**18 Natural Dyes**

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**18.1 Natural dyes in human history**

Natural dyes (in the text: NatD) from plants, animal (less often) and mineral resources, has long been used for dyeing of textile, leather, body, hair, for cosmetic purposes and craft as well as food colourings. It is not a coincidence that many of dye plants and colour pigments have been also used in witchcraft and religious ceremonies: dyeing is not far from magic, and some of the original secrets of alchemy are in fact recipes for dyes.

***Prehistory***

The beautiful and mystical paintings on the walls of caves that have been preserved for example in Lascaux (France) and Altamira (Spain), suggest that the use of natural dyes accompanied humans almost all of their history. The carbon from ash and clay is a coloured mineral pigment that survived many thousands of years. We can assume that creators of these cave paintings (prehistoric people of the Younger Palaeolithic period) were already sufficiently inventive in the utilization of natural resources for artistic purposes. They probably have decorated their bodies, hair, clothes and tools of daily use with dyes that nature offered them, similar to what to this day the indigenous peoples in Africa, New Guinea and the Amazon Rainforest.

***Antiquity***

Antiquity was a time when the use of NatD was a highly developed art, and the shreds of coloured fabrics found in the tombs of ancient Egyptians, Greeks and Romans are proof of that. The analysis of these fabrics confirmed the use of plants such as weld (*Reseda*), saffron (*Crocus*), buckthorn (*Frangula*) or safflower (*Carthamus*) and use of mineral pigments (like hematite, limonite, copper sulfate, ochre). The use of mordants, especially alum and tartar, is also known since ancient times. Prehistoric discoveries of textiles in Europe document for example the use of alizarin, purpurin, and indigo from the 4th century BC. This indicates the cultivation of madder and import of indigo or local use of woad (*Isatis tinctoria*) because same dyes were identified already about 800 years earlier in the Late Bronze Age on textiles found in graves in the Chinese Yanghai. [1]

***The Middle Ages***

The Middle Ages can be described as the golden age of natural dyeing. Not only a great amount of clothing and tapestries that reflect rich variety of dyes with different stability survived from this period, but also literature documenting that textile dyeing has become a real art and specialisation of human activity. The book "*Secreti*" by Italian author Alessio Piemontese (1555) is sort of a collection of prescriptions and various manufacturing technologies including dyeing techniques. We learn here, for example, how to achieve blue colours on linen using the juice of blueberries or elderberry fruit with the addition of aluminum, copper or ferric salts.

Natural (and not only natural!) dyes whose appearance resembles vine anthocyanins attracted (and still attract today) dishonest people to colour diluted or light red wine. For this purpose served e.g. elderberry juice, carcinogenic synthetic azorubine or juice of beets. American pokeweed (*Phytolacca americana*)[2] is a plant native to North America, it is grown in Europe as a decorative plant. Its fruits contain a reddish/purple betalain pigment phytolaccanin and the original Indians in Virginia used it for dyeing of fur, leather and wicker products. Europeans began to use it for food colouring and especially adulteration of wine soon after the discovery of America. There are records preserved in Portugal showing that the quality of wine stained with juice from these fruits suffered so much, so that in the 17th century in France under Louis XIV. adding of pokeweed into wine was punished by death. [3] [4]

***Modern history***

The advancement of science cannot be stopped, so in the second half of the 19th century ends the golden age of natural dyes: the chemical industry started to produce their synthetic substitutes. Although it took some time before synthetic dyes in Europe and the United States almost completely pushed out the NatD (to the beginning of the 20th century). The causes of their boom were mainly brilliance, rich palette of colours, gradually lower cost, easier colouring and greater stability. Deep blue **pittacal** (hexamethylaurine) is considered to be a first synthetic dye, accidentally discovered by German chemist Carl Ludwig Reichenbach in 1834. In 1878 another German chemist, Adolf von Baeyer, synthesized the holy grail of dyers – indigo. It was not the only reason why he got in 1905 the Nobel Prize for Chemistry (aspirin), but certainly he would have deserved it even for this single discovery. After centuries of tumultuous history of indigo the import of indigo from Asia and its laborious obtaining from European woad could end.

NatD currently account for only about 1% of the total amount of dyes used worldwide. In many countries, the use of NatD has a strong tradition (eg. India, Turkey, Mexico, Morocco, countries of West Africa). Countries such as Mexico, India, China or Peru are among the largest exporters of NatD, but the interest in NatD is growing even in countries that have forgotten about that people there had dyed only with plants a long time ago (e.g. Czech Republic). It's caused by a general environmental awareness and the increase of public interest in natural products.

 Main sources of synthetic dyes are limited (oil, coal), the production of synthetic dyes pollutes the water and the environment by toxic wastes. On the other hand, sources of NatD are continually renewed in nature and therefore natural dyes evoke the idea that their production and use are clean, non-toxic, harmless and "eco-friendly".

The increasing demand for natural dyes is also reflected in the amount of scientific literature and growing number of scientific publications about NatD: the tradition is one thing, but when we begin to consider utilising NatD on the industrial scale, we find that it is actually necessary to solve a number of problems associated with their production and use.

**18.2 Principle of natural dyes sorption on fibres**

NatD are primarily suitable for dyeing of natural fibres (animal - wool, silk), it is more difficult to dye plant (cellulose) fibres (cotton, flax, jute). We can also dye some synthetic fibres with polar groups (polyamide, modified acrylic fibres or viscose and in some cases even polyester).

Mordanting is one of the reasons why we cannot say with clean conscience that dyeing with NatD is a totally eco-friendly technology. The molecular structure of most NatD is not ideal for interaction with fibres - nature did not create them for this purpose! They are often small molecules resembling the **disperse dyes** suitable for dyeing of synthetic fibres and only sparsely soluble in water. At the same time, they are also considerably thermolabile and chemically unstable, so typical progressive applications (thermosolation or bath dyeing exceeding 100 °C) are not possible.

Although the plant and animal fibres dyed with NatD (by applying the **weak binding interactions -** hydrogen bonds and van der Waals forces), but their sorption is low. This interaction is similar to spotting of wool or cotton by disperse dyes and exceptionally, although only slightly, their sorption can be increased by additions of a neutral electrolyte to the bath. They are not therefore substantive (direct) dyes, although some of them are similar to direct dyes, especially those with longer chains in the molecules (e.g. curcumin that dyes the fibres to bright-yellow colour).

The acidification of wool and silk usually does not help (except for several dyes having anionic groups). The **ionic interaction** typically occurs in dyeing of wool with betalains that act as acid dyes. They contain three carboxyl groups gradually dissociating with the increasing alkalisation of bath. This bond is the strongest at pH 5 where the wool is maximally protonated and simultaneously all three carboxyl groups of betalain are dissociated.

The indigo from indigofera or isatis and Tyrian purple are dyes applicable for dyeing of fibres after the conversion on reduced “leuco” form. They are soluble in the water only in this enol form and can dye cotton and wool fibres. They act as **vat dyes**.

However, in terms of dyeing classifications, most of the NatD resemble disperse dyes – theoretically corresponding to the sorption isotherm (*see Chapter 6 – Sorption systems*): the distribution of dye in the extract of eucalyptus leaves (with tannin as a main component) between the fibre and the bath (dyeing near of equilibration condition), behaves according to Nernst isotherm (**Fig.1**).

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| **Fig.1:** Sorption isothermes after 120 min of dyeing of silk fabric (unmordanted) with eucalyptus leavesextract (main substance: tannin, adjoined flavanoids) at 30, 60 and 90 °C [5] |

The weaker binding interactions and nonoptimal shapes of molecules exhibit low fastness and low exhaustion of NatD in comparison with the synthetic dyes that are optimised for interactions with fibres. Fortunately, a long time ago, ancient dyers came up with the ingenious invention: mordanting. It improves fastness, often also exhaustion, and additionally it makes desirable deepening and interesting spectral alternation of a colour. Therefore, dyeing with NatD is usually not possible without mordanting.

**18.3 Mordants**

**Mordants** are auxiliary dyeing substances that are able to form complexes with molecules of dyes. This results in increased exhaustion or low-affine dye from the bath and thus improving the colour-fastness. This particularly improves the wet fastness and sometimes the light fastness.

The complexes are formed by reaction with mordant salts where a metal ion exhausted into the fibre is simultaneously bound with dye by coordinate covalent bond and these complexes induce bathochromic and hyperchromic shift in the colour. Mordant may be applied before dyeing or as additional stabiliser of dye after dyeing or may be applied directly to the bath during dyeing. The problem is that most commonly used mordants are metal salts (e.g. sulfates or chlorides of iron, tin and copper, or even chromium and lead!) and often in concentrations up to 15 g/litre![6] [7] Indeed, here arises a paradox: improved stability and deeper colour of fabrics can often be achieved only at the cost of using a high concentration of metal salt.

Some authors of publications about natural dyeing have deliberately avoided this topic in the effort to emphasize the environmental friendliness and the health safety of NatD and therefore they often do not mention the concentrations of mordants at all.

With the use of metal salts it is possible to differentiate variants with different toxicity, burdening the environment more or less. Perhaps the most controversial is the use of lead salts and chromates (potassium, sodium or ammonium dichromate).

 Compounds of lead and hexavalent chromium are toxic and carcinogenic!

Traditional inorganic mordants include **alums** that are hydrated double sulphate salts, commonly found in nature. As "alum" is often called the hydrated aluminum potassium sulphate (KAl(SO4)2 **.**12 H2O). This substance has an astringent effect and therefore is used to stop bleeding after cutting during shaving or as the adjuvant in vaccines.

The chemical toxicity is expressed as the lethal dose for a particular organism. LD50 is the dose at which half of the test animals die. LD50 of alum for mouse, rat and rabbit is 300, 980 and 3200 mg / kg of body weight at peroral administration. [8]

Another mordant often used is **tin chloride** (SnCl2), it is a water-soluble inorganic substance with strong reducing effects.

 The tin chloride is harmful to health (acute toxicity: LD50 by oral dose is in mice 250 mg/kg, in rats 700 mg/kg, in rabbits 10 000 mg/kg [9]). Tin chloride induces in test animal’s changes of blood count, bone demineralisation, inflammations and organ damage. And yet it is used for food purposes (designation E512): it is allowed in the Czech Republic, other EU countries and in the US. It is used e.g. as an antioxidant in beverages with carbon dioxide or in the preservation of asparagus. In the Czech Republic its use is permitted by the Decree No.4/2008 Coll. (annex 2). [10]

**Copper sulphate** (or its pentahydrate – blue vitriol, CuSO4 . 5H2O) andferrous sulfate (heptahydrate - green vitriol, FeSO4 .7H2O) are also often used as mordants. They easily form coordination complexes with dyes. The coordination number of copper sulphate and ferrous sulphate are 4 and 6, so some of the coordination places remain unoccupied in the interaction with fibre. Therefore, functional groups of dye, such as amino or carboxy groups can occupy these places. This means that metal can finally create a ternary complex in which metal binds with fibre and dye.

The boundary between mordant and dye is not always clear because mordants themselves can also be a source of fibres colour and in conjunction with dyes can greatly affect shifts of final hues; a plant itself can be a source of mordants in addition to dyes. These are the various kinds of vegetable **tannins** that are polyphenolic substances able to form complexes with metals and to bind with organic substances (proteins, alkaloids, hormones, carbohydrates, etc.) by a number of hydrogen bonds. Furthermore, there are so-called biomordant resources - plants with hyper accumulation of metals. There are many varieties of tropical trees and shrubs of the genus *Symplocos* containing alum (aluminum potassium sulphate), and these trees are used in folk medicine as well as in textile dyeing. [8]

**Tannins** (natural or synthetic) can be used as mordants, either alone or in collaboration with metal salts. The phenolic groups of tannins can form effective bonds with different types of fibres and dyes, and thus help in the fixation of dyes. Mordants based on tannin found their use in dyeing of cellulose fibres, especially in dyeing of cotton that has a very low affinity to most NatD. The classic method is two-phase, a fabric is soaked with tannins, then metal salts are applied, this is followed by dyeing. First tannin gets into fibres and subsequent application of metal salts leads to the formation of complexes (**Fig.2**), and it stabilises tannin on textile material. Subsequently, a natural dye is bound to the fibre through tannin with higher affinity.

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| **Fig.2:** Formation of complexes of o-phenolic groups with metal ions |

When dyeing with plant extracts, various forms of tannins present in the dye mixtures are often fundamentally involved in the resulting colour (**Fig.3**).

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| **Fig.3:** Exhaustion of tannins on cotton (CO), polyamide (PA) and wool (WO) fabric when dyeing with oak bark extract at 70 oC [11] |

**18.4 Main groups of natural dyes**

**18.4.1 Carotenoids**

Carotenoids are polyenes that contain eight isoprenoid units and belong among tetraterpenes. They are lipophilic dyes that are involved in photosynthesis of plants. Carotenoids absorb the dangerous UV radiation and thereby protect the plant tissues. They have yellow, orange and red colour and are divided into **carotenes** and **xanthophylls**. The typical representative of carotenes is the orange beta-carotene (**Fig.4**) in carrots, or the red lycopene in tomatoes. Xanthophylls are oxygenated derivatives of carotenes and they are also photosynthetic pigments. They can be found in plants and animals: the yellow lutein is contained in dandelions, sunflowers or egg yolk. Purple rhodoxanthin occurs in fruits of yew (*Taxus baccata),* it also colours leaves of trees in the fall or can be found in the feathers of some birds. Rhodoxantin is used as a food colourant in Australia and New Zealand (in the EU and the US it is not allowed).

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| http://butane.chem.uiuc.edu/pshapley/GenChem2/B2/4.png |
| **Fig.4:** β-carotene |

**18.4.2 Pyran dyes**

The pyran dyes include primarily **flavonoids** and **anthocyanins**, (or their aglycones anthocyanidins). The basic skeleton of these dyes consists of two substituted benzene rings A and B, the ring A is fused with the pyran ring C (**Fig.5**).

Flavonoids and anthocyanins are often bound to various sugars by glycosidic bonds and the sugar can be further acylated with organic acids. These are the natural substances of very diverse configuration that differ in hydroxylation, glycosylation and methoxylation. They are found in fruits, leaves and flowers of plants.

Flavonoids have number of biological effects; particularly they are strong antioxidants that are able to protect cells against harmful UV radiation and oxidative stress, they also act as "quenchers" of free radicals.

Flavonoids are further divided by the non-sugar substituents into flavonols, flavones, flavan-3-ols, anthocyanidins, flavanones, isoflavones, dihydroflavonol, flavan-3,4-diols and coumarins, structurally related compounds are chalcones, dihydrochalcones and aurones. [11] [12] Especially yellow flavones and flavonols (from Latin *flavus* = yellow) are important as vegetable dyes. Their name is the basis for the name of whole group. Chalcones and aurones are also yellow, flavanones are colorless or slightly yellow; anthocyanidins are red, pink, purple, blue, orange, as well as yellow and form a specific group. [13]

The best known and the most common flavonoid is yellow **quercetin** (**Fig.6**) that has a number of biogenic effects (e.g. anti-inflammatory, antioxidant, anticancer). It is very poorly soluble in water, but as a lipophilic substance penetrates cell membranes very well. In plants it occurs in the form of glycoside (e.g. rutin in buckwheat - *Fagopyrum*).

Yellow **luteolin** also occurs in plants most often as glucoside. We can find it e.g. in oregano, dandelion, *Rosmarinus*, millet, olive oil and others. [14]

**The name of anthocyanins** comes from the Greek *anthos* = flower and *kyanos* = dark blue, but their colour scale is much richer. Anthocyanins are contained e.g. in the plant family *Vitaceae* (grape vine), *Rosaceae* (plums, sweet and sour cherries, raspberries, strawberries, blackberries, Aronia, apples, pears), *Solanaceae* (eggplant, red-skinned potatoes), *Grossulariaceae* (black and red currants, red gooseberry), *Ericaceae* (blueberries, cranberries), *Brassicaceae* (red cabbage, radishes, red Kohlrabi), *Malvaceae* (hibiscus), *Rutaceae* (red varieties of oranges and grapefruits), *Poaceae* (red varieties of corn), etc.

There have been identified around 500 anthocyanins that are the cause of red, pink, purple, violet, blue or orange colour of many plants. The number of aglycone **anthocyanidins** alone is much smaller (about 17[15]), 6 of them occur most frequently: cyanidin (Fig.), delphinidin, pelargonidin, malvidin, peonidin and petunidin. [16] Their typical property is the change of colour according to pH, generally from red under acidic conditions, through purple to blue in alkaline medium.

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| http://www.mdpi.com/ijms/ijms-14-18711/article_deploy/html/images/ijms-14-18711f1-1024.png |  |
| **Fig.5:** Basic structure of anthocyanins | **Fig.6:** Quercetin |

Besides anthocyanins many plants contain also other dyes such as quercetin, chlorophylls or carotenoids that affect their resulting colour. Co-pigmentation is also a unique property for anthocyanins: they form weak bonds with flavonoids, alkaloids, amino acids, phenolic acids, ascorbic acid and others. This is called **intermolecular co-pigmentation**. So called **intramolecular co-pigmentation** is stronger, here acyls of anthocyanins react with their aglycone. Another important influence on the final colour of anthocyanins has an associative mechanism of their molecules and even the formation of complexes with metal ions present in plants. [17]

In 1966 it was discovered that high-molecular polysaccharide is present in cornflower. It is derived cyanidin in anionic form bound in the complex with the Al+3 and Fe+3 ions.[18]The more recent research based on X-ray analysis of crystal structure of the cornflower pigment specified that it consists from a complex of six molecules, each includes current cyanidin and flavone with one Fe+3 ion, one Mg+2 ion and two Ca+2 ions and this tetrametal complex is the true source of cornflower blue. [19]

Another nice example of the flower colour change depending on anthocyanin binding metal ions is hortensia (*Hydrangea*). Its colour change is associated with soil pH and aluminium content. The more acidic soil allows the higher absorption of Al+3 from the soil and this complex with anthocyanin in vacuoles changes pink colour of flowers to blue. [20]

Anthocyanins play a very important role in the food industry (E163). Brilliant hues, strong dyeing ability and relative health safety of anthocyanins are utilized in food colouring (dairy products, beverages, confectionery etc.). In the Czech Republic, their use is prohibited only in child nutrition. For this purpose are most frequently used extracts from elderberry, blackcurrant and cherries in the acidic environment (usually with citric or ascorbic acid) at a pH of 3 - 4.5, when anthocyanins are the most stable. At lower pH proceeds mainly glycosidic bond hydrolysis, at higher pH (already at pH> 5) starts their oxidation and in alkaline environment anthocyanins decompose.

The strong interest in anthocyanins is driven by the consumer demand for healthier food products. However, their instability at pH, instability to light and heat degradation are quite limiting for these purposes.[21]

**18.4.3 Quinoid dyes**

Quinone dyes are derived from benzoquinone, naphthoquinone and anthraquinone. Most of the quinoid dyes that are used for dyeing textiles, in cosmetics and food industry have a vegetable origin, except cochineal carmine:

- red **carthamin** is present in safflower (*Carthamus tinctorius*), it is also used as a food colourant (Natural Red 26), and in folk medicine. Carthemin dyes fabrics in yellow, orange, red or violet according to fibre type, pH and mordant;

- red **henna** (lawson) is a naphthoquinone derivative, it is contained in the leaves of tropical plant *Lawsonia inermis*, it dyes protein fibres (wool, silk) very well to orange, maroon, dark brown or burgundy hues and because it binds well with keratin, it is very popular among certain ethnic groups (especially in India and the Middle East) for skin and hair decorating;

- brown **juglone** (**Fig.7**) is an isomer of lawsone that occurs in the leaves, barks and epikard of walnut trees (genus *Juglans*). It is used as herbicide, dye for cloth and colouring agent for foods (Natural Brown 7) and cosmetics. Juglone dyes textiles (and hair) to various shades of brown and it was used even for the production of inks. It also has medicinal effects (anthelmintic, antimicrobial and possibly anticancer) and also acts as herbicide on many plants (walnut tree prevents the growth of other plants in its proximity;

- red **alizarin** (**Fig.8**) from the roots of the madder (*Rubia tinctorum*), it is an anthraquinone derivative, it dyes fabric to various shades of red (Turkey red), pink, purple or brown colour, depending on the pH and mordant;

Madder has been cultivated and used for dyeing in ancient Egypt and was very popular in the Middle Ages. However, the much cheaper production of synthetic alizarin from the coal tar ended his fame in the second half of the 19th century (German chemists Graebe and Liebermann, 1868).

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|  | http://www.sigmaaldrich.com/content/dam/sigma-aldrich/structure0/030/mfcd00001201.eps/_jcr_content/renditions/mfcd00001201-medium.png |
| **Fig.7:** Juglone | **Fig.8:** Alizarin |

- purple-red **carmine** occurs in cochineal insects (*Dactylopius coccus*) that are dried and cooked in water with addition of aluminum ions to precipitate carmine. Besides textile dyeing it is used as a food colourant (Natural Red 4, E120), but because cochineal carmine often causes allergic reactions, it has been replaced by synthetic one.

**18.4.4 Indolic dyes**

Indolic dyes are derived from heterocyclic indole. They include **indigoid dyes** and **betalains**.

**Indigoid dyes** are in general poorly soluble in water, for dyeing of fibres it is necessary to convert them to more soluble "colourless" (in fact only different and less colour) enol leuco-form. The most common reducing agent is sodium dithionite (Na2S2O4) for reduction of keto groups to phenols in an alkaline environment.Once attached to the fabric, the leuco dye is then oxidized to the insoluble state which is intensely coloured, while washing out of alkali. (*see Chapter 12.2 – Vat dyes*)

The best known is **indigo** contained in tropical indigo plants of genus *Indigofera* (*Polygonum tinctorium*) or Europan woad (*Isatis tinctoria*) and **Tyrian purple** that is produced by several species of predatory sea shellfish of *Muricidae* family. [22]

 Highly desirable indigo blue and royal purple were very expensive, because obtaining these dyes was extremely difficult. *Isatis* was the only source of indigo in Europe before the importation of indigo from Southeast Asia. But *Isatis* contains such a slight amount of indigo (0.2 – 0.5 %[3]), it must be processed from about a half ton of *Isatis* leaves to obtain 1 g of indigo powder! And what about Tyrian purple (chemically 6,6´ - dibromoindigo), to obtain 1 g of this dye more than 8000 shellfishes are needed!

Indigo is derived from plants in the form of precursors: ***indican*** (indoxyl-beta-D-glucoside) found in indigo-producing plants and ***isatan B*** (indoxyl-5-ketogluconate) found only in woad. [23] Both of these molecules can be naturally hydrolysed by native beta-glucosidase an acidic pH of 3 to yellow ***indoxyl*** (the enzyme beta-glucosidase is localised in the chloroplasts of mesophyll cells in the leaves of the indigo plants [24]). Finally, two molecules of indoxyl are oxidised to form indigo in alkaline solution (**Fig.9**).

 A reduction in alkaline medium is needed when dyeing the fabric with indigo - ancient dyers used the ammonia from fermented urine - so because of the odious stench they were not exactly welcome neighbours... In India, the indigo dyers were mostly representatives from the lowest castes and have been banished downriver of the city so they do not pollute it.

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| **Fig.9:** Formation of indigo |

In terms of fastness, indigoid dyes are an honorable exception from NatD: although they have relatively small molecules, they are "locked" in the fibres during the dyeing process, where they additionally crystallise in larger units. This results in high wash fastness and undeniably excellent light fastness (up to grade 8 of lightfastness blue scale).

**Betalains** contain in their structure the heterocyclic indole too, but here ends the similarity with indigoid dyes: they are water-soluble and can be used for dyeing without vatting. In contrast to indigoid dyes they have very poor light fastness, often less than grade 2 of light fastness blue scale. Some of them are also very thermolabile, so even though they are popular and health harmless dyes used in the food industry (E162), this limits their application to refrigerated, frozen and light protected products. They somewhat resemble anthocyanins, but compared with them, betalains are more stable in various acidic environments: while anthocyanins are very sensitive acidobasic indicators, betalains do not change their colour markedly according to the pH.

They occur in plants as glycosides that are contained e.g. in beetroot and red swiss chard (*Beta vulgaris*) [25], pigweed (*Amaranthus*) [26], prickley pear (*Opuntia*) [27] or some ornamental plants as four o'clock flower (*Mirabilis*), *Bougainvillea*.[28] Betalains occur in plants in the form of yellow or yellow-orange **betaxanthins** (e.g. vulgaxanthin is contained in beetroot, indicaxanthin was isolated from opuntia, betaxanthin musca-aurin was discovered even in toadstool (*Amanita)* [29]) and red-purple **betacyanins** (**Fig.10**) (e.g. betanidin and isobetanidin are present in beetroot, phytolaccanin in pokeweed (*Phytolacca americana*), amaranthine in pigweed (*Amaranthus*), bougainvillein in *Bougainvillea*). [3] [30]

Yellowish betaxanthin absorbs the light with wavelength in the range from 470 to 486 nm; red betacyanin has this peak shifted to around 540 nm. Both of these dyes have a similar metabolic pathway of formation, their precursor is the light yellow betalamic acid. [31]Betalamic acids bind with a variety of amines or amino acids and can theoretically bind with more than 200 known plant amino acids and, therefore, the structural formulae of "pure" betaxanthins are in fact only hypothetical. [32] However, it is reported that there are more than 50 types of betalains.[17]

**18.4.5 Pyrrolic dyes**

Pyrrolic, speciffically, tetrapyrrolic dyes are derived from the heterocyclic pyrrole. Four rings of pyrrole are connected by methine bridges to the aromatic cyclic structure (**porphyrins**) or in the linear structure (**bile pigments**). In the central part of porphyrins a metal ion is most often bound; typical representatives are metalloporphyrins: green plant pigments chlorophylls (the central ion is magnesium) and haem (the central ion is iron) that is the part of red haemoglobin, muscle protein myoglobin and certain redox enzymes (cytochromes, catalases, peroxidases).

**Chlorophyll** (**Fig.11**) itself is not very suitable for dyeing of fibres: it is soluble in organic solvents and experiments with dyeing of polyester fibres are not very successful; fastness is very poor. Some scientific papers describe the use of plant chlorophyll either as precursor to form a cationic dye (removal of the central ion forms so called pheophytin that is in the slightly acidic environment symmetrically protonated to form dication and thus acquires an excellent affinity to fibres with the content of amino acids, imino, nitro, or peptide groups) [33] or use of chlorophyll as mordant. The chlorophyll obtains the free binding capacity after removal of the central magnesium ion in acid environment and can work as any other, e.g. tannic complexation mordants. [34] We can find chlorophylls in its natural form as a ubiquitous impurity in plant extracts for textile dyeing, where they cause turbidity of shades similar to tannins.

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| **Fig.10:** Betanidin | **Fig.11:** Chlorophyll |

Even if we leave aside ethical, religious or aesthetic objections to the dyeing with animal or even human blood, haem (or blood pigment haemoglobin) is not very suitable for textile dyeing. Red **haemoglobin** does not have a good fastness and it is oxidised to bluish-brown methaemoglobin during its aging. To remain red, it would be necessary to convert it to carboxyhaemoglobin using a suitable reducing agent.

 A similar trick is used for meat sale: it is treated with preservative salt that contains carcinogenic sodium nitrite to remain nicely red. Also, smoking process of meat or fish in a reducing atmosphere of carbon monoxide can keep "healthy" reddish look of meat because of the chemical reduction of haem in haemoglobin and myoglobin.

Bile pigments are formed in the body due to the degradation of haem from destroyed red blood cells (green **biliverdin** colours the bruises, but we find it also in green avian egg shells, yellow-orange **bilirubin** accumulates in bile, straw-yellow **urobilin** gives the colour to urine, brown **sterkobilin** colours feces).

 As dyeing with blood, the idea of textile dyeing with these dyes evokes not exactly positive images and also the hue and stability obtained are very bad. Human or animal urine however was often used in the past for the processing and textile dyeing, although rather as "textile auxiliary agent". E.g. fermented urine served as a source of ammonia in vatting of indigo [35], fermentation of isatis leaves or lichen. Lichens contain precursor orcein that was used in dyeing of wool into brownish-red to purple shades [36] [37]. Camel or ovine urine was used as an additive to a mixture for textile dyeing to obtain red shade using the root of alkanet (*Alkanna tinctoria*) [38]. All additives, including alum were cooked directly in urine during dyeing of wool and linen to yellow with weld (*Reseda luteola*) [35] [39]; human urine was also used for wool washing.

**18.5 (Dis)advantages of natural dyes**

The main idea of the natural dyeing is based on the concept of inexpensive, non-toxic and renewable exploitation of natural resources with minimal impact on the environment. In fact, dyeing with NatD brings about a number of problems. NatD, unlike the synthetic ones:

**a/** have a limited range of colour shades, (prevailing are spectrally impure shades of brown, gray and greenish [40]), with their poor reproducibility. These are substances that do not have a standard composition. Their large **variability** lays not only in chemical composition but also in the quantitative content that relates to the natural conditions of cultivation (soil composition, nutrition, sunshine, irrigation) and genetic variability within the same plant species.

**b/** have a significantly lower affinity to fibres, which causes the lower dye - exhaustion from bath on fibers (often not higher than 10 % [41]). Low dye-exhaustion from bath and also low fastness of most NatD (except indigo) is due to their structure, and often hinders dispersion of synthetic pigments for colouring of synthetic fibre. They have mostly small, non-ionic polar molecules, with low water-solubility.

Therefore, the dose of colourants (by synthetic dyes is within 0.3 -3 % o.w.f.) must be at least one order of one magnitude higher. The vast majority of NatD remains in bath after dyeing, especially when trying to obtain dark shades.

**c/** attain even worse bath-exhaustion of mordants - their affinity to fibers is minimal - almost zero. Spoiling of effluents by these soluble salts of heavy metals or tannin is environmentally very undesirable. Use of the “old” dyeing and mordanting bathes for dyeing of other goods is possible, but rarely realised.

Low dye and mordant-exhaustion increases cost of dyeing, and also often removing residual dyes and auxiliaries from the waste water to meet regulatory limits for the textile waste water.

If we want to say that fabrics dyed with natural dyes are "eco" and "bio", which should be the main reason for their use, we should not use metal salts for mordanting (in most cases they are necessary) or other chemicals, e.g. sodium hydroxide, sodium hydrosulphite to vatting. So, shall we use fermented urine again?

d/ are contained in plants in small quantities. Logically, this creates a need to handle a large amount of biomass for obtaining them, thereby producing large quantities of waste. At the same time cost for transporting large volumes of plant material from the place of harvest to the place of processing is rising. Production cost of NatD from the direct harvest is very high.

These properties do not matter in occasional small textile dyeing at home. But in the daily production in workshops and industries, it is a complicated problem as handling huge volumes of natural (mostly bulky plant) material.

 Therefore, it is necessary to seek good practical compromises. Traditional recipes (often originating from historic ones), however, do not help in this direction - they are working with long processing times. We should seek effective new approaches utilising appropriate auxilliaries, effective use of temperature and the liquor ratio should be used as low as possible.

An interesting method for dyeing of silk or wool fabric with extract of eucalyptus leaves in professional workshops in Thailand was developed applying padding methods *Pad-Dry* or *Pad-Batch*: liquor ratio drops here below 1:1. The volumes of the remaining “loss” in bathes are negligible, the production times are short [42] [43] (see *eucalyptus application* below).

Besides the purposeful cultivation of dye plants, there is a much more progressive option, and that is the **utilisation of waste** from food industry, forestry and agricultural production. Industrial production of food and beverages produces huge amounts of biological waste, such as molded fruits, distillation residues, pomace and other residual by-products containing a large amount of vegetable dyes that can be used in the textile industry. Most of them are pomace from fruits rich in anthocyanins (red and black currants, cherries, purple grapes) and waste from colourful vegetables containing anthocyanins or betalaines (red cabbage, beetroot, red onion). Timber harvest provides a large amount of waste material in the form of bark that is a rich source of tannins. These can serve not only as mordants, but also as textile dyes because bark (e.g. oak, birch, alder, and chestnut) has the ability to dye especially natural fibres to various shades of brown colour.[44]

The use of waste materials from agriculture and forestry also has its risks. We should use only waste from organic farming for dyeing, because, for example, the grape pomace often contain high concentrations of copper, zinc and other organic toxic substances of sprays protecting vines from pests and fungi. Also bioaccumulation of heavy metals, radioactive elements and various pollutants in plants is well known - a method of phytoremediation is based on it. For example, barks of trees have this accumulation ability in relation to some metals - as evident from studies monitoring the different concentrations of radioactive caesium[45] [46],or hexavalent chromium in oak bark, depending on the area from which the analysed samples originated (nature, urban agglomeration or proximity of the former chromium processing company). [47] The **continuous monitoring of heavy metals and other harmful substances and pollutants content would be necessary** for dyeing with NatD, and especially with the coloured waste.

**18.6 Examples of dyeing using some natural dyes**

**18.6.1 General conditions of bath-dyeing**

Extraction of dyes from plant material

Fresh or dried plants and parts of plants (mostly bark, twigs, fruits, dried plants) finely chopped, soaked in water 24 hours before dyeing (start with hot water and allow to cool), only use flowers or leaves soaked in warm water 1-2 hours before dyeing.

Dyeing

Heat the extracting (leaching) bath with plant material and after 30 - 60 min. of boiling let it cool off. Filter through a colander to remove plant residues. Insert textile into the lukewarm extracting bath with material and boil, while stirring, 30 - 45 min (don´t heat fine woollen and silk materials – risk of shrinkage!). After cooling, remove material, squeeze and rinse until the water flows clear.

      If not mordanted in advance, apply mordant now (mostly at boil for 1h, silk max. 60 °C - risk: loss of lustre). Rinse, squeeze, dry.

Mordanting [6]

*a) protein fibres (wool, silk)*

For 100 g of washed wool or silk, add half to one and half tablespoon of mordant salt, e.g. alum + tartar 1:1, or copper sulphate acidified by vinegar; ferrous sulphate is inappropriate! (Silk - loss of gloss, soft wool – risk of felting); liquor ratio about 1:180. Start with cold water, bring to boil and cook for about one hour with occasional stiring. Let it stand in cooling bath for 2-12 hours. Then remove, rinse, dry or dye immediately.

Natural mordant: an extract from leaves and petioles of rhubarb (rich in oxalic acid) - (see recipe below); tannin is not suitable for the wool mordanting! [6] [48]

0.5 kg of sliced rhubarb, cook for 1 hour in 5 l of water, filter through a sieve, put 100 g of wool (liquor ratio 1:50), bring to the boil (put the wool only into cold or lukewarm water and bring to the boil; don’t put in hot water - risk of felting!) and boil 30 – 40 min. Remove, rinse, dry.

If the same bath is alkalised (added with soda) wool will be light pink – suitable for dyeing with fruits containing anthocyanins or birch bark. Ecologically, it is very gentle mordanting, used in Himalayas.

*b) cellulose fibres (cotton, linen)*

For mordanting of plant fibers it is necessary to use a higher concentration of mordants and to stain for longer time than for wool - the cellulose fibers absorb mordants very poorly!

For 100 g of washed cotton, add mordant salt: 4 tablespoons of alum + half tablespoons of soda, or half tablespoon of copper sulphate +vinegar, or half tablespoon of ferrous sulphate; liquor ratio about 1:100 – 180. Bring to a boil, let it cool for up to 24 hours. Remove, wring, dry.

Natural mordant: tannin from bark of oak, sumac (*Rhus*); or gall nuts: per 100 grams of cotton: 20 g of crushed gall nuts or bark, boil 1 hour in 2 litres of water, insert the cotton, let it cool for 24 hours. Remove, wring, dry.

It is possible to perform the extraction, mordanting and dyeing under these (or slightly modified) conditions e.g. with the following plants:

|  |  |  |  |
| --- | --- | --- | --- |
| **Plant – part used** | **Natural dye** | **Mordant** | **Colour** |
| walnut (*Juglans*)- leaves, pericarp | juglone | alum | brown |
| turmeric (*Curcuma longa*) - rhizome | curcumin | alum | yellow |
| CuSO4 (before) and alum (after dyeing) | pea green |
| blackberries (*Rubus*)- fruits | anthocyanins | alum | dark violet |
| alum + acetic acid | pink-purple |
| weld (*Reseda luteola*) - herb, flowers | flavonoids | alum | bright yellow |
| SnCl2 | sulphur yellow |
| K2Cr2O7 | yellow-orange |
| CuSO4 (before) and alum (after dyeing) | pea green |

**18.6.2 Red on cotton or wool fabric by alizarin from madder roots**

[49] [50]

Besides sugars and tannins, madder root contains about 36 anthraquinones, such as purpurin, purpuroxanthin, anthraflavin, pseudo-purpurin, dantron or rubiadin, but the most important is alizarin (Pigment Red 83, CI 75330). Not all these dye pigments are water-soluble, mixture of organic solvents (e.g. methanol, ethanol, ethyl acetate, ..) give extracts partially water-soluble, so a better way to obtain water-soluble root powder extract is to resort to an alkaline solvent.

Put 10 g of madder root powder in 0.5 litre of water at room temperature overnight (12 hours). After recovering the supernatant by centrifugation, washe the solid residue twice with water, collect all supernatants, add the initial dye-bath volume of water (0.5 litre) and dip 10 g of premordanted wool or cotton. Heat the bath to 90 °C (wool), or to boil (cotton) for 2 hours, with stirring regurlarly. Allow to cool off, rinse in tap water until the rinsed water is clear, then dry.

*The colour* of madder lake (*lake = an insoluble pigment made by combining a soluble organic dye and an insoluble mordant*) is influenced by the metallic salt used: alumina lake – rose red, calcium lake – bluish red, aluminium lake – Turkey red, tin lake – red-violet, chrome lake – red-brown.

*Mordanting*: 2.5 g of alum, 0.4 litre of water, add 10 g of wool, heat to 90 °C for 1 hour and then let it cool. Or 2.5 g of alum, 1 g of cream of tartar, 0.25 litre of watter, add 10 g of cotton, heat to boil for 2 hours, then let it cool. Squeeze and dry or directly put in dye – bath.

*CIELAB colour characteristics* of fabrics dyed with powder from madder root: L\* 26.8, a\* 20.9, b\* 15.1 (wool), L\* 39.6, a\* 9.7, b\* 14.4 (cotton). [49]

Light *fastness* 4 – 5, wash fastness 4 – 5.

**18.6.3 Blue on cotton or wool fabric by indigo from woad leaves** [51]

***Precursors extraction, conversion to indoxyl:***

5-15 g finely chopped leaves of *Isatis* (ideally with petioles removed - useless ballast, not dyeing), pour 50-100 ml of boiling water, cover, and let leach at 70 - 90 °C for 10 minutes maximum! Boiling water will also reduce foaming of bath (hot water partially deactivates plant surfactants). Filter extract (squeeze soaked leaves) and immediately cool this extract to about 40 °C. (Observe the times - danger of deactivation of indigo formation!)

***Formation of indigo from precursors:***

Alkalisation (add 0.1 g of NaOH to 50 ml of extract, i.e. create solution with concentration of 2 g of NaOH/litre, pH 10 - 12) and the intensive oxidation (shake, mix, spill over for 5-10 minutes) - solution changes colour to turquoise and indigo grains appear in the foam.

***Vatting:***

Time 20 min., temperature 45 oC, 0.2 – 0.3 g of sodium dithionite/50 ml of extract, the amount of dithionite is 2 - 3 times greater than in reduction of pure indigo because dithionite is inactivated by reaction with other plant components – don´t worry, unlike the pure indigo is not easy to "over-reduce" bath. When vatting continuously check pH of bath and possibly additionally alkalise if needed.

***Dyeing:***

If we dye at high pH (it is necessary to maximise the yield from plant indigo), we will achieve only a visually weak colour shade because indigo penetrates to a depth of fibres (*see Chapter 12.2.6 – Indigo „ring penetration” of cotton denim*). Therefore, the strongly alkaline extract with oxidised indigo should be slightly acidified (e.g. by acetic acid) and thean dyed at slightly alkaline pH of about 9. Due to the low concentration of indigo in *Isatis* leaves extract, the maximum utilization of surface dyeing with slightly dissolved indigo is only way to achieve a dark blue colour on the fabric. At weak alkaline pH indigo binds to the surface of fibre very quickly, producing unlevelness - at strongly alkaline pH, the fibre is slowly dyed in depth without unlevelness, but only to light shade of blue.

Insert textiles (cotton or wool) into the vat bath - liquor ratio 1:50 (1 g of cotton/50 ml of dye-bath); unlevelness can be improved by adding of auxiliary leveling chemical agent, dye for 30 minutes at max. 55 - 60 °C, let cool for another 30 minutes.

***Washing:***

The fabric is light green after removing from the dye bath, but in the air and during the subsequent wash in cold water under the action of oxygen. A blue colour is created successively while alkali is washed out.

**18.6.4 Dark brown on silk or wool fabric by eucalyptus leaves**

Water extract from eucalyptus leaves (*Eucalyptus camaldulensis*),major components: tannin, gallic and ellagic acids and minor flavanoids: quercetin, rutin, apigenin, hyperin, medicinal drugs.

Without mordant → very pale brown; with Fe (II) → dark browns; Cu, Al, Sn (II) → low effects.

Padding method [42] [43] developed for workshops and manufacturers (simultaneous padding/mordanting in padding mangle):

3 g/l of dry matter of eucalyptus water extract, 2 g/l FeSO4 andtenside. After very short impregnation (cca 1 sec) and squeezing, the fabric is:

 (*=****Pad-Dry***): directly dried (90 °C, 5 min.) or pre-dried in infrared field and fed into a *hot-flue* to fix the dye, or

 (=***Pad-Batch)***: the rolled fabric is kept at room temperature for 8 - 24 h, covered with a plastic sheet to prevent the drying and oxidation of the outer layers and rotated slowly to avoid percolation due the gravitational effect of the liquid that could distort the roll and create dyeing defects. (Also ***steaming*** is possible for intensification of diffusion into fibers and the mordanting reaction).

 The fabric is finally soaped in 50 °C bath of anionic washing tenside. Water - rinsing depending on local conditions. Fastness to washing (40 °C) 4-5, perspiration 4-5, light 4-5.

**18.7 Conclusion**

An extensive research and development in natural dyes is carried out all over the world, but the implementation of these technologies in modern practice is a rather long-term perspective. The reality is that natural dyes and mordants are rather used only on a small scale (craft industries, hobby associations, manufactures, home production) and their mass utilisation in the modern textile industry would be difficult. However, an emerging amount of literature about the environmental and economic aspects of textile natural dyeing shows that environmental impact can be minimized, and that the use of natural substances should contribute to sustainable development in the near future.

**Resources:**

[1] Kramell, A. et al.: Dyes of Late Bronze Age textile clothes and accessories from the Yanghai

 archaeological site, Turfan, China: Determination of the fibers, color analysis and dating. Quaternary

 international (2014), 348, p. 214-223

[2] Schliemann, W. et al.: Betacyanins from plants and cell cultures of *Phytolacca americana*.

 Phytochemistry (1996), 42(4), p. 1039-1046

[3] Schweppe, H.: Handbuch der Naturfarbstoffe. Ecomed Landsberg (1993). ISBN: 3-933203-46-5

[4] Mell, C. D.: *Phytolacca decandra*. Textile Journal (1922), 24, p. 436

[5] Mongkholrattanasit, R.: Dye extraction from Eucalyptus leaves and application for silk and wool

 fabrics dyeing. Dissertation, FT TUL, Liberec (2010)

[6] Bidlová, V.: Barvení pomocí rostlin. Grada Publishing, Praha (2005), ISBN 80-247-1022-6

[7] Bechtold, T., Mahmud-Ali, A., Mussak, R.: Anthocyanin dyes extracted from grape pomace for the

 purpose of textile dyeing. Journal of the Science of Food and Agriculture (2007), 87, p. 2589-2595

[8] Cunningham, A. B. et al.: Hanging by a thread: natural metallic mordant processes in traditional

 Indonesian textiles. Economic Botany, (2011), 35, s. 241–266

[9] Stannous chloride – material safety data sheet. Anachemia.

 On line: <http://www.anachemia.com/msds/english/8598> [retrieved 15.10.2015]

[10] Decree No. 4/2008 Coll. (annex 2) stipulating types and conditions of using additives and extraction

 solvents in foodstuffs production. On line: <http://www.zakonyprolidi.cz/cs/2008-4#p9> [retrieved

 15.10.2015]

[11] Vodrážka, Z.: Biochemie. Academia Praha (2002). ISBN: 80-200-0600-1

[12] Crozier, A., Jaganath, I., Clifort, M. N.: Dietary phenolics: chemistry, bioavailability and effects on

 health. Natural Product Reports (2009), 26(8), p. 965-1096

[13] Velíšek, J.: Chemie potravin. Ossis Tábor (2002). ISBN: 86659-00-3

[14] López-Lazaro, M.: [Distribution and biological activities of the flavonoid luteolin](https://www.bentham.org/mrmc/sample/mrmc9-1/0004N.pdf). Mini-Reviews in

 Medicinal Chemistry (2009), 9(1), p. 31-59

[15] Harborne, J. B., Grayer, R. J.: The anthocyanins. The Flavonoids. Chapman and Hall Ltd, London

 (1988). ISBN 978-0-412-28770-1

[16] Francis, F. J.: Food colorants: anthocyanins. Critical Reviews in Food Science and Nutrition (1989),

 28(4), p. 273-314

[17] Delgado-Vargas, F., Jiménez, A. R., Paredes-López, O.: Natural Pigments: Carotenoids,

 Anthocyanins, and Betalains – Characteristics, Biosynthesis, Processing and Stability, Critical

 Reviews in Food Science and Nutrition, (2000), 40(3), p. 173-289

[18] Bayer, E. et al.: Komplexbildung und Blütenfarben. Angewandte Chemie (1966), 78, p. 834-841

[19] Shiono, M., Matsugaki, N., Takeda, K.: Phytochemistry: Structure of the blue cornflower pigment.

 Nature (2005), 436(7052), p. 791

[20] Dangles, O., Elhabiri, M., Brouillard, R.: Kinetic and thermodynamic investigation of the aluminium

 anthocyanin complexation in aqueous solution. Journal of Chemical Society Perkin Transactions

 (1994), 2, p. 2587–2596

[21] Křížová, H.: Colour changes of anthocyanins. Diploma thesis. FT TUL, Liberec (2011)

[22] Cooksey, C. J.: Tyrian Purple: 6,6’-Dibromoindigo and Related Compounds: a review. Molecules

 2001, 6, p. 736-769

[23] Gilbert, K. G. et al.: Qualitative analysis of indigo precursors from woad by HPLC and HPLC-MS.

 Phytochemical Analysis (2000), 11, p.18-20

[24] Minami, Y. et al.: beta-Glucosidase in the indigo plant: intracellular localization and tissue specific

 expression in leaves. Plant Cell Physiology (1997), 38(9), p. 1069-1074.

[25] Kugler, F., Stintzing, F. C., Carle, R.: Identification of betalains from petioles of differently colored

 Swiss Chard (*Beta vulgaris* L. ssp. cicla Alef. Cv. Bright lights) by high-performance liquid

 chromatography – electrospray ionization mass spektrometry. Journal of Agricultural and Food

 Chemistry (2004), 52, p. 2975-2981

[26] Repo-Carrasco-Valencia, R. et al.: Flavonoids and other phenolic compounds in Andean indigenous

 grains: quinoa (*Chenopodium quinoa*), kañiwa (*Chenopodium pallidicaule*) and kiwicha

 (*Amaranthus caudatus*). Food Chemistry (2010), 120(1), p. 128–133

[27] Ali, N. F., El-Mohamedy, R. S. R.: Eco-friendly and protective natural dye from red prickly pear

 (*Opuntia Lasiacantha* Pfeiffer) plant. Journal of Saudi Chemical Society (2011), 15, p. 257–261

[28] Stintzing, F. C., Carle, R.: Functional properties of anthocyanins and betalains in plants, food, and in

 human nutrition. Trends in Food Science & Technology (2004), 15(1), p. 19-38

[29] Steglich, W.: Pilzfarbstoffe. Chemie in unserer Zeit (1975), 9, p. 117-123

[30] Gandía-Herrero, F., García-Carmona, F.: Biosynthesis of betalains: yellow and violet plant pigments.

 Trends in Plant Science (2013), 18(6), p. 334-343

[31] Strack, D., Steglich, W., Wray, V.: Betalains. Methods in Plant Biochemistry. Academic Press

 Orlando (1993), 8, p. 421-450

[32] Reznik, H.: Betalaine. Ber Berichte der Deutschen Botanischen Gesellschaft (1975), 88, p. 179-190

[33] Zvezdina, S. V. et al.: Natural dyes based on chlorophyll and protoporphyrin derivatives. Russian

 Journal of Coordination Chemistry (2010), 36(9), p. 711-714

[34] Guesmi, A. et al.: First application of chlorophyll-a as biomordant: sonicator dyeing of wool with

 betanin dye. Journal of Cleaner Production (2013), 39, p. 97-104

 [35] Frei, K. M. et al.: Removal of natural organic dyes from wool–implications for ancient textile

 provenance studies. Journal of Archaeological Science (2010), 37(9), p. 2136-2145

[36] Riley, M. E.: Clothing of the Ancient Celts (1997).

 On line: <http://www.marariley.net/celtic/SentToKass/Dyes.htm> [retrieved 15.10.2015]

[37] Abel, A.: The history of dyes and pigments: from natural dyes to high performance pigments. Colour

 Design (2012), p. 433-470

[38] Humphrey, J. W. et al.: Greek and Roman Technology: A Sourcebook. Routledge (1998), London

 and New York, ISBN 0-203-41325-3

[39] McKenna, N. M. et al.: Complex Weavers Medieval Textile Study Group. (2001). On line:

 <https://www.cs.arizona.edu/patterns/weaving/webdocs/mnm_mt29.pdf> [retrieved 15.10.2015]

[40] Ul Islam, S. et al.: Perspectives for natural product based agents derived from industrial plants in

 textile applications - a review. Journal of Cleaner Production (2013), p. 1-17

[41] Kryštůfek, J., Wiener, J., Machaňová, D.: Barvení textilií II. Textbook, TUL, Liberec (2011).

 ISBN 978-80-7372-796-3

[42] Mongholrattanasit, R., Kryštůfek, J., Wiener, J.: Dyeing of wool and silk by eucalyptus leaves

 extract. Journal of Naturals Fibers (2009), 6(4), p. 309-330

[43] Mongholrattanasit, R., Kryštůfek, J., Wiener, J.: Dyeing and fastness properties of natural dye

 extracted from eucalyptus leaves using padding techniques. Fibers and Polymers, (2010), 11(3),

 p.1229-9197

[44] Punrattanasin, N. et al.: Silk fabric dyeing with natural dye from mangrove bark (*Rhizophora*

 *apiculata* Blume) extract. Industrial Crops and Products (2015), 49, p. 122-129

[45] Zhiyanski, M. et al.: Cesium-137 contamination of oak (*Quercus petrae Liebl*.) from sub-

 mediterranean zone in South Bulgaria. Journal of Environmental Radioactivity (2010), 101(10),

 p. 864-868

[46] Fogh, C. L., Andersson, K. G.: Dynamic behaviour of 137Cs contamination in trees of the Briansk

 region, Russia. Science of the Total Environment (2001), 269(1-3), p. 105-115

[47] Minganti, V. et al.: The bark of holm oak (*Quercus ilex,* L.) for airborne Cr(VI) monitoring.

 Chemosphere (2015), 119, p. 1361-1364

[48] Křížová, H.: Testing of light fastness of wool fabric dyed by anthocyanins from blue grapes pomace.

 Waste Forum (2014), 2, p. 88-94

[49] De Santis, D., Moresi, M.: Production of alizarin extracts from *Rubia tinctorum* and assessment of

 their dyeing properties. Industrial Crops and Products (2007), 26, p. 151-162

[50] Önal, A.: Extraction of dyestuff from madder plant (*Rubia tinctorum* L.) and dyeing of wool,

 feathered – leather and cotton. Turkish Journal of Chemistry (1996), 20, p. 204-213

[51] Křížová, H.: Verification of the possibility of dyeing with extract of woad. Bachelor thesis, FT TUL

 (2009)