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Vpliv UV-sevanja na obarvanja bombažnih tkanin z naravnimi barvili

Izvirni znanstveni članek

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Izvleček

Človek si od nekdaj poskuša popestriti življenje z barvami. Naravna barvila so neobstojna, še zlasti če so neposredno izpostavljena soncu, zato so se najbolj ohranili predvsem izdelki, ki so jih našli zakopane v zemlji ali globoko v jamah. Cilj raziskave je bilo barvnometrično vrednotenje sprememb obarvanj z barvili iz naravnih virov, ki so jih ljudje najpogosteje uporabljali, po različnih časih izpostavljenosti UV-sevanju. Uporabljena so bila barvila, pridobljena iz rdeče pese (*Beta vulgaris*), rdečega zelja (*Brassica oleracea*), črnega ribeza (*Ribes nigrum*), čebule (*Allium cepa*), hibiskusa (*Hibiscus*) ter žafranike (*Carthamus tinctorius*). Raziskava je pokazala, da so barvila iz skupine derivatov kinona, ki so prisotna v žafraniki, najbolj obstojna na UV-sevanje v primerjavi z drugimi izbranimi naravnimi barvili.

Ključne besede: naravna barvila, UV-sevanje, barvna metrika, barvanje bombaža

Influence of UV Radiation on Cotton Fabrics Dyed with Natural Dyes

Original Scientific Paper

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Abstract

The human being has always tried to variegate its life with colours. All natural dyes are not resilient, especially when they are directly exposed to sunlight. In most cases, only those products have remained preserved which were found buried in soil or in deep caves. The aim of this research was a colorimetric evaluation of the changes in the colourings from natural sources people have been using most frequently with regard to different periods of exposure to UV radiation. The dyes used were obtained from red beet (Beta vulgaris), red cabbage (Brassica oleracea), black currant (Ribes nigrum), onions (Allium cepa), hibiscus (Hibiscus) and safflower (Carthamus tinctorius). The research has shown that the dyes from the group of derivatives from quinone present in safflower are the most resistant to UV radiation in comparison with the rest of the chosen natural dyes.

Keywords: natural dyes, UV radiation, colorimetry, dyeing of cotton

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1 Uvod

Naravna barvila so del svetovne kulture in imajo velik zgodovinski pomen. Uporabljajo se dalj časa kot katerokoli sintetično barvilo. V zadnjem času postajajo zopet čedalje bolj aktualna, saj so prijazna do okolja, zdravju neškodljiva in biorazgradljiva, zato naravna barvila zamenjujejo tudi zdravju škodljiva sintetična barvila v živilski in farmacevtski industriji. Lastnosti in učinki naravnih barvil so razmeroma slabo raziskani. Zadnje raziskave kažejo na zdravilne učinke naravnih barvil, predvsem tistih iz skupine an-

1 Introduction

Natural dyes represent a part of the global culture and are of a great historical importance. They have been used for a longer period of time than any other synthetic dye. Lately, they are again becoming more present, since they are environment-friendly, harmless to health and biodegradable. Natural dyes are thus replacing also the synthetic dyes which are hazardous to health in the food and pharmaceutical industry. The characteristics and effects of natural dyes are relatively poorly investigated. The latest researches point to healthy effects of natural dyes, above all those from the group of anthocyanins and carotenoids, since they are supposed to function as antioxidants protecting cells from injuries. They are very interesting for the dyeing of textiles from natural fibres; however, due to the complicated and longer procedures of preparation, limited colour shades and higher prices in the industry, they did not win recognition [1, 2]. After a few years of decreased interest, the researches in the field of textile dyeing with natural dyes are once again becoming more feasible, above all they aim at the studying of the use of natural dyes in the dyeing of textiles from different sources, also from the waste products in the food industry [3]. Furthermore, the researchers are directed towards the study of the effects of pretreatment processes with various metal salts using various natural dyes, both on the colouring shades as well as on their resilience to the washing and UV radiation [2–4]. Apart from other positive effects, the colouring with individual natural dyes is a prospective outlook towards the functionalization of textiles as a protection against harmful UV radiation [5, 6] and in some cases, to obtain antimicrobial effects [6].

1.1 Natural dyes and ultraviolet radiation

Ultraviolet (UV) radiation is a part of optical radiation and covers the wavelength region 100–380 nm [7]. One quant corresponds to the energy from 2.5—12.5 eV. The UV ranges are presented in Table 1. The most energetic UV range is the so called "Schumann UV" or "vacuum UV", which is strongly absorbed in

tocianov in karotenoidov, saj naj bi delovala kot antioksidanti ter tako varovala celice pred poškodbami.
Zelo zanimiva so za barvanje tekstilij iz naravnih vlaken, vendar pa se zaradi zapletenih in daljših postopkov priprave, omejene palete barvnih tonov in višje cene v industriji niso uveljavila [1, 2]. Po nekajletnem zmanjšanem zanimanju postajajo raziskave na področju barvanja tekstilij z naravnimi barvili zopet čedalje bolj aktualne, predvsem so osredinjene na proučevanje uporabe naravnih barvil za barvanje tekstilij iz različnih virov, tudi iz odpadkov živilske industrije [3]. Nadalje so raziskave usmerjene na proučevanje vpliva predobdelave tkanin z različnimi kovinskimi solmi na obarvanja z uporabo različnih naravnih barvil, na odtenke obarvanj in na njihovo obstojnost na pranje in UV-sevanje [2–4].
Poleg drugih pozitivnih učinkov so obarvanja s posameznimi naravnimi barvili perspektivna za funkcionalizacijo tekstilij kot zaščito pred škodljivim UV-sevanjem [5, 6] in v nekaterih primerih za dosego protimikrobnih učinkov [6].

1.1 Naravna barvila in ultravijolično sevanje

Ultravijolično sevanje (UV) je del optičnega valovanja z valovno dolžino med 100 ter 380 nm [7]. Energija enega kvanta je enaka 2.5 do 12.5 eV. UV-območja so prikazana v preglednici 1. UV z največjo energijo, tako imenovano „Schumann UV" ali „vacuum UV", se močno absorbira v atmosferskih plinih. Ta sevanja imajo na Zemlji malo vpliva, prava moč se pokaže šele v odprtem vesolju. Najpomembnejši naravni vir UV je sonce, ki proizvaja cel spekter UV-sevanja. Ozonski plašč absorbira večino UV-C-sevanja tako, da na zemeljsko skorjo večinoma prodirata UV-B ter UV-A. Tanjšanje ozonskega plašča posledično vodi do manjše zaščite pred kratkovalovnim sevanjem. Tako lahko večja količina tega sevanja prodre na Zemljo, kar povzroča poškodbe celic živih organizmov.

Table 1: UV ranges [7]

Wavelength of UV ranges		
Wavelength (nm)	*Quants of energy (eV)*	*Name*
100–200	*12.5–6*	*vacuum UV, Schumann UV*
200–280	*6–4.4*	*UV-C*
280–315	*4.4–4*	*UV-B*
315–380	*4–3.3*	*UV-A*

Ultravijolično sevanje je pomemben naravni mutagen. Vpliv UV--sevanja na organske spojine je lahko kompleksen, saj je ponavadi prisotnih več različnih kemijskih molekul, prav tako posamezne kemijske vezi povzročijo različno absorpcijo UV-sevanja. Najbolj *the atmospheric gases. It has only a small influence on the Earth, while its true significance is in space. The most important natural source of UV radiation is the sun, which emits UV radiation over the whole spectral range. The ozone layer absorbs most of the UV-C radiation, thus only the UV-B and UV-A radiation seems to be of importance. The thinning of the ozone layer leads to a reduced protection against shortwave radiation. Consequently, a larger amount of harmful solar radiation reaches the Earth, causing damages to the cells of living organisms.*

UV radiation is an important natural mutagen. Its influence on organic compounds can be complex, since many various chemical molecules are usually present. Moreover, each chemical bond absorbs UV radiation differently. Carbon compounds which include π-electron systems are the most susceptible to the UV absorption. The π-electron system in natural organisms has the most significant protective function [8].

Textiles can also offer protection against UV radiation. Their protective ability depends on their chemical structure and structural parameters (porosity, mass per unit area, thickness, production process). Also the presence of dyes, pigments and other auxiliary agents, reducing or blocking the harmful UV radiation in the wave range 290–400, influence the protection against UV radiation [5, 6, 9].

UV radiation also affects dyed fabrics or products. It can be seen from the literature that the colourfastness of natural dyes to UV radiation depends on several factors, i.e. chemical structure, physical state, dye concentration, fibre type, mordant type, light source, exposure conditions and the presence of other substances on textiles. Natural dyes from the flavonoids group are much less resistant to UV radiation than the natural dyes from the anthraquinones and indigoids group [10].

1.2 Chemical structure of chosen natural dyes

Natural dyes are colouring matters that are produced in the cells of living organisms. They can be divided into five main groups, i.e. quinone derivatives, pyrrole derivatives, pyran de-

dovzetne za UV-absorpcijo so ogljikove spojine, ki vsebujejo π elektronske sisteme. Prav π elektronski sistem ima najpomembnejšo funkcijo zaščite pri naravnih organizmih [8].

Zaščito pred UV-sevanjem lahko dajejo tudi tekstilije, kakovost zaščite pa je odvisna tako od njihove kemične sestave kot tudi od strukturnih parametrov (poroznosti, mase, debeline in proizvodnega procesa). Zaščita pred UV-sevanjem je odvisna tudi od prisotnosti barvil, pigmentov in drugih pomožnih snovi, ki imajo možnost zmanjšanja ali blokiranja škodljivega UV-sevanja v območju 290–400 nm [5, 6, 9].

UV-sevanje negativno vpliva tudi na obarvane tkanine oz. izdelke. Iz literature je razvidno, da je obstojnost naravnih barvil na UV-sevanje odvisna od več dejavnikov: kemične strukture, fizikalnega stanja, koncentracije barvila, vrste vlaken, kovinskih soli, vira svetlobe, pogojev izpostavitve in prisotnosti drugih substanc na tekstilijah. Naravna barvila iz skupine flavonoidov so v primerjavi z barvili iz skupin antrakinonov in indigolov veliko slabše obstojne na UV-sevanje [10].

1.2 Kemijska struktura izbranih naravnih barvil

Naravna barvila so barvilne snovi, ki nastajajo v celicah živega organizma. Delimo jih na pet glavnih skupin: derivati kinona, derivati pirola, derivati izoprena, derivati pirana in derivati pirimidina [11]. V raziskavi smo se osredotočili na skupine naravnih barvil, ki so jih ljudje najpogosteje uporabljali.

Rdeča pesa (*Beta vulgaris*) vsebuje naravno barvilo betalain. Betalaini so vodotopni pigmenti, ki vsebujejo dušik in jih uvrščamo v skupino derivatov pirola [12, 13]. Njihove vodne raztopine ob spremembi pH-vrednosti spreminjajo barvo, zato jih uporabljamo kot naravne pH-indikatorje. Zanje so značilni rumeno-oranžni barvni toni, če so prisotni betaksantini ali močni rdeče-vijoličasti barvni toni, v primeru betacianinov, med katerimi je najbolj navaden betanin (slika 1). Ta je v največjem deležu prisoten v rdeči pesi, delež vsebnosti drugih barvil iz skupine batalainov je odvisen od vrste rdeče pese.

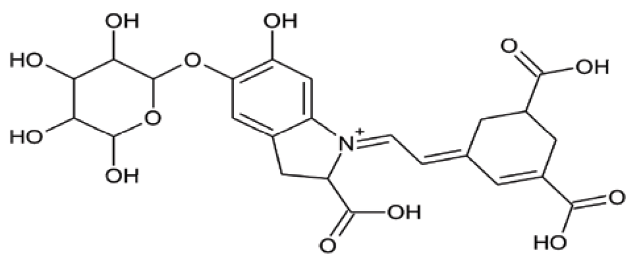

Figure 1: Structural formula of betanin [11]

Rdeče zelje (*Brassica oleracea*)**, črni ribez** (*Ribes nigrum*)**, čebula** (*Allium cepa*) in **hibiskus** (*Hibiscus*) vsebujejo naravna barvila iz skupine antocianidinov, ki so najobsežnejša skupina flavonoidov in jih uvrščamo med derivate pirana. Flavonoide kot vodoto-

rivatives and pyrimidine derivatives [11]. The research focuses on those natural dyes which have been in use most frequently.

Red beet (Beta vulgaris) contains the natural dye betalain. Betalains are water-soluble dyes that contain nitrogen and are classified as pyrrole derivatives [12, 13]. Their water solutions change the colour when the pH changes; therefore, they are used as natural pH indicators. They usually appear in yellow-orange colour shades in the presence of betaxanthins and in red-violet colour shades in the presence of betacyanins, the most common being betanin (cf. Figure 1). The latter occurs most naturally in red beet. The percentage of other compounds from the betalain group depends on the cultivar of red beet.

Red cabbage (Brassica oleracea), black currant (Ribes nigrum), onions (Allium cepa) and hibiscus (Hibiscus) contain natural dyes from anthocyanidins, which represent the largest group of flavonoids and are classified as pyran derivatives. Flavonoids as water-soluble dyes in strong yellow, red, violet and blue colours mainly appear in plant flowers and fruits. Anthocyanidins strongly absorb light in the visible spectral range. Various colours of particular anthocyanidin dyes are a result of a double bond and hydroxyl group shifts on the main structure. The basic chemical structure of anthocyanins is presented in Figure 2.

Black currant contains a mixture of anthocyanins, more specifically cyanidin and delphinidin (cf. Figure 3) or their derivatives. Among them, delphinidin-3-glucoside is prevailing. The black currant extract gives blue-violet to violet colour shades [12, 14].

Hibiscus flowers contain malvidin, which is one of the delphinidin derivatives and is classified as anthocyanidin. The chemical structure of malvidin is presented in Figure 4. While this dye is less soluble in water, it is completely soluble in ethanol.

Researches showed that red cabbage contains a mixture of natural dyes from the flavonoid group, with anthocyanins prevailing, mainly malvidin derivatives (cf. Figure 4), malvidin-5-glucoside and malvidin 3,5-diglucoside [15].

Onion skin contains a mixture of flavonols and anthocyanins, the most important being

pna barvila močnih rumenih, rdečih, vijoličastih in modrih barv najdemo zlasti v cvetovih in plodovih rastlin. Antocianidini močno absorbirajo svetlobo v vidnem delu spektra. Različne barve posameznih antocianidinskih barvil so posledica zamenjav dvojnih vezi in hidroksilnih skupin na osnovnem skeletu. Osnovna kemijska struktura antocianov je prikazana na sliki 2.

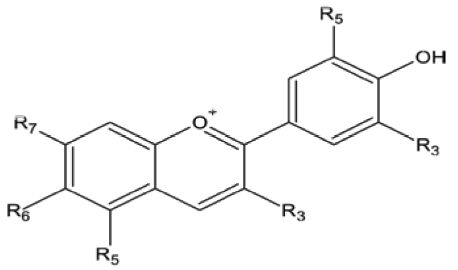

Figure 2: Structural formula of anthocyan [11]

Črni ribez vsebuje mešanico antocianinov, in sicer cianidin in delfinidin (slika 3), oziroma njune derivate. Delfinidin-3-glukozid med njimi prevladuje. Z ekstraktom črnega ribeza dobimo modro-vijoličaste do vijoličaste barvne tone [12, 14].

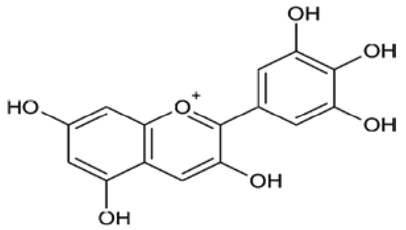

Figure 3: Structural formula of delphynidin [12]

Cvetovi hibiskusa vsebujejo barvilo malvidin, ki spada v skupino antocianov in je eden od derivatov delfinidina. Kemijska struktura malvidina je prikazana na sliki 4. Barvilo je slabo topno v vodi, popolnoma pa v čistem etanolu.

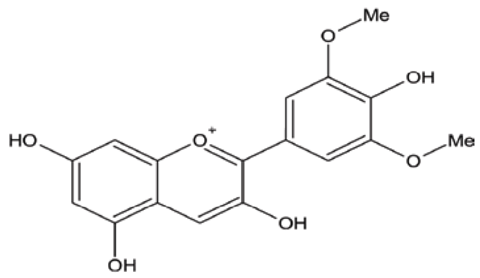

Figure 4: Structural formula of malvidin [11]

Raziskave so pokazale, da rdeče zelje vsebuje mešanico naravnih barvil iz skupine flavonoidov, prevladujejo pa antociani, predvsem derivati malvidina (slika 4), malvidin 5-glukozid in malvidin 3,5-diglukozid [15].

quercetin derivatives [16]. One of them is also quercitrin, which is shown in Figure 5. With onion skin extracts, yellow to yellow-red colour shades can be obtained.

Flowers of safflower (Carthamus tinctorius) can appear in yellow, orange or red colours. Safflower is highly valued in cooking as it can be used for the colouring of different foods as a cheaper substitute for saffron. It is also used in the dyeing of textile fibres, especially natural fibres, gaining various colour shades from yellow, orange, red to olive green. The flowers of safflower contain 0.3–0.6% of red dye – Carthamin, also known as C.I. Natural Red 26 and 25–30% of yellow dye (C.I. Natural Yellow 5) [12]. Carthamin natural dye, the structural formula of which is presented in Figure 6, is classified as a quinone derivative.

Researches that include the investigation of the effect of time of the UV radiation exposure on the changes in the colourings with natural dyes are rare. Therefore, the goal of the research was a colorimetric evaluation of the change in the colourings of a fabric dyed with chosen natural dyes after different exposure times.

2 Experimental

2.1 Fabric

For dyeing, a bleached cotton fabric was used in atlas weave with 295 g/m² mass per unit area and density of 40 threads/cm in warp and 30 threads/cm in weft direction.

2.2 Mordanting process

Mordanting was performed with the exhaustion process with the addition of $KAl(SO_4)_2 \times 12\ H_2O$ (50 g/l) at boiling for 5 min and the liquor ratio 1 : 20.

2.3 Dyeing

In this study, we used 6 different natural dye extracts from safflower (Carthamus tinctorius, Sample A), onion (Allium cepa, Sample B), hibiscus (Hibiscus, Sample C), black currant (Ribes nigrum, Sample D), red beet (Beta vulgaris, Sample E) and red cabbage (Brassica oleracea, Sample F). The dyeing baths were prepared from natural juices with 65% of fruit content (Samples D, E and F) and from the ex-

Čebulni olupki vsebujejo mešanico flavonolov in antocianov, med katerimi so najpomembnejši derivati kvercetina [16]. Eden od njih je tudi kvercitrin, ki je prikazan na sliki 5. Z ekstraktom iz čebulnih olupkov dobimo rumene do rumeno rdeče barvne tone.

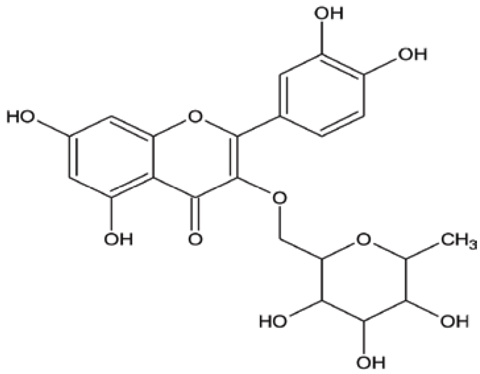

Figure 5: Structural formula of quercitrin [11]

Cvetovi **žafranike** (*Carthamus tinctorius*) so lahko rumenih, oranžnih ali rdečih barv. Žafranika je zelo cenjena v kulinariki, saj z njo obarvamo različne jedi in nadomešča uporabo dražjega žafrana. Uporablja se tudi za barvanje tekstilnih vlaken, predvsem je bolj primerna za barvanje naravnih vlaken, pri čemer lahko dobimo različne barvne tone od rumenega, oranžnega, rdečega pa do olivno zelenega. Cvetovi žafranike vsebujejo 0,3–0,6 % rdečega barvila – Carthamin, znanega tudi kot C.I. Natural Red 26 in 25–30 % rumenega barvila (C.I. Natural Yellow 5) [12]. Naravno barvilo kartamin, katerega strukturna formula je prikazana na sliki 6, spada v skupino derivatov kinona.

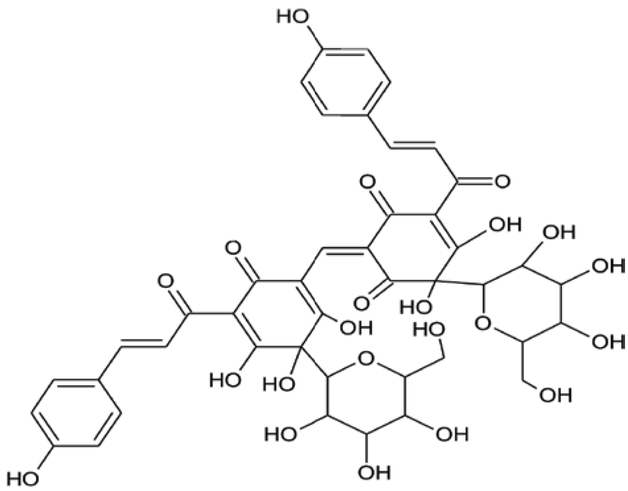

Figure 6: Structural formula of carthamin [12]

Raziskave, ki vključujejo spremljanje vpliva časa izpostavljenosti UV-sevanju na spremembo obarvanj z naravnimi barvili, so redke, zato je bilo cilj raziskave barvnometrično vrednotenje sprememb *tracts of dried materials (Samples A, B and C). The latter were prepared with the boiling of 0.5 g of dry mass in 200 ml of distilled water.*

The dyeing baths prepared in this way were heated to boiling. Afterwards, the soaked and wrung out textile fabrics were put inside. The dyeing was performed in a beaker with the exhaustion process at boiling for 15 min and the liquor ratio 1: 20. During the dyeing, we were constantly stirring the dyeing baths. After the dyeing, the textiles were wrung out and air dried, followed by ironing.

2.4 Illumination of samples

Two parallels of dyed cotton samples were illuminated in the apparatus Xenotest Alpha (Atlas, USA) according to the SIST ISO 105-B02 standard. The light source represents an air-cooled xenon lamp with an output of radiation 0.8–2.5 kVA and the area of UV radiation above 320 nm (using filter Xenochrome 320), which simulates the operation of sunlight behind the window glass. The samples with 4.5 × 13 cm in size were inserted into the chamber where a constant temperature of 35 °C and 70% relative humidity were established. After 2, 4, 6, 9, 12, 14, 16 and 22 hours of exposure to illumination, the samples were evaluated colorimetrically.

2.5 Colorimetric evaluation of colourings

The difference in the colour of textile samples before and after the artificial illumination was determined with a two-ray spectrophotometer Spectraflash 600 PLUS-CT (Datacolor, Switzerland). In accordance with the EN-ISO 105-J01 standard, the instrument gives the sample reflection values in a visible range on the basis of the relationship between the incoming light and the light reflected from the sample. The measurements were performed under the following conditions: aperture size 9 mm, standard light D65, standard observer 10°, number of sample layers 4. Each sample was measured 5 times.

The total colour difference, ΔE^*_{ab}, was calculated from the differences in coordinates in all three directions of the CIELAB colour space according to Equation 1 [17].

obarvanj tkanin z izbranimi naravnimi barvili po različnih časih izpostavljenosti UV-sevanju.

2 Eksperimentalni del

2.1 Tkanina

Za barvanje smo uporabili beljeno bombažno tkanino v vezavi atlas, ploščinske mase 295 g/m^2 in gostote 40 niti/cm po osnovi in 30 niti/cm po votku.

2.2 Postopek predobdelave s kovinskimi solmi

Predobdelavo smo izvedli po izčrpalnem postopku s $KAl(SO_4)_2 \times 12\ H_2O$ (50g/l) pri vrenju 5 min in kopelnem razmerju 1 : 20.

2.3 Barvanje

V raziskavi smo uporabili šest različnih naravnih ekstraktov barvil iz žafranike (*Carthamus tinctorius*, vzorec A), čebule (*Allium cepa*, vzorec B), hibiskusa (*Hibiscus*, vzorec C), črnega ribeza (*Ribes nigrum*, vzorec D), rdeče pese (*Beta vulgaris*, vzorec E) in rdečega zelja (*Brassica oleracea*, vzorec F). Barvalne kopeli smo pripravili iz naravnih sokov s 65-odstotnim sadnim deležem (vzorci D, E in F) in iz ekstraktov suhih snovi (vzorci A, B in C). Le-te smo pripravili tako, da smo 0,5 g suhe mase snovi prekuhali v 200 ml destilirane vode.

Tako pripravljene barvalne kopeli smo segreli do vrenja. Vanje smo vložili omočene in ožete tkanine in jih nato barvali po izčrpalnem postopku v čaši med vrenjem 15 min in kopelnem razmerju 1 : 20. Med barvanjem smo barvalne kopeli ves čas mešali. Po končanem barvanju smo tkanine oželi in posušili na zraku. Sušenju pobarvanih vzorcev na zraku je sledilo likanje.

2.4 Osvetljevanje vzorcev

Po dve paralelki pobarvanih bombažnih vzorcev smo osvetljevali v aparatu Xenotest Alpha (Atlas, ZDA) v skladu s standardom SIST ISO 105-B02. Svetlobni vir je zračno hlajena ksenonska žarnica z močjo sevanja 0,8–2,5 kVA z območjem UV-sevanja nad 320 nm (uporabljeni filter Xenocrome 320), ki ponazarja delovanje sončeve svetlobe za okenskim steklom. Vzorce z velikostjo 4,5 × 13 cm smo vstavili v komoro ter v njej vzpostavili stalno temperaturo 35 °C in 70-odstotno relativno vlažnost. Po 2, 4, 6, 9, 12, 14, 16 in 22 urah smo osvetljevane vzorce tudi barvnometrično ovrednotili.

2.5 Barvnometrično vrednotenje obarvanj

Razliko v barvi vzorcev tkanine pred umetnim osvetljevanjem in po njem smo določili z dvožarkovnim spektrofotometrom Spectaflash 600 PLUS-CT (Datacolor, Švica). Instrument v skladu s standardom EN-ISO 105-J01 poda refleksijske vrednosti vzorca v vidnem območju na podlagi razmerja med vpadlo svetlobo in svetlobo, odbito od vzorca. Meritve smo opravljali pri naslednjih po-

The differences between the sample, V, and standard, S, were calculated using Equations 2–4. A non-illuminated dyed fabric was used as the standard.

3 Results and discussion

Table 2 presents the CIELAB values of dyed samples before and after the illumination. By applying the dyes from safflower and onion onto a cotton fabric, yellow hues were obtained. The dyes from hibiscus gave a light violet colour, those from red beet and black currant a red-violet colour and those from red cabbage a blue-violet hue.

3.1 Lightness, L*, of dyed fabrics after illumination

Figure 7 presents the values of lightness, L, after different illumination times for the dyed samples. Before the exposure to light, the highest values of lightness were measured on Sample A, dyed with safflower, and the lowest on Sample F, dyed with red cabbage (cf. Table 2). After 22 hours of illumination, the fabrics dyed with safflower (Sample A) reached the highest value of lightness among all samples, despite the fact that the lightness increased only by 2.07 units.*

gojih: velikost merilne odprtine 9 mm, standardna svetloba D_{65}, 10° standardni opazovalec, število plasti vzorca: 4. Na vsakem vzorcu smo opravili pet meritev.
Celotno barvno razliko, ΔE^*_{ab}, smo izračunali iz razlik koordinat v vseh treh smereh barvnega prostora CIELAB po enačbi 1 [17].

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (1)$$

Razlike med vzorcem, V, in standardom, S, smo izračunali po enačbah od 2 do 4. Standard je bila neosvetljena obarvana tkanina.

$$\Delta L^* = L^*_B - L^*_S \qquad (2)$$

$$\Delta a^* = a^*_B - a^*_S \qquad (3)$$

$$\Delta b^* = b^*_B - b^*_S \qquad (4)$$

3 Rezultati in razprava

V preglednici 2 so zbrane vrednosti CIELAB koordinat obarvanih vzorcev pred osvetljevanjem. Z barvili iz žafranike in čebule smo na uporabljeni bombažni tkanini dobili rumeno obarvanje, z barvili iz hibiskusa svetlo vijoličasto obarvanje, iz rdeče pese in črnega ribeza rdeče vijoličasto obarvanje in iz rdečega zelja modro vijoličasto obarvanje.

3.1 Svetlost, L*, obarvanih tkanin po osvetljevanju

Table 2: Measured values of L^*, a^*, b^*, C^*_{ab} and h_{ab} of dyed samples

Origin of dyes	L^*	a^*	b^*	C^*_{ab}	h_{ab} (°)
Safflower (A)	89.92	–2.39	17.37	17.53	97.89
Onion (B)	86.03	0.09	26.80	26.80	89.84
Hibiscus (C)	72.59	4.46	–6.69	8.04	303.71
Black currant (D)	69.77	12.54	–5.19	13.57	337.51
Red beet (E)	74.16	17.08	–4.93	17.78	343.90
Red cabbage (F)	52.63	5.19	–23.85	24.41	282.29

The results also show that after 22 hours of exposure, the increase in lightness was the most evident on Sample F, dyed with red cabbage, as the lightness of this sample increased by 23.53 units. Nevertheless, the lightness of this sample remained the lowest.
For the fabrics dyed with hibiscus (Sample C), black currant (Sample D) and red beet (Sam-

Na sliki 7 so prikazane vrednosti L^* po različnih časovnih obdobjih osvetljevanja obarvanih vzorcev. Najvišje vrednosti svetlosti smo pred osvetljevanjem izmerili na vzorcu A, obarvanem z žafraniko in najnižje vrednosti pri vzorcu F, obarvanem z rdečim zeljem (preglednica 2). Po 22 urah osvetljevanja je tkanina, obarvana z žafraniko (vzorec A), dosegla največjo svetlost, ki se je spremenila samo za 2,07 enote. Iz rezultatov je tudi razvidno, da je tkanina, obarvana z rdečim zeljem (vzorec F), po 22 urah dosegla najnižjo *ple E), the highest increase in lightness was observed during the first six hours of illumination. Afterwards, it was increasing more slowly.*

3.2 Chroma, C*ab, of dyed fabrics after illumination

The most intensive colour and the highest values of chroma were reached with the dyes obtained from onion (Sample B) and red cabbage (Sample F). The lowest values were measured on Sample C, dyed with hibiscus (cf. Figure 8).

After the exposure to light, the values C^*_{ab} decrease and the colour becomes less intensive on all samples, which is in accordance with our expectations. The most evident changes appear already after 2 or 5 hours. It is evident (cf. Figure 8) that after two hours of illumination, the decrease in chroma is especially obvious on yellow samples (Sample A – safflower and Sample B – onion), followed by Sample E (red beet), C (hibiscus), D (black currant) and F (red cabbage).

After 22 hours of illumination, the biggest difference in chroma was found on Sample F (red cabbage) as it exceeded 20 units, followed by Samples B, A, E and D. The smallest change in chroma was measured on Sample C (hibiscus), which gave at the beginning the least intensive colour.

3.3 Change in hue after illumination

Figure 9 presents the change in values a and b* on the samples during the process of illumination. The direction of change is presented with arrows.*

The biggest change in hue appeared on Samples E (red beet) and F (red cabbage), and the smallest on Sample A (safflower). The most evident change in hue appeared already after two hours of illumination. Very similar changes were observed on the samples dyed with red beet (E) and black currant (D). Both of them gradually lost their red-blue hue and gained a yellowish one.

Samples A (safflower) and B (onion) lost their yellow hue during the illumination and became very neutral in colour.

vrednost L^* in da je pri tem vzorcu povečanje svetlosti najbolj izrazito, saj se je vrednost L^* povečala kar za 23,53 enote. Pri tkaninah, obarvanih s hibiskusom (vzorec C), črnim ribezom (vzorec D) in rdečo peso (vzorec E), se svetlost bolj povečuje v prvih šestih urah, nato pa narašča počasneje.

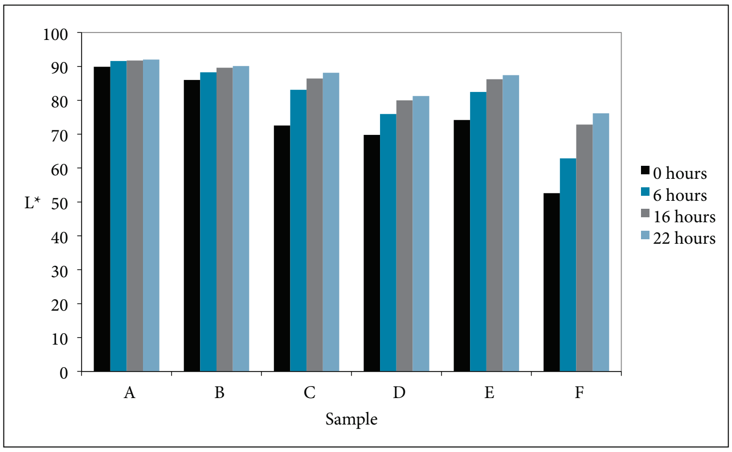

Figure 7: Lightness, L, of dyed samples after different illumination times*

3.2 Kroma, C^*_{ab}, obarvanih tkanin po osvetljevanju

Najbolj izrazito obarvanje smo dobili z barvili iz čebule (vzorec B) in rdečega zelja (vzorec F) in najmanjše z barvili iz hibiskusa (vzorec C) (slika 8). Z osvetljevanjem se vrednosti C^*_{ab} znižujejo in barve vzorcev v vseh primerih postanejo manj nasičene, kar je bilo skladno z našimi pričakovanji. Največje spremembe so opazne že po dveh (petih) urah. Iz slike 8 je tudi razvidno, da se je že po dveh urah najbolj spremenila nasičenost pri vzorcih A in B, obarvanih z barvili iz žafranike oziroma čebule, torej pri rumenih vzorcih, sledijo vzorec E (rdeča pesa), vzorec C (hibiskus), vzorec D (črni ribez) in vzorec F (rdeče zelje). Največja razlika v nasičenosti bar-

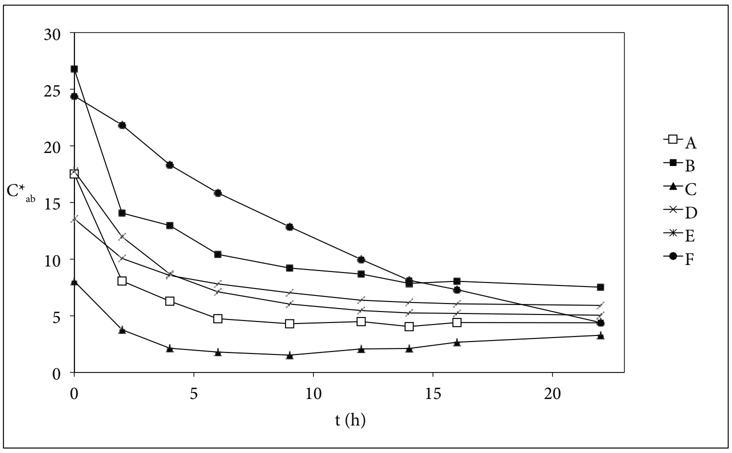

Figure 8: Chroma, C^*_{ab}, of dyed samples in dependence of time, t

3.4 Total colour difference after illumination

According to the results (Figure 10), UV radiation caused the most evident changes on Sample F, dyed with red cabbage, as it reached the highest values of ΔE^*_{ab}. The smallest differences after the illumination were measured on Sample A (safflower). The differences are expressed mostly as the changes in b (Samples A and B) and a* (Sample E) values showing a relatively big change in hue. At other samples (C, D, F), the colour difference was expressed mostly as an increase in lightness.*

4 Conclusions

As expected, already a short-term exposure of dyed cotton samples to UV radiation has a significant impact on the change in the CIELAB values of the colourings with selected natural dyes. The study showed that among all the selected natural dyes, UV radiation has the smallest influence on the total colour difference of the dye from quinone derivatives, which is present in safflower. Therefore, this dye is the most resistant to UV radiation compared to other dyes from the groups of pyrrole derivatives, present in red beet, and pyran derivatives, present in onions, hibiscus, black currant and red cabbage.

Note

The study was conducted within the final project work by the students from the University of Ljubljana, Faculty of Education, chemistry and biology programme, during the course Methodology of Chemical Education.

ve se je po 22 urah pokazala pri vzorcu F, kjer je nastala razlika v nasičenosti, ΔC^*_{ab}, za 20,01 enote, sledijo vzorci B, A, E, D in najmanjša pri vzorcu C, s katerim smo dosegli sicer najmanj izrazito obarvanje.

3.3 Sprememba barvnega tona po osvetljevanju

Na sliki 9 je prikazan potek spremembe vrednosti *a** in *b** od začetka do konca osvetljevanja, kar je prikazano s puščicami. Največje spremembe barvnega tona so razvidne pri vzorcih E (rdeča pesa) in F (rdeče zelje), najmanjše pa pri vzorcu A (žafranika). Pri vseh vzorcih je največja sprememba vidna že po dveh urah osvetljevanja. Zelo podobne so spremembe pri vzorcih, obarvanih z barvili iz rdeče pese (vzorec E) in črnega ribeza (vzorec D), oba izgubljata rdeče modri odtenek in pridobivata rumenega. Vzorca A (žafranika) in B (čebula) izgubljata rumeni odtenek in sčasoma postaneta neizrazito obarvana.

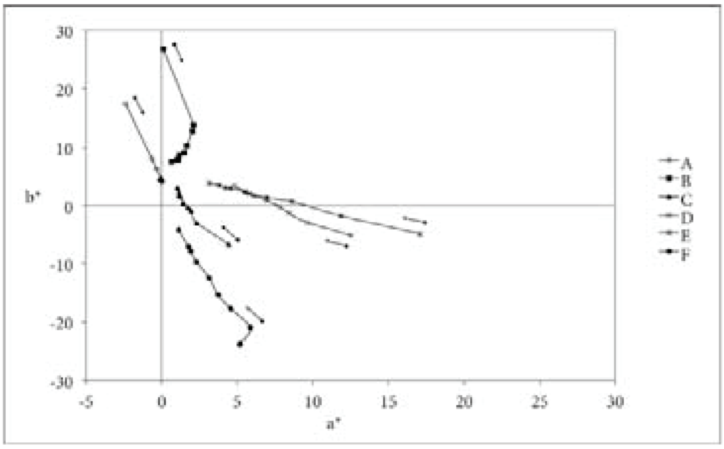

Figure 9: Values a and b* of dyed samples after different illumination times (2, 4, 6, 9, 12, 14, 16 and 22 hours)*

3.4 Celotna barvna razlika po osvetljevanju

Iz slike 10 je razvidno, da je osvetljevanje najbolj vplivalo na obarvanje z rdečim zeljem (vzorec F) in najmanj na obarvanje z žafraniko (vzorec A). Največji delež k vrednosti ΔE^*_{ab} pri obarvanjih z žafraniko in čebulo (vzorca A in B) prispeva sprememba v vrednosti *b** ter pri obarvanjih z rdečo peso (vzorec E) vrednost *a**, torej gre v teh primerih za razmeroma veliko spremembo barvnega tona. Pri preostalih vzorcih (C, D in F) pa se barvna razlika pretežno odraža kot povečanje svetlosti obarvanih vzorcev.

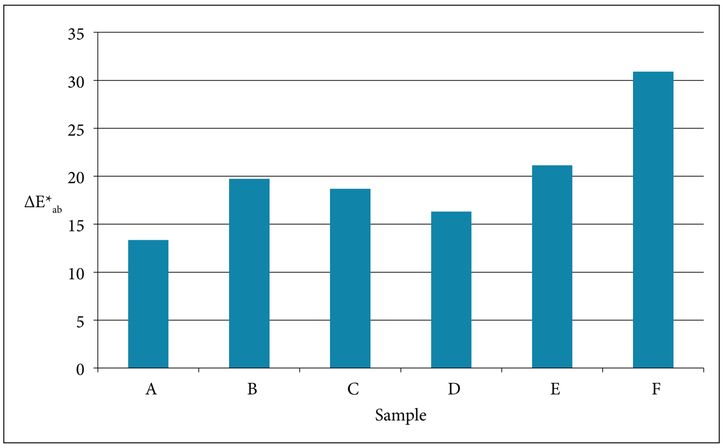

Figure 10: Total colour difference, ΔE^*_{ab}, of dyed samples after 22 hours of illumination

4 Sklepi

Po pričakovanjih že kratek čas izpostavljenosti pobarvanih bombažnih vzorcev UV-sevanju močno vpliva na spremembo CIELAB vrednosti obarvanj z izbranimi naravnimi barvili. Raziskava je pokazala, da med izbranimi naravnimi barvili UV-sevanje najmanj vpliva na spremembo celotne barvne razlike barvila iz skupine derivatov kinona, ki je prisotno v žafraniki, kar pomeni, da so najbolj obstojna na UV-sevanje v primerjavi z drugimi barvili iz skupin derivatov pirola, prisotnih v rdeči pesi, in derivatov pirana, prisotnih v čebuli, hibiskusu, črnem ribezu in rdečem zelju.

Opomba

Raziskava je bila narejena v okviru sklepnega projektnega dela študentov Pedagoške fakultete, smeri kemija-biologija, pri predmetu Metodologija kemijskega izobraževanja.

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