DYEING COTTON FABRICS WITH NATURAL MORDANT DYES PLANT ORIGIN

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Abstract: *Given the global problems of the textile industry, there is increasing interest in revitalizing the use of natural dyes, with an emphasis on cellulose materials. This investigation presents the dyeing of cotton with natural mordant dyes plant origin. The following dye sources were selected: Stems and leaves of goldenrod, willow bark, stems with leaves and flowers of St. John's wort, hawthorn twigs with leaves and oak galls. All selected plants belong to the group of acid-mordant dyes due to their dyeing properties and bind to the fabric by forming a complex with metal salts (mordants). For this reason, the cotton material was treated with potassium aluminium sulphate dodecahydrate* $KAl(SO_4)_2 \cdot 12H_2O$ *and iron(II) sulphate heptahydrate* $FeSO_4 \cdot 7H_2O$*. Through the formation of the ligand: cotton fibre – metal ion – natural mordant dye, a wide range of harmonious shades was obtained. The dyes obtained were evaluated by subjective and objective spectrophotometric analysis. In addition, the fastness to laundering and artificial light was tested, which guarantees both the aesthetic and functional quality of the cotton fabrics dyed in this way.*

Key words: natural dyes, mordants, cotton, heritage, colour fastness, spectrophotometry.

BOJENJE PAMUČNIH TKANINA PRIRODNIM MOČILSKIM BOJAMA BILJNOG POREKLA

Sažetak: *S obzirom na svetske probleme tekstilne industrije sve više se javlja interes revitalizacije primene prirodnih boja sa naglaskom na celulozne materijale. Ovo istraživanje prikazuje bojenje pamuka biljnim prirodnim močilskim bojilima. Odabrani su sledeći izvori bojila: stabljike i listovi zlatnice, kora vrbe, stabljike sa listovima i cvetovima kantariona, grančice gloga sa listovima i hrastove šišarke. Sve odabrane biljke pripadaju grupi kiselo-močilskih boja zbog svojih svojstava bojenja i vezuju se za tkaninu formirajući kompleks sa solima metala (mordantima). Iz tog razloga je pamučni materijal tretiran kalijum aluminijevim sulfatom dodekahidratom* $KAl(SO_4)_2 \cdot 12H_2O$ *i gvožđe(II) sulfatom heptahidratom* $FeSO_4 \cdot 7H_2O$*. Formiranjem liganda: pamučno vlakno – metalni jon – prirodna močilska boja, dobijen je širok raspon harmoničnih nijansi. Dobijene boie vrednovane su subjektivnom i objektivnom spektrofotometrijskom analizom. Pored toga, testirana je postojanost na pranje i veštačko svetlo, što garantuje estetski i funkcionalni kvalitet obojenih pamučnih tkanina na ovaj način.*

Ključne riječi: prirodna bojila, močila, pamuk, baština, postojanost obojenja, spektrofotometrija.

1. INTRODUCTION

The use of natural dyes and pigments goes back thousands of years, in all civilizations from Asia, Africa, Europe to North and South America (Fig. 1). Even before people began to decorate textiles, primarily for protection, they were painting with earth pigments in caves such as Niaux in France and Altamira in Spain. Another example is the Egyptian pyramids and temples, which were also painted with natural colours. In the ancient cultures of the Mediterranean, among the

Phoenicians, Egyptians, Greeks and Romans, painting was established as a craft. The members of these cultures valued finely dyed silk and woollen fabrics. In medieval Europe, dyers had already developed well-established and organized guilds (Fig. 2). They reached their peak at the end of the 13th century, even before the Renaissance, thanks to guild systems that maintained a high standard of quality. In addition to the master dyers, who worked to the highest possible standards, apprentices also worked and learned in the guilds. The masters were responsible for dyeing textiles destined for the nobility and clergy (Fig. 3). For those who were not members of the guild, there were prohibitions on owning or using dyes [1-5].

Figure 1: Archaeological discovery of 4,000-year-old kermes-dyed textiles found in caves in the Judean Desert in 2016 (Middle Bronze Age between 1,954 and 1,767 BC) [6]

Figure 2: Coat of arms of the dyers' guild in the German town of Mammingen [7]

Figure 3: Polychrome velvet with a variation of a Medici emblem [8]

In the middle of the 19th century, the first synthetic dyes came onto the market and the need to use natural dyes diminished and practically disappeared. Nowadays, however, we know that synthetic dyes lead to an increased accumulation of toxic components in organisms at every stage of the food chain due to their persistence in the environment. These components are not only harmful and even carcinogenic, but have also been linked to degenerative diseases in animals. This is also linked to the problem of modern agriculture and food growing, which also have devastating effects on soil, water, humans and animals. These industries are closely linked, so it is not surprising that they are already having a negative impact on humans. Another major problem is the energy required for conventional dyeing processes. Large amounts of energy, coal to be precise, are required to keep the bath temperatures constant. As a result, this phase of the process alone accounts for 75-90% of energy emissions. The above is a condensed version of the problems facing the modern textile industry. Therefore, working with natural dyes and local nature wherever possible is one of the best solutions to preserve and restore biodiversity and strengthen the connection of consumers with the processes that lead to the final product [9-11]. To deepen the knowledge and connection with local habitats, this investigation will focus on researching invasive plants and plant pests as well as other species of native and waste plants.

Natural dyes can be classified according to their colouring properties, their chemical composition, their origin (from plants, animals, minerals), their hue or their fields of application (food industry, pharmaceutical industry, textile industry, etc.) [1-3, 12]. In terms of their colouring properties, most natural dyes are classified as acid dyes, less frequently in the group of direct dyes (e.g. turmeric), and plants from the indigo family belong to the vat dyes. Chemical compounds that are extracted from plants and belong to the group of mordant dyes are mostly flavanoids and tannins [1-3, 12]. Mordant dyes give different colours by complexing with metal salts (mordants) - these dyes have polygenetic properties. Aluminum, copper, iron and tin salts are most commonly used as mordants. These dyes are most commonly used for protein fibers with: pre-treatment of the fibers (before dyeing), simultaneous (together with the dyeing) or post-treatment (after dyeing). This can be seen in the colouriation of the folk costumes (Fig. 4). Cellulosic materials (flax, hemp, nettle, cotton) were bleached, and wool and silk protein fabrics were dyed with mordant natural dyes of plant origin [3, 4, 12, 13].

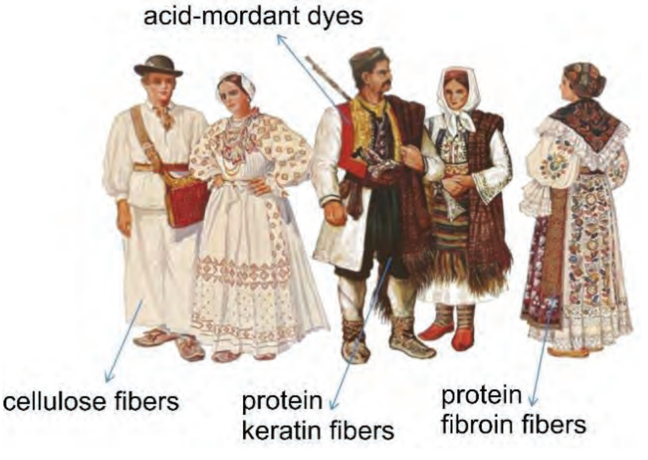


Figure 4: The presence of acid-mordant dyes in folk costumes [3, 4]

However, considering the demands of today's market and fashion designs, recent scientific research has focused intensively on the application of mordant dyes for cellulosic textiles [5, 14]. The colouration of cellulosic materials and their properties are the result of the formation of ligands between the hydroxyl group of cellulose, metal ions and hydroxyl groups of cellulose and chemical compounds extracted from selected plants (Fig. 5) [1-3, 12, 15, 16]. Furthermore, textiles with natural dyes are now expected to have multifunctional properties in addition to beautiful harmonious tertiary colours. This refers to antibacterial, antiinflammatory, antiallergic, antimutagenic and anticarcinogenic properties and protection against dangerous UV radiation. These properties of textiles are based on the properties of chemical compounds extracted from plants [16-22].

2. EXPERIMENTAL

2.1. Textile material

It was used 100 % chemically bleached cotton fabric in plane weave from producer Čateks d.o.o., Čakovec, Croatia. Textile has the following structural characteristics: weight 140.00 g/m^2, density in warp direction 32.4 cm^{-1}, density in weft direction 32.4 cm^{-1}.

2.2. Natural dyes sources selection

Local and readily available plants collected in the Croatian in the rural surroundings of the city of Zagreb were selected as a source of dyes. The focus was on the use of local invasive plants, forest litter and pests that occur on other plants and trees. To preserve natural habitats, the plants for the work were collected with great care from nearby fields and forests. The plants were cut with scissors so that the roots were not torn out of the ground and so that the quantity of plants harvested in one place could be controlled. When we collect plants in nature, it is important to take less than we need so that the plants can self-seed the following year. When collecting tree bark, care was taken to ensure that only bark from already visited trees and fallen branches was collected, at no point was bark removed from living and healthy trees.

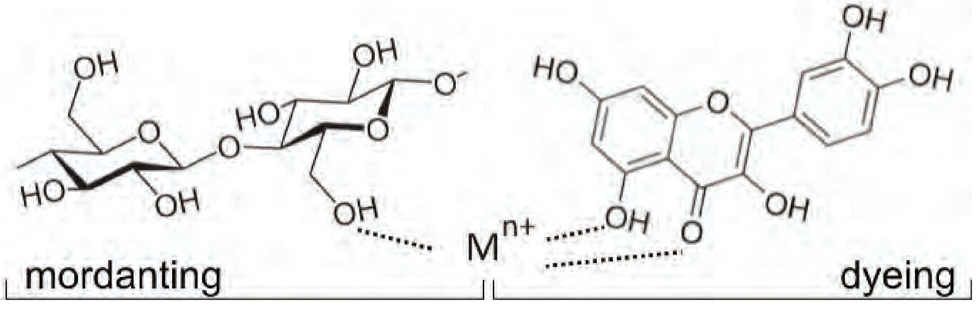


Figure 5: Schematic representation of the formation of the ligand: cotton fiber – metal ion – natural mordant dye [5]

The following dye sources were selected for the work: goldenrod stems and leaves, willow bark, St. John's wort stems with leaves and flowers, hawthorn twigs with leaves and oak galls.

Goldenrod *(Solidago, L.)* is known as an invasive species because it spreads rapidly, especially in open areas such as fields, meadows and roadsides, where it forms dense clumps that prevent the growth of other plants (Fig. 6). Goldenrod also has the ability to change the composition of the soil, affecting the diversity and abundance of other plant species. For all these reasons, goldenrod can have a negative impact on the ecosystems in which it has colonised. The goldenrod used for the study was harvested in early June, i.e. not in the flowering phase, and fresh stems and leaves were used. Goldenrod is a herbaceous perennial of the sedge family that branches only in the upper part and grows up to 120 cm tall, while some species can reach a height of 250 cm. Goldenrod grows in the temperate regions of Europe, Asia, North Africa and North America. In phototherapy, the above-ground part of the plant is used, which is carefully collected and dried during the flowering period. Many people in North America, including the Hopi and Navajo Indians and the Dutch in Pennsylvania, valued golden root as a source of dye. Its dyeing and medicinal properties are due to its chemical composition, which contains flavonoids and tannins. In addition to its dyeing properties, this plant also has significant medicinal properties. Goldenrod has been used to treat tuberculosis, diabetes, asthma, arthritis and more. It has also been used to treat urinary tract infections, kidney stones and bacterial infections of the urinary tract [2, 23, 24].

Figure 6: Goldenrod plant [25]

The ***willow tree*** *(Salix, L.)* is a deciduous shrub or small tree from the willow family (Fig. 7). It can grow up to 12 m high and has a dense and irregular crown. It is widespread in Europe and Southwest and Central Asia. It prefers sunny and semi-shady, moist locations along rivers, streams or lakes and on forest edges. It has medicinal properties and is a good honey plant. The bark is collected in spring and peeled from the thin twigs. It is used to reduce fever, relieve pain, promote sweating and aid the elimination of toxins from the body. Due to its content of salicylic compounds, it is also used for problems with rheumatism and gout [2, 26, 27]. In this work, the bark was collected from a local field after the owners had felled the trees and left them behind. In addition to the outer, exposed bark, the bark from the roots was also collected after the trees were felled, which preserves the pigment even more due to the higher moisture content. The bark used for this work was collected in the fall of 2022.

Figure 7: Willow tree [25]

St. John's wort *(Hypericum perforatum, L.)* - in this work, the entire stem was used for dyeing, with the exception of the roots (Fig. 8). The plant was collected in several places in late June and early July and cut with scissors to preserve its natural habitat [18]. St. John's wort is a perennial herbaceous plant from the hypericaceae family. The stem is erect, branched in the upper part, glabrous and grows up to 80 cm high, in the local habitat even up to 100 cm. It often grows in groups, sometimes as a solitary plant. It likes sunny meadows and nutrient-poor grasslands, forest edges. The plant was called St. John's wort because of the red pigment hypericin, which is released when the bud is crushed. The colour that is released symbolizes the blood of John the Baptist. Over the centuries, various magical and mystical properties have been attributed to the plant itself. It is in full bloom on June 24, Midsummer's Day, during the summer rituals. Scientific research has shown that it has stronger antidepressant properties than some medicines. In Germany, it has a medical license, so it is prescribed for depressive conditions and sells eight times more antidepressants than Prozac. It has antiseptic and anti-inflammatory properties, heals wounds quickly and is often used to make oils and creams. Care should be taken when using it on the skin when exposed to the sun as it can cause skin sensitivity and irritation [2, 28].

Figure 8: St. John's wort [25]

Hawthorn *(Crataegus, T.)* belongs to the genus of shrubs or small trees in the rose family (lat. Rosaceae) (Fig. 9). There are several species, the most important of which are the hawthorn and the redthorn. They grow up to 15 meters high, although on average they are only about 5 meters tall. They grow wild on the edges of forests and fields, often among other shrubs and bushes. Hawthorn was associated with festivals to celebrate summer as it blooms in May, hence the English name mayblossom. Hawthorn was considered a sign of good and bad luck. In Europe, it is an important medicinal plant. It is known for its effect on the circulation, strengthening the heart and lowering blood pressure. In addition to its medicinal uses, it was also used in food. In the past, the leaves and berries were eaten as a spread and the young shoots were cooked in sour puddings. Fresh flowers were added to whipped cream and creamy desserts because of their special aroma. The flesh of the hawthorn, which ripens in the fall, is dry and mealy. The berries taste sour, but become tasty after the first frosts. They can then be used to make jams or compotes and jellies [2, 29]. Twigs cut with scissors from the local hawthorn habitat at the edge of the forest were used for the work. The harvest time was early July, so the berries were not yet ripe.

Oak galls or cecidia are smooth or spiky spherical formations on oak leaves, a round or spherical growths on the plant tissue that varies in size (Fig. 10). They are

Figure 9: Hawthorn [25]

formed by the action of some species of insects, mites, roundworms, phytopathogenic fungi and bacteria. The formation of cecidia on oak leaves is caused by the wasp *cynips gallae*. The females lay their eggs in the tissue of the host plant, where the larva develops, which then secretes substances to which the plant organism reacts with an increased accumulation of tannins, deformations and abnormal growth. During the biochemical process that takes place in the infested plant, specific chemical substances accumulate, such as: tannins, flavonoids, anthocyanins, phenolic acid, saponins, alkaloids, etc. They have antibacterial, antifungal, antiviral and antiparasitic properties. They are used to treat various inflammations, infections, acute diarrhea and bleeding. In addition to their excellent medicinal properties, they have also been used since time immemorial for the production of ink and for tanning. Oak gall ink, also known as gall ink, is a type of ink traditionally made from oak cones – oak galls. The galls are collected from oak trees, dried, ground and then boiled with vinegar and water to release the tannins contained in the galls. The first Bibles were written with this ink because it was resistant to water and light [2, 26, 30, 31]. Oak galls collected between fall 2021 and spring 2023 were used for this work. After collection, they were left outside to dry and ground by hand in a marble mortar before dyeing.

2.3. Natural dye extraction

Dye extraction was performed in soft water (1.27 µS) in a 1:40 bath ratio (considering the mass of the plant) at 100 °C for 60 min. The bath was then allowed to cool for 24 h and the extract was decanted.

Figure 10: Oak galls or cecidia [25]

2.4. Mordanting

All selected plants belongs to the group of acid-mordant dyes due to their dyeing properties and bind to fabric by forming a complex with metal salts (mordants). For this reason, cotton material was treated with potassium aluminium sulphate dodecahydrate $KAl(SO_4)_2 \cdot 12H_2O$ and ferrous (II) sulphate heptahydrate $FeSO_4 \cdot 7H_2O$; (Kemika, Zagreb, Croatia). Mordanting with metal salts was performed with 5% mordants (based on the mass of the material) in a bath ratio of 1:30 at 50 °C for 30 min. Treatment with aluminium salt was preformed as pre-dyeing process, and treatment with iron salt was preformed as post-dyeing process.

2.5. Dyeing with natural dyes

Dyeing with natural dyes was performed with a bath ratio of 1:30 at 100 °C for 60 min. After dyeing, the cotton material were rinsed with cold water and soaped with comercial detergent Burti Liquid, Burnus GmbH, Germani.

2.6. Colour Analysis

Colour characteristics were measured using a remission spectrophotometer, Datacolour 850, measuring geometry d/8°, illumination D65, and measuring aperture of 9 mm. The coordinates used to determine colour values are L* for lightness, a* for redness (positive value) and greenness (negative value), b* for yellowness (positive value) and blueness (negative value), C* for chroma and h° for hue angle in the range of 0° to 360°. Colour coordinates of undyed and dyed cotton yarns were determined according to ISO 105-J01:1997 Textiles-Tests for colour fastness-Part J01: General principles for measurement of surface colour. All results were measured on samples by repeating the measurement procedure at random locations. Thus, the colour measurements were made using the Datacolour Tools computer program and "Measuring until tolerance" command, which means that at least 10 measurements must be made, and the results are accepted only if the total colour difference between each measurement is less than 0.1 (dE* < 0.1).

2.7. Colour fastness to laundering

Colour fastness to laundering of printed materials were tested in a laboratory apparatus for wet processes Polycolour (Mathis, Switzerland). The test was performed according to standard ISO 105-C06:2010 (A2S) Textiles-Tests for colour fastness-Part C06: Colour fastness to domestic and commercial laundering, using 2 g/L of standard detergent (James Heal ECE A, without optical brighteners and without phosphates), with a bath ratio of 1:20, temperature of 40 °C, time of 30 min. The results of fastness to laundering are given as numerical values of total colour difference (DE) calculated according to equation (1).

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

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

2.8. Colour fastness to artificial light

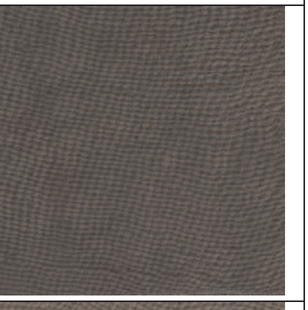
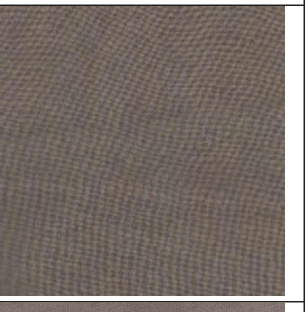
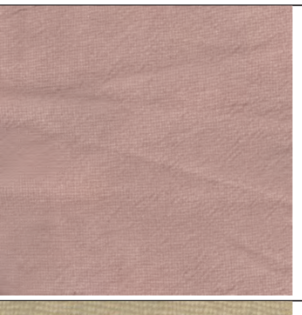
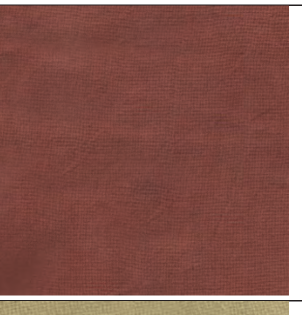
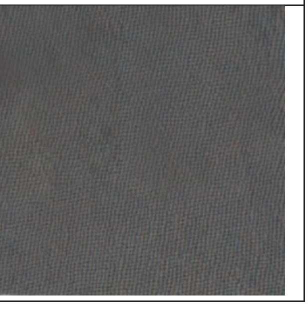
Colour fastness to artificial light were performed on Xenotest 440 ((SDL Atlas, Rock Hill, SC, USA). Xenotest 440 is used for laboratory simulation of external weather influences on the stability and durability of textile and other materials. Analysis was evaluated according to the modified ISO 105-B02 and 13 B04 test methods using Xenotest 440. Test conditions simulated in this research were: Total light time: 41:10 h, Radiant exposure: 6226 kJ/m2, Irradiance control: 300–400 nm, Filter system: B04, E: 42 W/m2 (± 2 W/m2), CHT: 32 °C (± 3 °C), BST: 47 °C (± 8 °C), RH: 40 % (± 8 %), no spray, fan speed: 2000 rpm. Using the same equation as for the fastness to laundering (1), the artificial light fastness properties was also evaluated by calculating total colour difference values (DE).

3. RESULTS AND DISCUSION

It should be emphasized that this research represents an important contribution to the revival of natural plant dyes for textiles and their application to cellulosic materials. The results presented show the importance of spectrophotometric measurements for the evaluation of the obtained colourations and their fastness. However, subjective experience is very important in the application of natural dyes.

The visual subjective evaluation of the cotton fabrics dyed with natural mordant dyes is shown in Table 1. It can be seen that the obtained colourations have good uniformity. All the observations seen in Table 1 were also confirmed by objective spectrophotometric

Table 1: Samples of cotton fabrics dyed with natural mordant dyes

Plant [32]	**Mordant**		
	—	**Al**	**Fe**
Goldenrod 			
Willow 			
St. John's wort 			
Hawthorn 			
Oak galls 			

measurements. The obtained colouristic parameters lightness (L*), chroma (C*) and hue (h°) are listed in Tables 2 to 6, and Figure 11 shows the colour analysis in the a*/b* colour space. All colourations are the result of two parameters: the choice of plants and metal salts (mordants). As explained in Figure 5, the ligand is formed during dyeing: cotton fiber – metal ion – natural mordant dye. The use of a dye extracted from the golednrod plant without mordant results in an achromatic, greyish colour, while the addition of aluminum results in a bright yellow and iron in a dark brown colouration. However, analysis of the colour parameters in Table 2 and Figure 11 shows that all three samples are in the yellow range, i.e. h°>88. In the case of the willow plant, it is already subjectively apparent that pinkish to brownish-red tones were obtained, with h° (Table 3, Figure 11) in the range 57.34 to 64.51. Without mordant, the St. John's wort plant gives a grayish colour with an indistinct tone, with the addition of aluminum ochre and with the addition of iron a gray-brown colour. However, the spectrophotometric tone is in the range of yellow tones (Table 4) from 74.82 to 81.41. With the hawthorn plant (Table 5, Figure 11) in combination with aluminum, the brightest red colour was obtained (h°=43.69), while without mordant and with the addition of iron, the colour intensity visibly decreases. Oak galls produced the expected dark colour with iron. Table 6 shows that the colour hue is in the yellow range.

When comparing the samples in Table 1 with the indicated tone values determined by spectrophotometric measurements, it becomes clear that the subjective perception of natural dyes is also significantly influenced by other colouristic parameters, i.e. lightness (L*) and chroma (C*). The colours obtained with aluminum as a mordant have the highest chroma value for each plant, with the colouration obtained from goldenrod standing out for yellow hues (C*=50.17). For red shades, the colouration obtained from the hawthorn plant has a C*=32.57. It can also be observed that the lightness value (L*) is significantly influenced by the addition of iron. All samples in Table 2 are dark brown, without a specific tone.

Table 2: Spectrophotometric analysis of cotton fabrics dyed with a dye extracted from goldenrod stems and leaves

Mordant	L*	a*	b*	C*	h°
–	68.85	0.60	20.51	20.52	88.34
Al	68.27	1.32	50.15	50.17	88.50
Fe	49.85	-0.48	12.50	12.51	92.21

Table 3: Spectrophotometric analysis of cotton fabrics dyed with a dye extracted from willow bark

Mordant	L*	a*	b*	C*	h°
–	70.15	10.21	15.93	18.92	57.34
Al	64.53	9.84	20.64	22.86	64.51
Fe	50.34	2.43	4.01	4.69	58.75

Table 4: Spectrophotometric analysis of cotton fabrics dyed with a dye extracted from St. John's wort stems with leaves and flowers

Mordant	L*	a*	b*	C*	h°
–	61.21	3.90	14.36	14.88	74.82
Al	55.97	5.28	28.21	28.70	79.39
Fe	48.84	1.38	9.12	9.22	81.42

Table 5: Spectrophotometric analysis of cotton fabrics dyed with a dye extracted from hawthorn twigs with leaves

Mordant	L*	a*	b*	C*	h°
–	69.69	13.49	9.6.	16.56	35.46
Al	41.28	23.55	22.49	32.57	43.69
Fe	52.97	3.53	4.83	5.98	53.89

Table 6: Spectrophotometric analysis of cotton fabrics dyed with a dye extracted from oak galls

Mordant	L*	a*	b*	C*	h°
–	70.93	4.10	21.23	21.63	79.06
Al	66.78	3.50	26.90	27.12	82.58
Fe	42.25	1.48	3.75	4.03	68.44

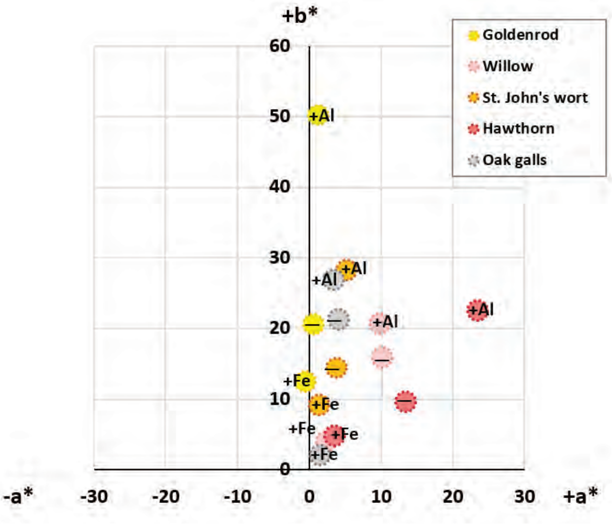


Figure 11: Colour analysis in the a*/b* colour space

In view of the interest of the fashion industry and the market for natural dyes on cotton fabrics, the fastness of the dyes to laundering and artificial light was tested. In addition to the selection of plants for dye extraction, the influence of metals was also monitored. The fastness value provides indirect information about the strength of the resulting bonds.

Fastness is indicated by the value of the total colour difference (dE), which comprises the difference between the fabrics before and after treatment for all coloristic parameters; a larger colour difference indicates poorer fastness.

Figure 12 shows the wash fastness and it can be seen that the addition of metals significantly improves the fastness of the dye. The influence of aluminum and iron is different for different plants due to the chemical structure of the plant pigment. Figure 13 shows the results of the artificial light fastness test. It can be observed that the addition of metal reduces the fastness, i.e. coloured compounds are formed that are unstable when exposed to light for a longer period of time. This applies in particular to the aluminum stain in all plants except oak galls. Of the plants tested, oak galls contain the most tannins and the formation of compounds between plant pigments and metal ions is more stable.

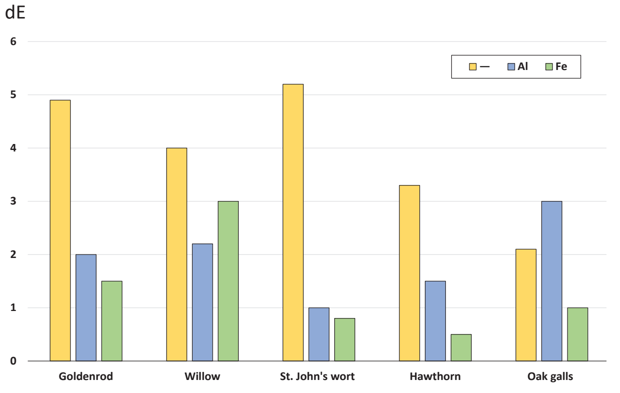


Figure 12: Fastness to laundering

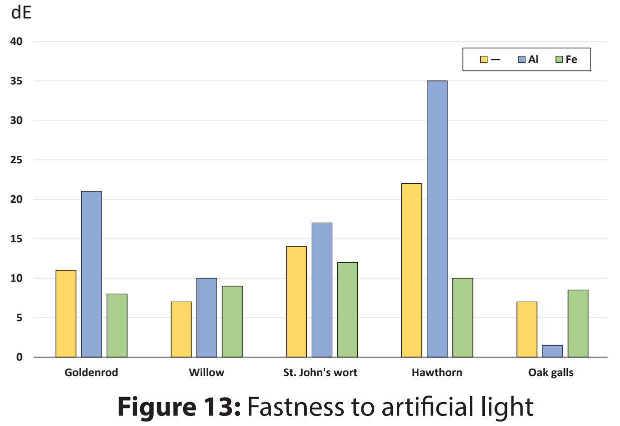


Figure 13: Fastness to artificial light

4. CONSLUSION

On the basis of the investigations carried out, it can be concluded that natural mordant dyes can be successfully used for dyeing cotton fabrics. When selecting and collecting plants, attention should be paid to the environment and the preservation of the plants' habitat.

By choosing different plants and metal salts as mordants, a wide range of beautiful, harmonious shades can be achieved. However, the intended use of such materials should be taken into account. Depending on the function and desired fastness, suitable metal salts should be selected that form stable complexes with the plant pigments. In order for cotton fabrics dyed with natural plant dyes to have a satisfactory functionality in addition to aesthetics and to find their place on the market, it is necessary to carry out laboratory tests in advance, i.e. to optimise all process parameters.

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