same as when dyeing in the extraction bath without the added metal salt, which means that the NaCl salt affects the bath exhaustion, however, less if compared with metal salts – ferric sulphate addition in the nut tree fresh leaves dyeing (cf. Table 4). The colour fastness properties of the fresh nettle leaves extract dyed samples were similar to the samples dyed with plant extracts. The poorest colour fastness was demonstrated when dyeing without the added metal salts (grade 1–2) and the best with the copper sulphate after-treatment (max. grade 3–4).*

4 Conclusion

On the basis of extensive experimental work and the dyed sample evaluation with the CIE colour system, it can be concluded that the plant dyes extracted from birch tree leaves provide tones yellow in colour, lady's bedstraw roots red, nut leaves brown and big nettle green colour shades. The aluminium salt addition into the extraction bath or to the dyeing bath created lively and saturated colour shades when compared with the dyeing without any added metal salts. The copper sulphate and tartrate combinations addition created more blue-green colour tones and the ferric sulphate addition provided darker and less saturated colour shades. The addition of chemicals into the extraction bath or into the dyeing bath had a great impact on the colour shade, colouration depth and particularly on the obtained colour fastness properties. The bath extraction ratio affected the colouration intensity; a higher bath rate provided lighter and less saturated colourations. On the other hand, more intensive colourations of lively warm colours (yellow and red) were achieved when dyeing in the acidic pH. Cold and dark colourations became precious when dyeing in the alkaline pH. However, it is important to emphasize that due to the growing environment conditions, the amount of the dye can vary and the colourations are difficult to reproduce. All colour fastness properties to washing at 40 °C were low (visual estimation using the grey-scale

vzorci (vzorci od 36 do 43) so tudi manj rdeči. Dodajanje NaCl v kopel pri barvanju (vzorci od 40 do 42) vpliva na povečanje nasičenosti, svetlost se zmanjša, barvni ton pa ostane enak kot pri barvanju v ekstrakcijski kopeli brez dodanih kovinskih soli, kar pomeni, da NaCl vpliva na izčrpanje kopeli, vendar manj kot dodatek kovinske soli – železovega sulfata pri barvanju s svežimi listi navadnega oreha (preglednica 4).

Barvne obstojnosti vzorcev, obarvanih z ekstraktom iz listov sveže koprive, so podobne obstojnostim vzorcev, barvanih z drugimi rastlinskimi ekstrakti; najslabše so pri barvanju brez dodanih kovinskih soli (ocena med 1 in 2) in najboljše pri poobdelavi z bakrovim sulfatom (maks. ocena 3–4).

4 Sklep

Na podlagi obsežnega eksperimentalnega dela in vrednotenja obarvanih vzorcev s pomočjo barvnega sistema CIE lahko povzamemo, da rastlinska barvila, ekstrahirana iz brezovih listov, dajejo rumene barvne tone, iz korenine navadne lakote rdeče, iz listov navadnega oreha rjave in iz listov velike koprive zelene barvne tone. Dodajanje kombinacije aluminijeve soli in tartrata pri ekstrakciji oz. pri barvanju vpliva na nastanek živahnejših, nasičenih barvnih tonov kot pri barvanju brez kovinskih soli; dodajanje bakrovega sulfata je vzrok za bolj modro zelene barvne tone, z železovim sulfatom pa dosegamo temnejše, manj nasičene barvne nianse. Dodajanje kemikalij pri ekstrakciji oz. barvanju ima pomemben vpliv na barvni ton, globino izbarvanja, predvsem pa na barvno obstojnost. Kopelno razmerje ekstrakcije pomembno vpliva na intenzivnost obarvanj; z večjimi kopelnimi razmerji dosegamo svetlejša in manj nasičena obarvanja. Na drugi strani pa dosegamo bolj intenzivna obarvanja živahnih toplih barv, (rumene in rdeče) z barvanjem v kislem *pH*, hladne in temne barve pa postanejo žlahtne pri barvanju v alkalnem *pH*. Pri tem pa je treba poudariti, da so ta izbarvanja pri ponovni ekstrakciji težko ponovljiva, saj rastline glede na razmere in okolje, v katerem rastejo, vsebujejo različne količine barvil. Barvne obstojnosti vseh vzorcev na pranje pri temperaturi 40 °C so slabe (vizualne ocene po sivi lestvici so bile med 1 in 3), odvisno od vrste postopka in dodanih kovinskih soli, medtem ko so spremljevalne tkanine ostale neobarvane oz. rahlo obarvane (ocene med 4 in 5). Pri eksperimentalnem delu smo opazili, da nekateri barvni toni s pranjem pridobijo na nasičenosti in barvni pestrosti, drugi postanejo svetlejši, spet tretji ostanejo nespremenjeni.

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was 1–3), depending on the procedure type and metallic salts addition, while the adjacent fabrics stayed un- or slightly coloured (estimations 4–5). During the experimental work, it could be observed that with several washes, some colour shades gained on saturation and colour diversity, others became lighter, and again the third remained unchanged.

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