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NATURAL DYES PAST, PRESENT, FUTURE AND VIABILITY

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1. INTRODUCTION

Natural colorants and dyestuffs are an important group of non-wood forest products which find use in industries producing confectionery, other food products, textiles, cosmetics, medicines, leather, paper, paint, ink, etc. This article reflects on comparison of natural and synthetic dyes because number of problems and questions arise in connection with the use of natural dyes. Are natural dyes really an environmentally friendly alternative of synthetic dyes? Is industrial and general use of natural dyes in the textile industry practicable, beneficial and Viable? Let's try find some answers with regard to the modern scientific knowledge.

2. ISSUES OF DYEING WITH NATURAL DYES

Natural dyes - their golden age return

Nature is full of beautiful colors that attract human attention. Natural dyes have been used since ancient times for dyeing of body, food, walls of caves, textiles, leather and objects of daily use. A large number of plant, animal, insect or mineral sources have been identified for extraction of dyes and pigments. The art of dyeing is as old as human civilisation. Dyed textiles found during archaeological excavations at different places all over the world provide evidence to the practice of dyeing in ancient civilizations. Earliest written record of the use of dyestuffs in China comes from year 2,600 BC. The use of cochineal as a textile and paint dyestuff in Mexico and Peru dates back almost 3,000 years. Alizarin, purpurin and indigo were identified in the Late Bronze Age on textiles found in Chinese Yanghai. [1] Prehistoric discoveries of textiles in Europe document the use of alizarin and purpurin from the 4^{th} century BC. In 55 BC Romans found painted people "*picti*" in Gaul dyeing themselves with woad (same chemical content of colour as indigo). Start of 16^{th} century was the time when France, Holland and Germany began the cultivation of dye plants as an industry. Natural dyes were used for colouring of textiles till the 19^{th} century when synthetic dyes pushed them out. It is only since few decades ago that textile industries have turned to synthetic dyes, but they were so successful that natural dyes currently account only for about one percent of the total amount of dyes used worldwide. [2] And this is so even thought that the use of natural dyes has a strong tradition in many countries (e.g. India, Turkey, Mexico, Morocco or countries of West Africa).

First European book on dyeing *Mariegola Dell'Arte de Tentori* published in Italy comes from 1429. The book *Secreti* from 1555 is a collection of prescriptions and various

manufacturing technologies including dyeing techniques. Italian author Alessio Piemontese describes there, for example, how to use the juice of blueberries or fruit of elderberry with the addition of aluminum, copper or ferric mordant salts, to reach blue colours on linen.

Dyeing with plants enjoyed a rebirth of popularity in the United States in the 60s and 70s. In 1960 Conley and Lewis published simple, basic dyeing methods with use of acorns, onion skins, rhododendron leaves and other plant sources. In 1971 Adrosko [7] published in New York another book on natural dye sources and processes for their application to textiles at the household level. There are about 50 recipes simply describing, e.g. how to extract dyestuffs from common trees, flowers, lichens, and weeds, and how to dye textiles. They include how to obtain brown dyes from the bark of apple, birch, hemlock, hickory, and maple trees; yellows from a wide variety of sources such as arsemart, white ash bark, barberry bark, sassafras, lichens, camomile flowers, and coffee beans; reds from madder, cochineal, Brazilwood, and alkanet; blues from woad, orchil and cudbear, as well as from the popular indigo; and blacks most commonly made from logwood and soot.

DOBAG is the Turkish acronym for Natural Dye Research and Development Project, launched in Turkey with German assistance in cooperation with the Marmara University, Istanbul in 1981. Project was initiated by the German teacher and doctor of chemistry Harold Böhmer. He discovered that older rugs used traditional vegetable dyes, while many of carpets made after the 1880 were coloured with artificial aniline dyes, which had come to Turkey from Europe (primarily Germany), and whose colour either faded to mud grey or remained garish. He initiated the natural dyes research and development project for the preparation of dyes in a village setting, old dyeing methods were newfound, and the vast majority of dye plants are now farmed in the Anatolia region (e.g.weld, madder, acorn). Project DOBAG have had a far-reaching effect on the Turkish carpet sector and it was a big success in reviving the lost art of producing naturally dyed carpets. [9] [10] [11]

Dyes traditionally used in the Scottish Highlands were reviewed by Grierson et al. [12] [13] There is documented that fruits of privet (*Ligustrum vulgare*) were used in Scotland for dyeing of wool mordanted from aluminum or iron salts with the addition of soda to achieve a deep blue colour. Wool was also dyed to violet-blue shade with fruits of crowberry (*Empetrum nigrum*) in the Shetland Islands until in the 1840's.

The Weaver's Garden from Rita Buchanan (1987) is a practical guide that provides information to weavers and gardeners on e.g.: growing plants for use in weaving and dyeing projects; how to use soap plants for cleaning textiles; information on fragrant plants for scenting and protecting textiles; what plant materials to use as tools; how to plan and create a garden containing cottn, flax, indigo, madder, fuller's teasel, woad, and many other.

Research efforts by individuals and organisations and exchange of available information through various seminars, symposiums, workshops, and research articles have now revealed various natural dye sources. Plenty of information about different sources of natural dyes is now available in the literature. [14] [15] [16] [17] [18]

As it is evident from the increase of scholarly and popular literature about natural dyeing, the interest in natural dyes today is growing even in countries where the use of natural dyes is no more than history. It's caused by a general environmental awareness and the increase of public interest in natural products. Today natural dyes have a variety of applications. They are used not only in textile dyeing and functional finishing (antimicrobial, antifeedant, deodorising or UV protective), but also as food and cosmetic colourants, cosmetic healing additives, pH indicators and in several other uses. [19]

Although we can apply common basic principles to dyeing with natural dyes, but their high variability leads to the necessity of individual approach for each of them. It is necessary to optimise these dyeing conditions: time, temperature, liquor ratio, dosage and type of mordant, preparation of plant material, choice of suitable fibres. This is probably what makes the dyeing with natural dyes exciting adventure with a touch of Alchemy.

We can get colouring matter from almost all vegetable sources. However, only a few of these sources yield colourants, which can be extracted and work out to be commercially viable. Coloured parts of plants (flowers, fruits, barks, stems or leaves) can yield colour, but the question is, what do these extracted colours: do they adhere to the fabric and do they have good fastness properties?

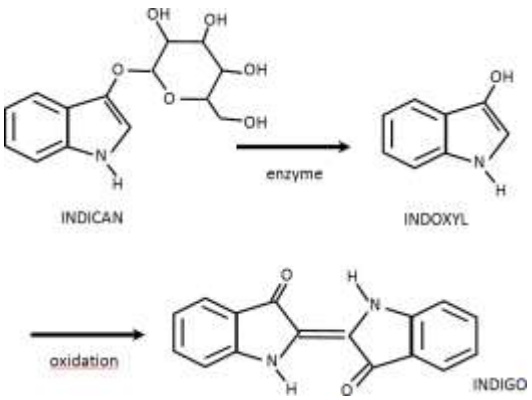

Figure 1: Formation of indigo from precursor indican (indoxyl-beta-D-glucoside)

The only viable choice among the blue natural dyes is indigo from *Indigofera* or *Isatis* (Figure 1). Its direct extract can't be use as a dye because indigo is present only in the form of precursors in these plants. Natural indigo is obtained by fermenting the leaves, running off the liquor and oxidising it to precipitate the dye. There is a certain amount of procedures and redox reaction, and only after it is kind of oxidised the dye actually comes up with its true colour. The woad, which is *Isatis tinctoria*, is grown mostly in North Europe and British Isles.

Yellow dyes are available from several plant resources: curcumin is extracted from turmeric (*Curcuma longa)* rhizomes, saffron is obtained from the dried stigmas of the plant *Crocus sativus*, annatto comes from seeds of small tree *Bixa orellana* (Figure 3) and it is used for the dyeing of cotton, wool, and silk and also used for colouring butter and cheese. Yellow colours on the fibres have mostly mild to moderate fastnesses, except flavonoids. Weld (*Reseda luteola*) was a very important yellow dye plant in Europe. Its colouring matter is a flavonoid and it produces a good yellow colour on natural fibre textiles that have very good fastness properties, similarly as quercitrin (CI 75720 / Natural Yellow) isolated from North American oak *Quercus velutina* [3] that is a glycoside formed from the flavonoid quercetin and the deoxy sugar rhamnose.

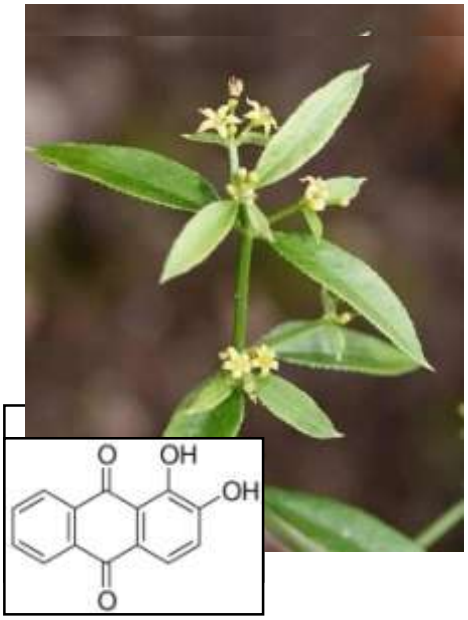

Figure 2: Madder (*Rubia tinctorum*) and structure of quinoid alizarin from its roots

Figure 3: Mature pods of the achiote tree (*Bixa orellana*) and structure of apocarotenoid bixin from its seeds (annatto)

The green colour is often achieved by a combination of indigo and various yellow pigments. Quinone dyes such as lawsone (from henna, *Lawsonia inermis*) or structurally similar juglone (from various walnuts), are also good sources of popular brown shades with good fastness properties. Thank to the good ability to bind with protein fibres and materials (wool, skin, hair, silk) it is very popular in Arabic world and India as body painting or "henna tattoo" (Figure 4). Black colour is obtained from the barks and leaves of trees and shrubs that are rich in tannins, in combination with ferric or ferrous salts. Tannins, generally in combination with various mordant salts, provide a wide range of brown, reddish, gray or black shades with good fastnesses. [3] [21] [22]

[weheartit.com]
Figure 4: Henna tattoo (body painting) and structure of henna dye (lawsone) from *Lawsonia inermis* leaves

Market requirements - only contest of price and quality

Countries such as Mexico, India, China or Peru are the largest exporters of natural dyes and it appears that it is well developing business: e.g. a conservative estimate for total world trade of annatto (dried seed of *Bixa orellana*, a source of pigments which impart a red or orange hue) is at about 7 – 9,000 tonnes, calculated in seed equivalents with the trade price of about US$ 800-1,000 per tonne of top quality seeds (1992). The main exporters are Peru and Kenya, the main importers are the United States and Canada. An annual world trade of henna (dried, whole or powdered leaves of *Lawsonia inermis* that contains the pigment lawsone, 2- hydroxy-l,4-napthaquinone) does at least 9,000 tonnes of dried leaf with price ranged from approximately

Business with natural dyes is still growing, but only its small part is applied to textile dyeing. Greater part consists of dyes for food colouring, because the pressure on healthier foods is growing, and there is thus a need to replace synthetic colourings by healthier natural products. Table1 provides an overview of the natural colourant permitted for foods by European Community.

Table 1: Colorant of natural origin permitted for foods by EC [23]

Designation	**Natural colourant**
E100	Curcumin
E101	Riboflavin
E120	Cochineal/carminic acid
E140	Chlorophyll
E141	Copper complexes of chlorophyll
E150	Caramel
E153	Vegetable carbon
E160 (a)	α-, β-, γ-carotene
(b)	Annato extract
(c)	Paprica extract
(d)	Lycopene
E161 (a)	Flavoxanthin
(b)	Lutein
(c)	Cryptoxanthin
(d)	Rubixanthin
(e)	Violaxanthin
(f)	Rhodoxanthin
(g)	Canthaxanthin
E162	Beetroot red, betanin
E163	Anthocyanins

Many factors decide on the commercial success of the fashion and textile products, among them is the kind of textile agents. Besides print and pattern, consumers demand basic characteristics of textiles: resistance to agents that cause fading of textiles (washing, light, perspiration, etc.). Textiles must offer a great range of colors and must be cost effective.

The high number of synthetic dyes is justified due to the demands of industry and consumers. However, most of synthetic dyes or dyeing methods are considered little viable partly due to effluents associated to these finishing processes, which can be harmful to the environment and human health. Fortunately, due to the general growth of education and awareness, responsible customer is beginning to form: costumer interested in the impact of purchased product on the environment. Textiles and fashion industry's negative impacts on the entire ecosystem are varied: spinning, weaving and industrial production are associated with non-renewable energy and waste; finishing processes, as dyeing and printing, consume vast amounts of water and chemicals, releasing numerous volatile agents into the environment. [19]

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 natural dyes are continually renewed in nature. So it might seem that natural dyes are not only environmentally friendly, health friendly, but above all cost-friendly. This is not the case at all!

Disadvantages - natural dyes

Industrial use of dyes from plants for dyeing of fibres is considerably limited by their high costs. Why? First of all, natural dyes have a significantly lower affinity to fibres, which causes the lower dye-exhaustion from bath on fibres. The dose of dyes must be at least one order of one magnitude higher and the majority of natural dyes remain in bath after dyeing, especially when trying to obtain dark shades. Moreover, the natural dyes and pigments are contained in plants in small quantities. We can also generally say that when dyeing a textile, we need one kilogram of dye plant for one kilogram of fibres. This creates a need to handle a large amount of biomass for obtaining them, thereby producing large quantities of waste. Where to put it? At the same time cost for transporting large volumes of plant material from the place of harvest to the place of processing is rising. Fortunately, some dyeing plant wastes are suitable as fertilizer or fuel.

Wild plants from open nature are certainly not usable for industrial textile production. Many dyes are obtained from tree bark, wood, and roots and it is difficult to obtain them without damaging the plant. Output of natural dyes as by-products from the timber industry may be viable but indiscriminate harvesting and tree cutting to get these materials only for dyeing purposes is sure to damage trees and lead to deforestation. Use of flowers has the danger of disturbing the natural pollination and reproduction cycle of plant species. Their harvest wouldn’t be quantitatively industrial effective, it would cause substantial destruction of the ecosystem and the many plants could additionally become endangered. [24]

To sum up: production cost of natural dyes from the direct harvest is very hight, use of plants from nature isn’t realistic.

Mordents - dyes bite

The term mordant comes from the present participle of French “*mordre*”, (to bite). Mordants cause the colour to 'bite' the fabric. And the need to use mordants is another serious problem in the dyeing with natural dyes.

This necessity arises from the fact that the molecular structure of most natural dyes is not ideal for interaction with fibers. The nature did not create them for this application, of course. Natural dyes have often small molecules resembling the disperse dyes suitable for dyeing of synthetic fibers and only slightly soluble in water. Those that have longer chains of molecules may slightly resemble the direct dyes. They bind to the fibres usually via hydrogen bonds and other weak interactions. In any event, generally, the sorption of natural dyes on the fibres is low, and thus is also related to poor fastness. Their sorption can be sometimes increased by additions of a neutral electrolyte to the bath like sodium chloride (NaCl) or Glauber's salt (Na2SO4), and especially by use of mordents.

Mordanting generally improves the dye-exhaustion to the fibres and achieves a broad spectrum of colours with large shade ranges and better fastness properties. Mordants are

not the only metal salts, such as sulphates (magnesium, aluminium, zinc, copper, cobalt, nickel, manganese or stannous sulphate), chlorides (stannic, ferric, copper, zinc, aluminium chloride and even rhenium, neodymium or zirconium trichloride or oxychloride), nitrates (aluminium nitrate), but also various hydroxides (calcium hydroxide) and oxides (ferric or lanthanum oxide). Most commonly used mordants in natural dyeing are aluminium potassium sulphate (alum, $KAl(SO4)2{\cdot}12H2O$), potassium dichromate ($K2Cr2O7$), stannous chloride ($SnCl2{\cdot}2H2O$), ferrous sulphate (green vitriol, $FeSO4{\cdot}7H2O$) and copper sulphate (blue vitriol, $CuSO4{\cdot}5H2O$). [25]

Mordants are one of the reasons why we cannot say that dyeing with natural dyes is an eco- friendly technology; the improved stability and deeper colour of fabrics can be achieved mostly with their very high concentrations (up to 15 g/litre) [26] 27] [28]! Same as natural dyes, the mordanting salts do not have affinity to the fibres and therefore only a small part of them is bounded with fibres. All the remnants are carried off by water after dyeing and final rinsing.

Many of metals are important micronutrients (they are necessary for the body in trace amounts), but generally, metals in soluble form (metal ions) acts on the organism as poisons. Depending on the dose, they block activity of enzymes; form deposits in the bones and tissues; form inactive or harmful structures by replacing some elements (e.g. lead replaces calcium in the bones, ions Cd^{+2} displace Zn^{+2} from native proteomic binding sites resulting in the formation of a Cd-proteome [29]), excess of iron, copper or zinc has a pro-oxidant effect and leads to increased oxidative stress via formation of harmful radicals or reactive oxygen species (ROS) molecules such as superoxide, hydrogen peroxide, the hydroxyl radical, and others.

Free iron, largely in the Fe^{+2} state is the toxic species that interacts with oxygen to form powerful oxidants, which directly damage protein and DNA. Toxic free iron levels occur in the presence of iron overload. Exposure to iron over time is associated with increased mortality, increased morbidity, risk of diabetes, and risk of cancer. The oxidative damage from iron comes mainly from the interaction of Fe^{+2} with $H2O2$ to produce hydroxyl radical ($HO\bullet$; Fenton reaction). Thus, when non-transferrin bound iron levels are high, severe oxidant damage can occur. [30]

Copper ion toxicity contribute to many health problems; including fatigue, premenstrual syndrome, depression, anxiety, migraine headaches, allergies, childhood hyperactivity and learning disorders [31].

Let us recall some of the reasons why in the recent years have been a trend to revive the art of natural dyeing: natural dyes should be non-toxic, harmless, environmentally friendly....

Do you see the paradox?

Improving traditional mordanting processes and selecting new mordants to replace traditional heavy-metal ions must be an important part in the development of natural dyeing of textiles.

So much water - natural dyes thirsty

The old technologies of dyeing consist of various steps that do not address modern demands and disregard the new possibilities offered by modern textile chemistry. The number of steps and duration of baths seem to be too high and non-productive: several hours soaking of fabrics before dyeing, multiple washing.

A large consumption of water and heat is used when washing, which is necessary to eliminate non-fixed dyes, reaction products or printing pastes. The reduction of water consumption also means a significant saving of heat. It is possible to apply more economical modern washing technologies - discontinuous (so-called "intelligent washing": in devices with very low liquor ratio that use recirculation of water) or continuous (e.g. controlled flow, stop valves, counter current washing, when heavily soiled fabrics come into contact with the dirtiest wash water). Installation for the mechanical dewatering at the output from the individual stages of tubes or machine reduces the transfer of pollution to the next stage of washing. It also saves water as it opens possibilities for reuse and recycling of waste water. These are modern technologies also require appropriate investment in the production. [33]

Traditional dyeing technologies are based on the bath dyeing when the fabric is completely immersed into dye liquor during dyeing. It means the bath ratio of 1:50, 1:100 and more, this causes a large consumption of water. This water should be cleaned from the remains of mordants before being discharged or ideally recycled. Of course, the high water consumption and water pollution from dyes and auxiliary chemicals is also the problem of bath dyeing with synthetic dyes. However, nobody claims that dyeing with synthetic dyes is an ecological dyeing! Moreover, an amount of synthetic dyes in the dye bath is much smaller. In contrast to synthetic dyes, natural dyes are considerably thermolabile and chemically unstable, so use of typical progressive applications (thermosolation, pressure dyeing or dyeing exceeding 100°C) is not possible. The most of natural dye in the bath is not used at all, it decomposes and becomes part of waste water together with the unused mordant salt. Storage of baths with residual mordanting salts for future use seems to be impractical possibility, due to the large volume of stock reservoirs.

To sum up: long time of material soaking before dyeing could be greatly reduced by wetting in a bath with suitable wetting agent as well as reducing of water consumption is possible with the use of modern technology such as e.g. smart washing and application of dye baths with very low liquor ratio.

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. This is an example of very progressive application of modern techniques in dyeing with natural dyes that is actively promoted by dr. Mongholrattanasit. [34]

Advantages - natural dyes

After all the negatives enumerated in previous chapters, some of the positives should be listed, they militate in favour of usage of natural dyes: [35]

- Experimental evidence for allergic and toxic effects of some synthetic dyes is available. Natural dyes are mostly non-toxic, non-allergic. Some of the natural colours have added value for its medicinal effects on skin and are more than skin friendly.
- Natural dyestuff can produce a wide range of colours by mix and match system. A small variation in the dyeing technique or the use of different mordants with the same dye (polygenetic type natural dye) can shift colours to a wide range or create totally new colours, which are not easily obtainable with synthetic dyestuffs.
- Unlike non-renewable basic raw materials for synthetic dyes, the natural dyes are usually renewable, being agro-renewable/vegetable based and at the same time biodegradable.
- Many plants thrive on wastelands. Thus, wasteland utilisation is an added merit of the natural dyes.
- In some cases the waste in the process becomes an ideal fertiliser for use in agricultural fields.
- This is a labour intensive industry, thereby providing job opportunities for all those engaged in cultivation, extraction and application of these dyes on textile. Natural dyes generate viable employment and income for the weaker section of population in rural and sub-urban areas both for dyeing as well as for non-food crop farming to produce plants for the natural dyes.
- Application of natural dyes has potential to earn carbon credit by reducing consumption of fossil fuel (petroleum) based synthetic dyes.
- The shades produced by natural dyes are usually soft, lustrous and soothing to the human eye.
- Natural dyes are suitable for protecting and preserving the ancient and traditional dyeing technology and for studying the ancient dyeing methods, coloured museum textiles and other textiles recovered by archaeology for conservation and restoration of heritage of old textiles.

Are all this arguments sufficiently strong to justify a large consumption of water and its contamination with metal ions?

3. CONCLUSION

The organising principle for viability is viable development, which includes ecology, economics, politics, culture, social impact and human health.

Availability and use of natural dyes in the current state raises big concerns about the viability of the concept. Less expensive production of natural dyes and affordable industrial application methods are needed. Also large water consumption and the amount

of often unnecessary or unnecessarily long working operations should be reviewed in the context of cost savings and considerate approach to nature.

Only selected natural dyes and pigments (e.g. indigo, alizarin dyes, tannins, flavonoids) may compete with synthetic dyes for quality and stability. At the current level of world textile production, natural dyes can replace only a fraction of the total consumption of textile dyes.

Coloured waste utilisation mainly from food, beverage and timber industries is practically applicable only in limited cases, growing dye plants is particularly important when using marginal soils. Land availability for growing natural dyes is limited in view of the first preference to food and fodder crops. Some important dye plants, including madder and indigo or woad, can be cultivated on marginal and wastelands to enhance their availability. Use of metallic mordants with natural dyes is incompatible with the concept of eco-friendliness of natural dyes. Seasonal availability of natural resources, tedious process of their processing and extraction of dyes, necessity of processing and possibly transport of large amounts of plant materials and subsequent problem with resulting waste, ineffective dye exhaustion from the dye bath, contamination of land and water resources by metallic mordants, unstable and not reproducible hues and often bad fastness together with high costs are the main reasons hindering the wider use of natural dyes in textile dyeing. Sum up: implementation of the current methods of natural dyes production and their use in the textile dyeing industry in global dimension would lead to an environmental disaster.

At the level where scientific developments stand today, natural dyes are a viable option only for small-scale applications and they can only complement synthetic dyes. They can be considered as best suitable on the cottage level, for small scale industries, manufactories, hobby groups, and craftsmen.

REFERENCES

[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: 214-223

[2] Gulrajani, M. L.: *Present status of natural dyes.* Indian Journal of Fibre and Textile Research (2001), 26.1(2): 191-201

[3] Furry, M. S., Viemont, B. M.: *Home dyeing with natural dyes.* U. S. Dept of Agriculture (1935), (reprint. by Thresh Publications)

[4] Kierstead, S. P.: *Natural dyes*. Bruce Humphries, Inc., Boston (1950)

[5] Davidson, M. F.: *The Dye-Pot*. Gatlinburg, Tenn.: privately printed (1950)

[6] Conley, E., Lewis, M.: *Vegetable Dyeing*. Paperback, Panland School of Crafts, Penland, N.C. (1960)

[7] Adrosko, R. J.: *Natural dyes and home dyeing. (formerly titled: Natural Dyes in the United States).* Courier Corporation, New York (1971), Vol. 281

[8] Buchanan, R.: *A Weaver's garden: growing plants for natural dyes and fibers.* Dover, New York (1987)

[9] Glassie, H. H.: *Turkish Traditional Art Today* (No. 11). Indiana University Press (1993)

[10] Ayliffe, R.: *The rough guide to Turkey*. London: Rough Guides (2003)

[11] Böhmer, H. et al.: *Koekboya- Natural Dyes and Textiles: a Colour Journey from Turkey to India and Beyond*. Remhöb-Verlag, Ganderkesee, Germany (2002)

[12] Grierson, S, Duff, D. G., Sinclair, R. S.: *Natural dyes of the scottish highlands.* Text Hist (1985), 16(1): 23–43

[13] Grierson, S.: *Vegetable Dyes of Scottland*. J Soc Dyers and Colourists (1984), 100: 209-211

[14] Bechtold, T., Mussak, R.: *Handbook of Natural Colorants*. John Wiley and Sons (2009)

[15] Siva, R.: *Status of natural dyes and dye-yielding plants in India*. Current Science-Bangalore *(2007), 92*(7): 916

[16] Samanta, A. K., Priti, A.: *Application of natural dyes on textiles*. Indian Journal of Fibre & Textile Research (2009), 34: 384-399.

[17] Hill, D. J.: *Is there a future for natural dyes?* Review of Progress in Coloration and Related Topics (1997), 27(1): 18-25

[18] Cardon, D.: *Natural dyes: sources, tradition, technology and science*. London: Archetype (2007)

[19] Carvalho, C., Santos, G.: *Global Communities, Biotechnology and Sustainable Design – Natural / Bio Dyes in Textiles*. Procedia Manufacturing (2015), 3: 6557-6564

[20] Vankar, P. S.: *Chemistry of natural dyes*. Resonance (2000), 5(10): 73-80

[21] Punrattanasin, N. et al.: *Silk fabric dyeing with natural dye from mangrove bark (Rhizophora apiculata Blume) extract*. Industrial Crops and Products (2013), 49: 122– 129

[22] Mongkholrattanasit, R., Kryštůfek, J., Wiener, J.: *Dyeing of wool and silk by eucalyptus leaves extract*. Journal of Natural Fibers (2009), 6(4): 319-330

[23] Green, C. L.: *Natural colourants and dyestuffs. A review of production, markets and development potential. Non-wood forest products, No.4.* Food and Agriculture Organization of The United Nations, Rome (1995, reprinted 2003)

[24] Saxena, S., Raja, A. S. M.: *Natural Dyes: Sources, Chemistry, Application and Sustainability Issues*. In: Roadmap to Sustainable Textiles and Clothing: Eco-friendly Raw Materials, Technologies, and Processing Methods, Springer Singapore (2014): 37-80

[25] Shahid, M., Shahid-ul-Islam, Mohammad, F.: *Recent advancements in natural dye applications: a review*. Journal of Cleaner Production (2013), 53: 310-331

[26] Karaboyaci, M., Uğur, S. S.: *Ecological wool dyeing with pulps of lavender, broom, and red wine*. The Journal of The Textile Institute (2014), 105(8): 821-827

[27] 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: 2589-2595

[28] Arroyo-Figueroa, G. et al.: *Cotton fabric dyeing with cochineal extract: influence of mordant concentration*. Coloration Technology (2011), 127: 39–46

[29] Ali, M. et al.: *Toxic metal proteomics: Reaction of the mammalian zinc proteome with* Cd^{2+}. Journal of Inorganic Biochemistry (2014), 136: 115-121

[30] Puliyel, M. et al.: *Iron toxicity and its possible association with treatment of Cancer: Lessons from hemoglobinopathies and rare, transfusion-dependent anemias*. Free Radical Biology and Medicine (2015), 79: 343-351

[31] Shahat, A., Ali, E. A., El Shahat, M. F.: *Colorimetric determination of some toxic metal ions in post-mortem biological samples.* Sensors and Actuators B: Chemical (2015), 221: 1027-1034

[32] Brewer, G. J.: *Copper toxicity in the general population*. Clinical Neurophysiology (2010), 121: 459–460

[33] Oborový manuál prevence a minimalizace odpadů. Výroba textilu. Inotex, s.r.o. Dvůr

Králové n.Labem. On line: <http://www.inotex.cz/docs/oborovy_man.pdf>

[34] 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): 1229-9197

[35] Samanta, A. K., Konar, A.: Dyeing of Textiles with Natural Dyes. Natural Dyes (2011), 3: 29-56

[36] 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

[37] Shahid-ul-Islam, Shahid, M., Mohammad, F.: *Perspectives for natural product based agents derived from industrial plants in textile applications – a review*. Journal of Cleaner Production (2013), 57: 2-18

[38] Minganti, V. et al.: *The bark of holm oak (Quercus ilex, L.) for airborne Cr(VI) monitoring*. Chemosphere (2015), 119: 1361-1364