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Suitability of apple tree bark as a natural source for cotton dyeing

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Abstract: *Suitability of apple tree bark as a natural source for cotton dyeing*. The study of dyeing cotton fabric with apple bark extract with the use of mortars - inorganic aluminum, tin, iron and copper salts, moreover oxalic acid and without mortar. The color of the fabric was determined using the CIE L*a*b* system. The result was a yellow color of varying shades, ranging from lemon to warm, intense yellow. In the case of iron and copper, a significantly different color was obtained, dark khaki and rusty brown respectively. Color fastness tests were carried out using hot water, mineral acid, mild and hot washing, dry cleaning and natural exposure to sunlight. It has been found to have excellent resistance to dry cleaning and good to a gentle wash. Dyed fabric showed the weakest resistance to sunlight and to mineral acid.

Keywords: apple bark, dye, mordant, color fastness

INTRODUCTION

Natural dyes have been known and commonly used since the prehistoric era for coloring such materials as wood, leather and natural fibers like linen or cotton (Samanta & Agarwal 2009). By using different parts of plants people were able to create many different colors and shades, which gave them variety of options. However, in 1856 synthetic dyes got invented and due to their low price, wide range of colors and better color fastness (El-Nagar et al. 2005), nowadays they almost completely dominate fashion industry. Although synthetic dyes have many advantages, producing and using them causes pollution by releasing toxic chemicals and producing a huge amount of waste, which creates a threat to human health and natural environment (Samanta & Konar 2011), making this solution non-ecological. For this reason, the fashion industry is known for being one of the most polluting ones (Niinimäki 2020).

Nowadays, the world is more focused on spreading awareness about the environment and ecology. As people expand their knowledge and become more aware of the dangers caused by pollution, they become more interested in buying products that are made from natural and eco-friendly friendly materials. Due to low toxicity, being less harmful to the environment, more biodegradable and causing less allergic reactions (Ali & El-Mohamedy 2011), natural dyes start coming back to use. They are not as durable as synthetic ones, therefore, to receive a satisfactory effect, they require the use of mordants in order to create a bond between the dye and the fibers of the material. Mordants are also supposed to improve the quality and fastness of the resulting color (Saxena & Raja 2014). There is a range of inorganic mordants, used for centuries, like iron, copper or tin salts (Singh & Bharati 2014). In antiquity they were coming form metal vessels for dyeing (Abdel-Kareem 2012), today are added on purpose, including environmental harmfull chromium(VI) salts or alum (Clark 2011). Mordants of natural origin are considered as well, like oxalic acid containing plants (rhubarb) or tannin sources (bark) (Wangatia et al. 2015, Clark 2011).

Apple trees have little industrial importance, but large amounts of trees from the renewal of fruit orchards can be a potential source of raw material. Apple tree bark is bitter, due to the presence of phloridzin (phloretin-2′-β-D-glucopyranoside) (Táborský et al. 2021). It contains a number of color substances, like chlorogenic acid (green when oxidized) or yellow

quercetin derived rutin (quercetin-3-O-rutinoside) and quercitrin (quercetin O-glycoside) (Adamcová et al. 2022). Extract of tree bark is know of antimicrobial activity (Švarc-Gajić et al. 2021) and is proposed as a component of anti-ageing cosmetics (Leconte & Leclere 2013), which confirms that it can be safely used on human clothing.

MATERIALS

Materials

Commercial white fabric (100 % cotton) was used in all tests.

Apple tree branches (*Malus domestica* Borkh.) were cut from the garden tree in Rembertow district of Warsaw. Relative moisture content of the bark was determined as 4,1 % by oven drying at 105 °C. Bark extract was obtained by boiling 40 g of bark in 300 cm³ of tap water. Fresh bark was placed in a glass vessel, then in a water bath and kept at 98 °C for 90 min. Obtained extract was filtered with fast filter paper.

Chemicals used as mordants were 2 % solutions of a single of following compounds (p.a. class):
Ferric chloride ($FeCl_3 \cdot 6H_2O$),
Stannous chloride ($SnCl_2 \cdot 6H_2O$),
Alum ($AlK(SO_4)_2 \cdot 12H_2O$),
Copper(II) sulfate ($CuSO_4 \cdot 5H_2O$),
Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$)

Chemicals used for color fastness testing:
Hydrochloric acid (HCl p.a),
Perwol Renew liquid laundry detergent for synthetic & athletic clothes (Henkel),
Cyclohexane, p.a.

Tap water was used in all experiments (from a private well), having following parameters: total hardness 15.3°, alkalinity 7.2° (both German scale), pH 8.4.

Mordanting

Cotton fabric was cut into six strips of 40 × 210 mm. Five strips were placed in PP 50 cm³ vials and then 40 cm³ of appropriate pure analytically mordant solution was poured into each vial. Each vial was placed in a water bath and kept at 95 °C for 30 min. Each vial was shaken by hand every 10 min. Next, each vial was left for 30 min. to cool down and then each piece of material was pressed to remove the excess of mordant solution. No rinsing with water was applied. One strip of fabric was not treated in this process.

Dyeing

All strips of fabric were placed in PP 50 cm³ vials and then 30 cm³ of birch bark extract was poured into each vial. Each vial was placed in water bath and kept at 95 °C for 60 min. Each vial was shaken by hand every 15 min. Next, each vial was left for 30 min. to cool down and then each strip of fabric was rinsed with tap water.

Testing color fastness

After dyeing every strip of fabric was cut into seven 30 × 40 mm pieces. Color fastness tests were performed in a following way:

1. **Hot water**

One piece of fabric from untreated strip and from each mordant was placed in PP 50 cm^3 vials and then 30 cm^3 of tap water was poured into each vial. Each vial was placed in water bath and kept at 95 °C for 30 min. Each vial was shaken by hand every 10 min. Next, each vial was placed in cold water bath for 5 min and then each piece of fabric was rinsed with tap water.

2. Laundry in 50 °C

Liquid laundry detergent solution was prepared by diluting 4 ml of liquid laundry detergent with 800 ml of distillated water.

One piece of fabric from untreated strip and from each mordant was placed in PP 50 cm^3 vials and then 20 cm^3 of liquid laundry detergent solution was poured into each vial. Each vial was placed in an oven and kept at 50 °C for 70 min. Each vial was shaken by hand every 10 min. Next, each vial was placed in cold water bath for 5 min. and then each piece of fabric was rinsed with tap water.

3. Laundry in 95 °C

One piece of fabric from untreated strip of fabric and from each mordant was placed in PP 50 cm^3 vials and then 20 cm^3 of liquid laundry detergent was poured into each vial. Each vial was placed in water bath and kept at 95 °C for 60 min. Each vial was shaken by hand every 15 min. Next, each vial was placed in cold water bath for 5 min. and then each piece of fabric was rinsed with tap water.

4. Dry cleaning

One piece of fabric from untreated strip and from each mordant was placed in PP 50 cm^3 vials and then 10 cm^3 of cyclohexane was poured into each vial. Each vial was placed in water bath and kept at 37 °C for 30 min. Next, each piece of fabric was placed in dryer and kept at 105 °C for 5 min.

5. Mineral acid

0.5% hydrochloric acid solution was prepared by diluting 40 ml of 5 % hydrochloric acid with 360 ml of distilled water.

One piece of fabric from untreated strip and from each mordant was placed in PP 50 cm^3 vials and then 20 cm^3 of hydrochloric acid was poured into each vial. Each vial was placed in water bath and kept at 98 °C for 30 min. Each vial was shaken by hand every 10 min. Next, each vial was placed in cold water bath for 5 min. and then each piece of fabric was rinsed with tap water.

6. UV exposure

One piece of fabric from untreated strip and from each mordant was placed on PVC board and pinned with a clothes clip. The PCV board was then exposed to natural sunlight while being kept outdoors for seven days. The weather during that week was:

Day 1: full sun
Day 2: full sun
Day 3: full sun
Day 4: overcast, moderate rain
Day 5: mostly sunny
Day 6: full sun
Day 7: mostly sunny

Color determination

All samples were tested for color change due to dyeing and color fastness testing. The determination of color was conducted using a Spectromaster Model 565-D spectrophotometer, in the CIEL*a*b* system (L* - brightness level coordinate, a* - coordinate of the yellow color, b* - coordinate of the red color).

RESULTS

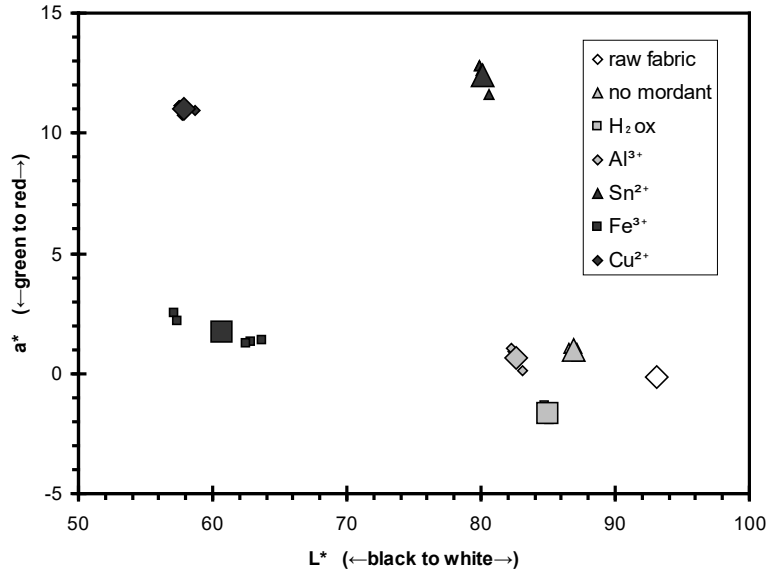
Dyeing

The uniformity of the color of the raw fabric was tested and the results were presented in Table 1. The fabric is characterized by a very uniform color, because the standard deviations do not exceed the value of 0.1 in any case.

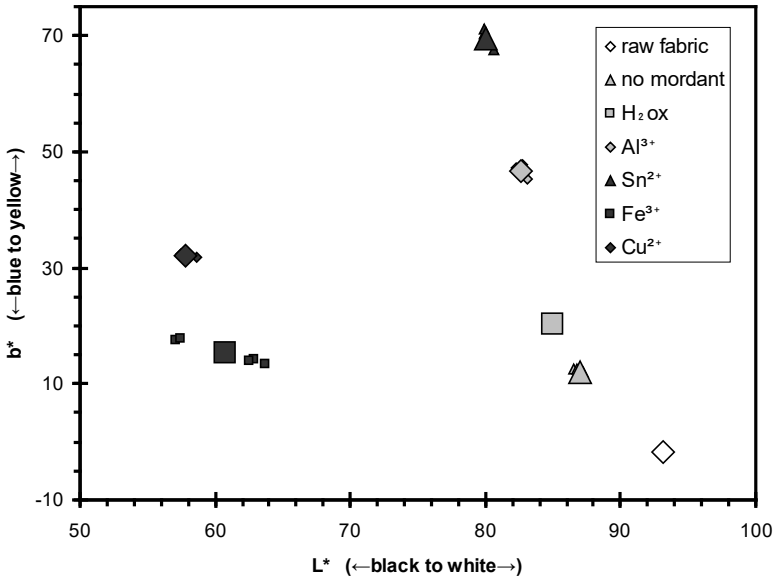
Table 1. CIEL*a*b* parameters of raw fabric

	L*	a*	b*
Mean	93.10	–0.14	–1.80
SD	0.08	0.06	0.05

The results of dyeing are presented in Figure 1. For better readability, the data are presented in two coordinate systems of L*–a* and L*–b*. Small points represent individual measurements, while big point denotes the mean values.



A



B

Figure 1. Color for dyed fabrics in L*-a* (A) and L*-b* (B) coordinate systems

No mordant: In the case of non-mordant treated samples, the smallest color change for each coordinate was found.

Oxalic acid: In the case of oxalic acid, the change was also slight, not much greater than in the no-mordant samples. In this case, the color obtained is very light yellow in a cold shade, as evidenced by the coordinate a, which has slightly shifted towards green. This is the only such case. In all the others there was a smaller or larger shift of the a coordinate towards red.

Alum: There was a strong change of the b* coordinate towards yellow and a slight change of the a* coordinate towards red. This corresponds to the sample intensely lemon yellow.

Tin: In this case, the samples obtained a very intense, deep warm yellow color, which is visible after the strongest change of parameter b* towards yellow, but at the same time the strongest change in the color of parameter a* towards red.

Iron: A characteristic feature of apple bark staining using iron mordant is a large divergence of the obtained colors, the largest among all the tested series of samples with a much wider distribution. This may be due to the properties of iron(III) compounds, which easily hydrolyze. In this case $Fe(OH)_3$ is precipitated, which may result in the non-uniformity of the color of the fibers. The use of iron confirmed its recognition in literature as a color modifier, because the color obtained in this case was not yellow, but close to dark khaki. It is noticeable after a very visible reduction of the L* parameter with a relatively small change of parameter a* towards red and b* towards yellow.

Copper: A very interesting effect was obtained, where both a very strong darkening of the sample and a strong change of color occurred. In this case, however, the change of parameter b* towards yellow is clearly smaller than for tin and alum, although stronger than for the other samples, while the change in the color of parameter a* towards red is the second strongest right after the tin. As a result, the color observed is an intense rusty brown. Based on the results, mordant containing copper compounds can be treated not only as a mordant, but also as a modifier.

Color fastness

Six color fastness tests were carried out for each sample series dyed with or without the use of mordants. Due to the amount of data, the results are presented separately for each type of mordant.

No mordant (Figure 2): The untreated samples (without mordant) were very weakly colored, therefore all the aging methods used did not cause a very strong color change, but it can be seen that in the case of dry clean the color was slightly deepened. In the remaining cases, the discoloration of the sample is rather the case, with the use of hot water the weakest, followed by mild wash and acid. The strongest discoloration was obtained for the hot wash and the next one for weathering (UV exposure).

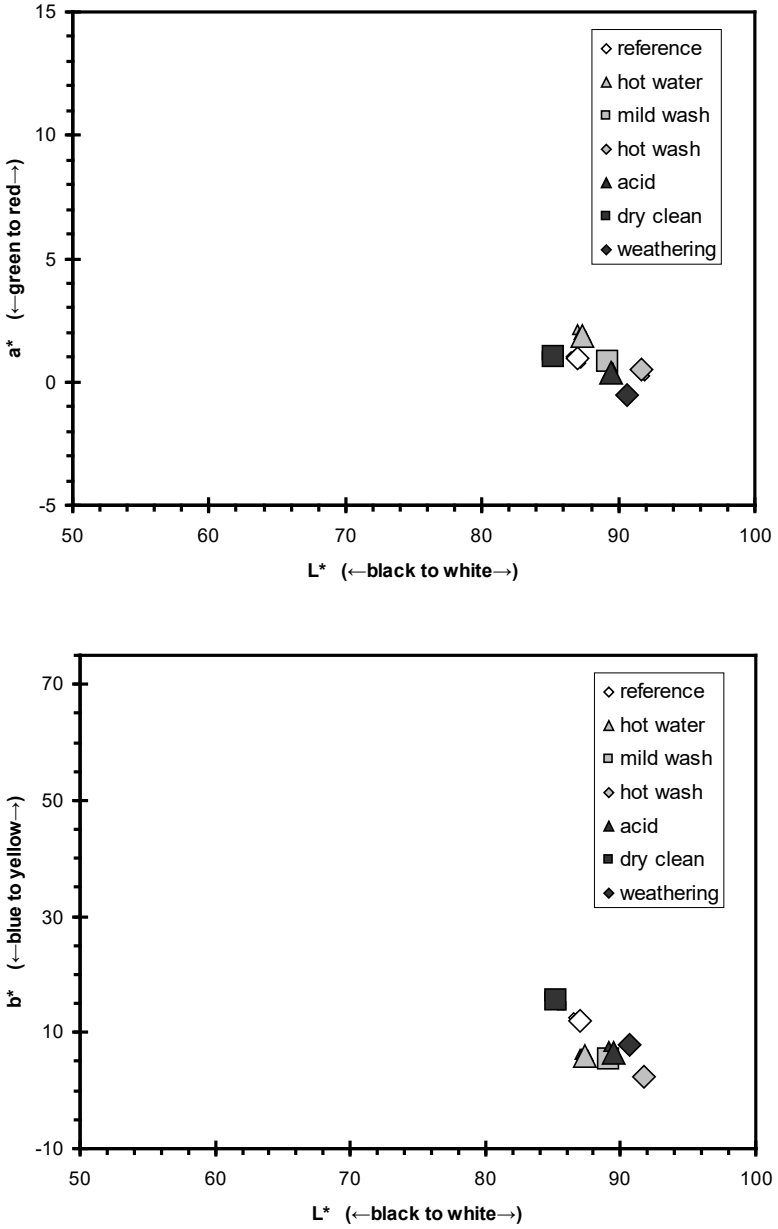


Figure 2. Color fastness for untreated fabrics in L*-a* (A) and L*-b* (B) coordinate systems

Oxalic acid (Figure 3): In the case of oxalic acid, the weak, cold yellow color obtained turned out to be similarly resistant as in the case of untreated samples. Samples after dry clean do not show a significant difference from the reference samples, while hot water causes the slightest lightening of the sample, but at the same time quite a strong change of shade. Mild wash, weathering and acid will cause slight discoloration. The strongest discoloration is observed with the hot wash.

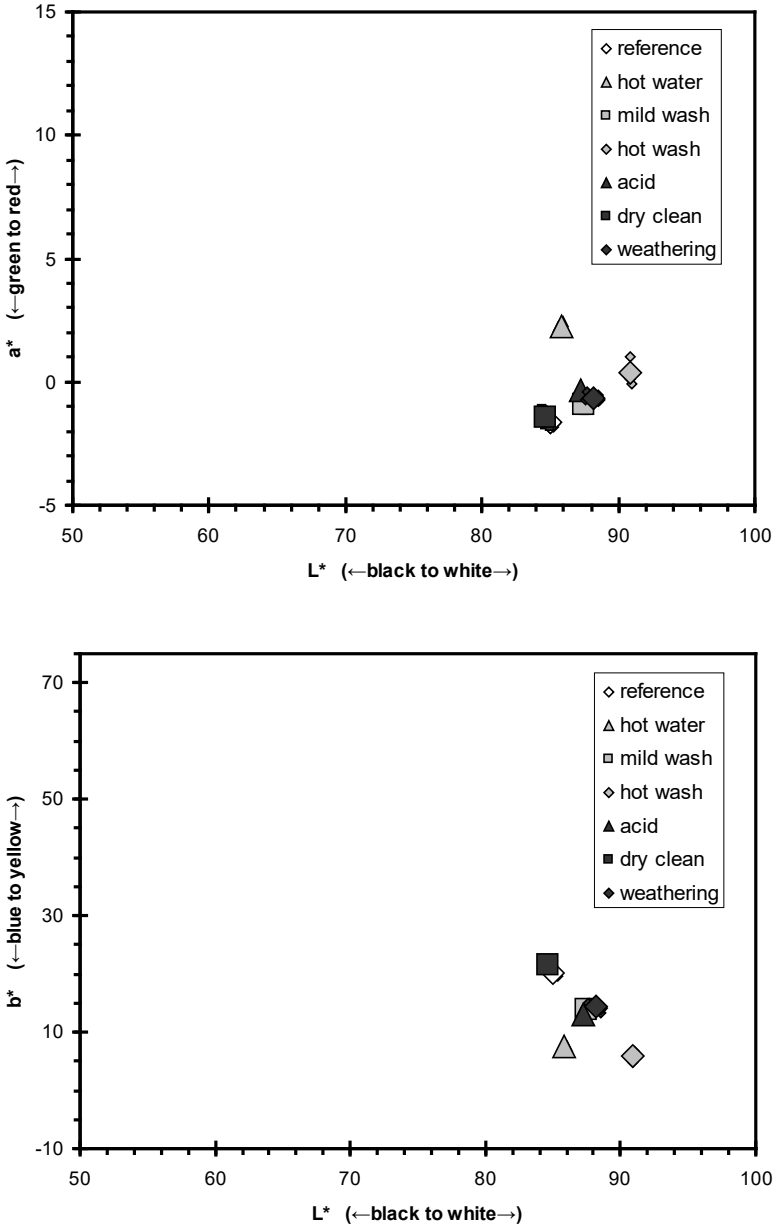


Figure 3. Color fastness for oxalic acid treated fabrics in L*-a* (A) and L*-b* (B) coordinate systems

Alum (Figure 4): The samples had a more intense yellow color than in the previous two cases and the obtained relationships in this case are slightly different. Dry clean does not significantly change the color, and even slightly increases its intensity. Mild wash does not cause a noticeable color change. Hot water does not significantly lighten the samples, but slightly changes their shade, which is especially visible on the b coordinate. Hot wash causes a noticeable lightening of the samples combined with a color change slightly smaller than in the case of hot water. Natural exposure to UV and acid causes the strongest discoloration and lightening of the samples. Interestingly, the action of the acid in this mordant is much stronger than in the case of untreated or oxalic acid treated samples.

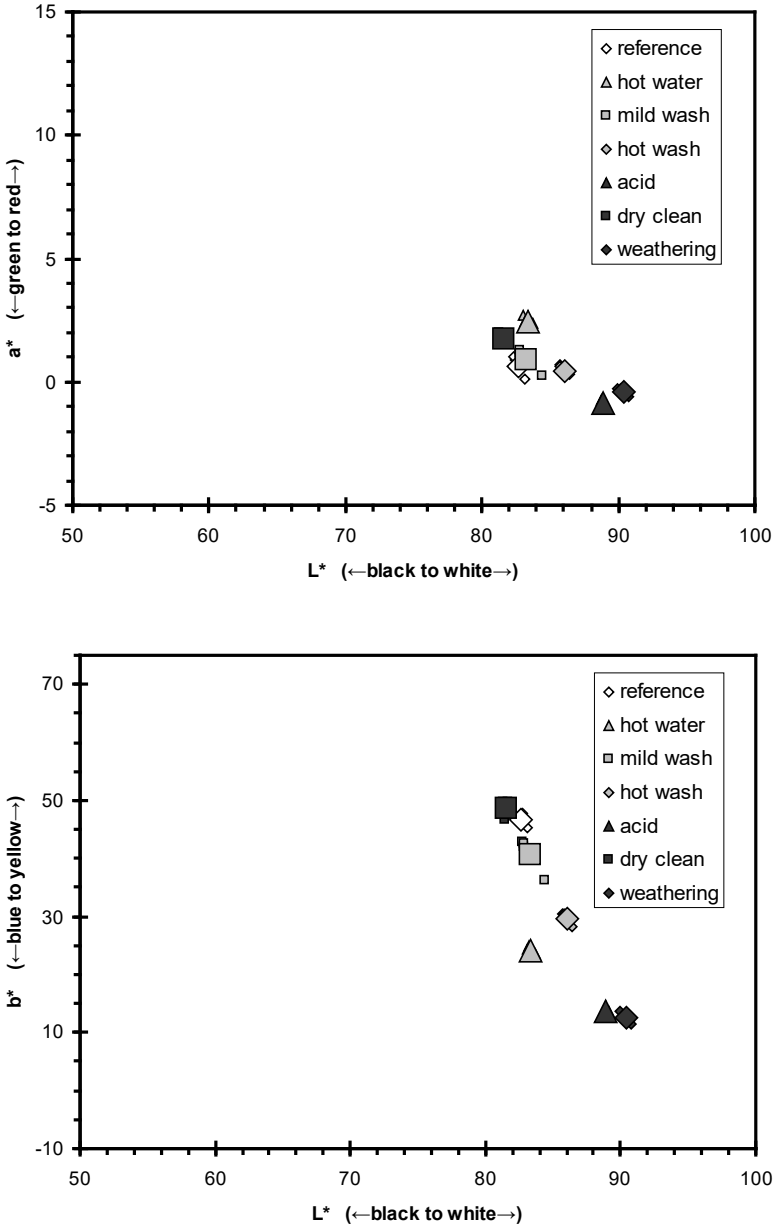


Figure 4. Color fastness for alum treated fabrics in L*-a* (A) and L*-b* (B) coordinate systems

Tin (Figure 5): In the case of tin, a deep yellow color was obtained, which, as in other cases, proved to be resistant to dry clean. Mild wash and hot water cause slight discoloration. Much greater discoloration is caused by hoy wash, while the acid causes a strong change of shade and quite significant lightening of the sample. The biggest change occurred in the case of UV exposure, in this case the dye turned out to be completely non-resistant and after 7 days of exposure the samples were almost completely discolored and the color of the material was similar to that of raw fabric.

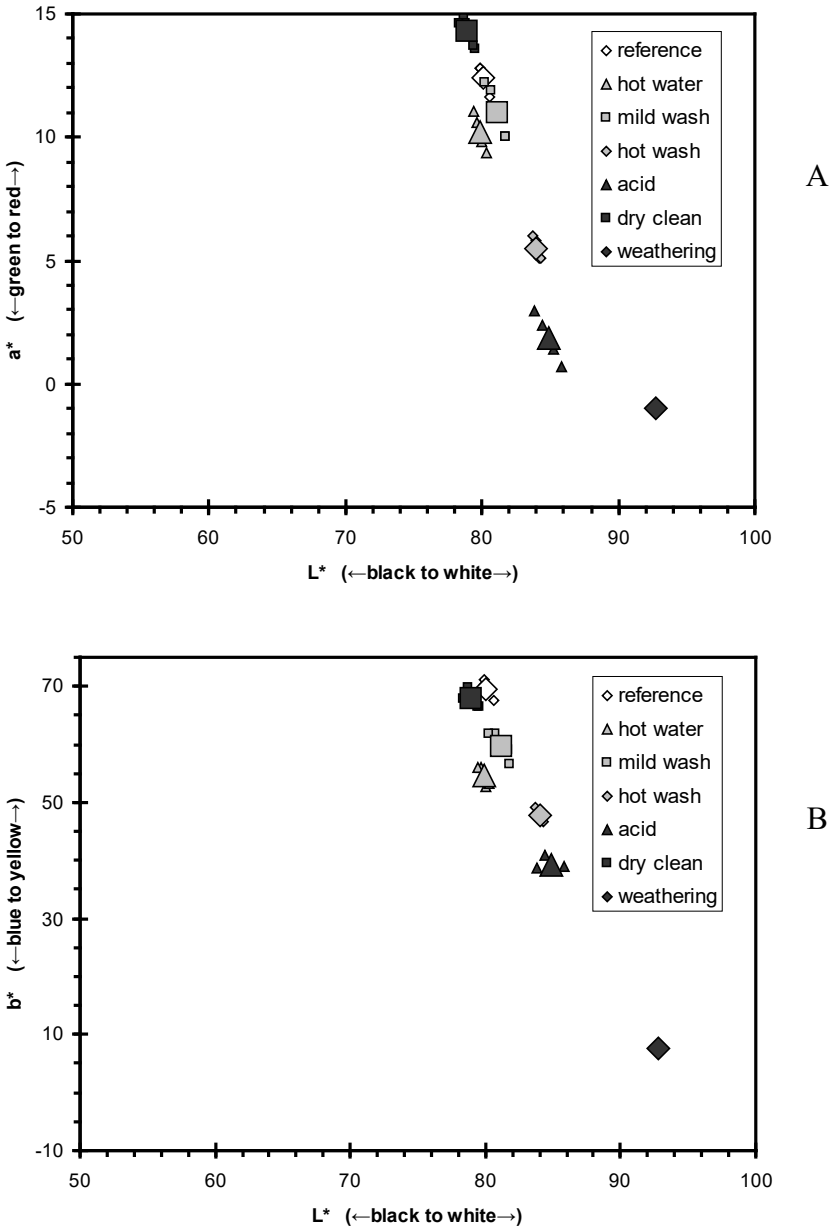


Figure 5. Color fastness for tin chloride treated fabrics in L*-a* (A) and L*-b* (B) coordinate systems

Iron (Figure 6): The obtained color dark khaki is well resistant to dry clean and mild wash. In the case of hot water and hot washing, further darkening of the samples and an increase in color intensity were observed. The only conditions in which there was a significant discoloration of the samples were weathering and acid. In the case of weathering, the samples did not change their shade, but they brightened significantly. The samples are the least resistant to acids. In this case, there is a slight change in the shade, but very strong lightening of the samples.

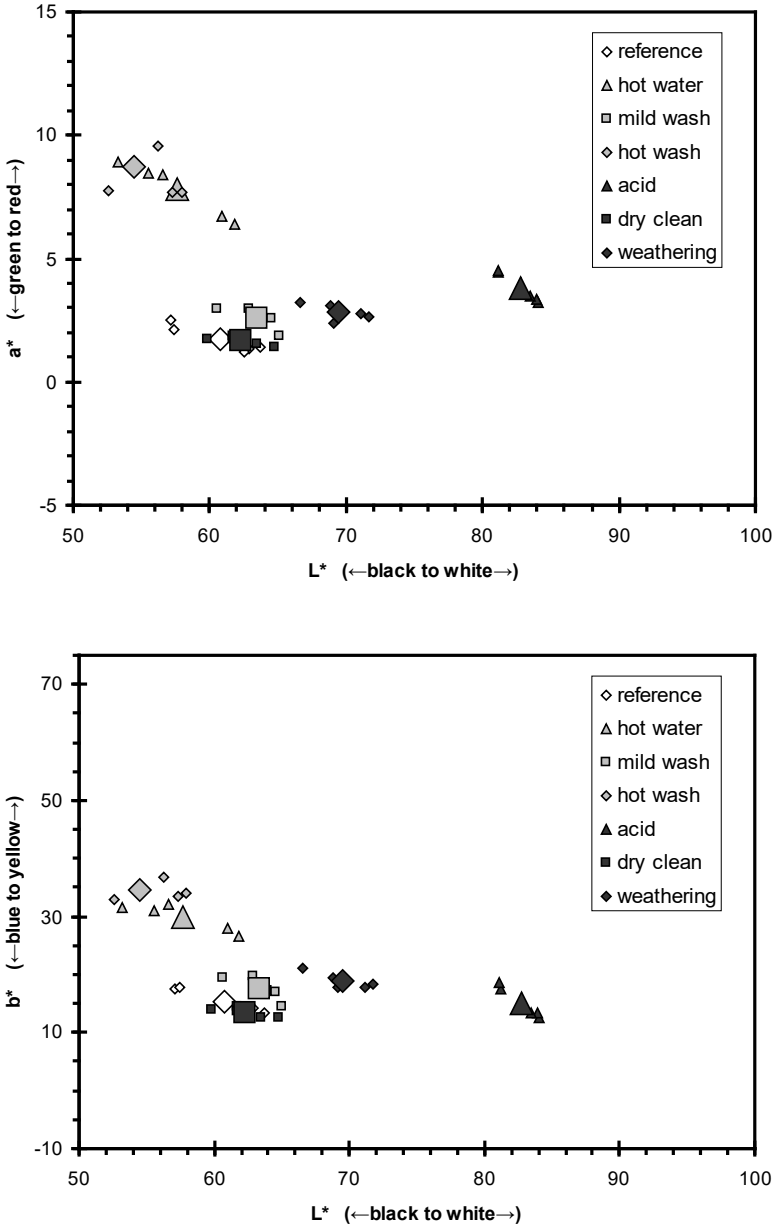


Figure 6. Color fastness for ferric chloride treated fabrics in L*-a* (A) and L*-b* (B) coordinate systems

Copper (Figure 7): A deep rusty bronze was obtained which, like all others, is resistant to dry clean. Unlike other samples, it is also resistant to hot water and slightly less resistant to mild wash and hot wash. Relatively it is the most UV resistant of all samples. This is the only case where the shade change and lightening are less than with hot washing. As in the case of iron, the color is not resistant to acids. In this case, both the greatest loss of color and lightening of the sample were observed.

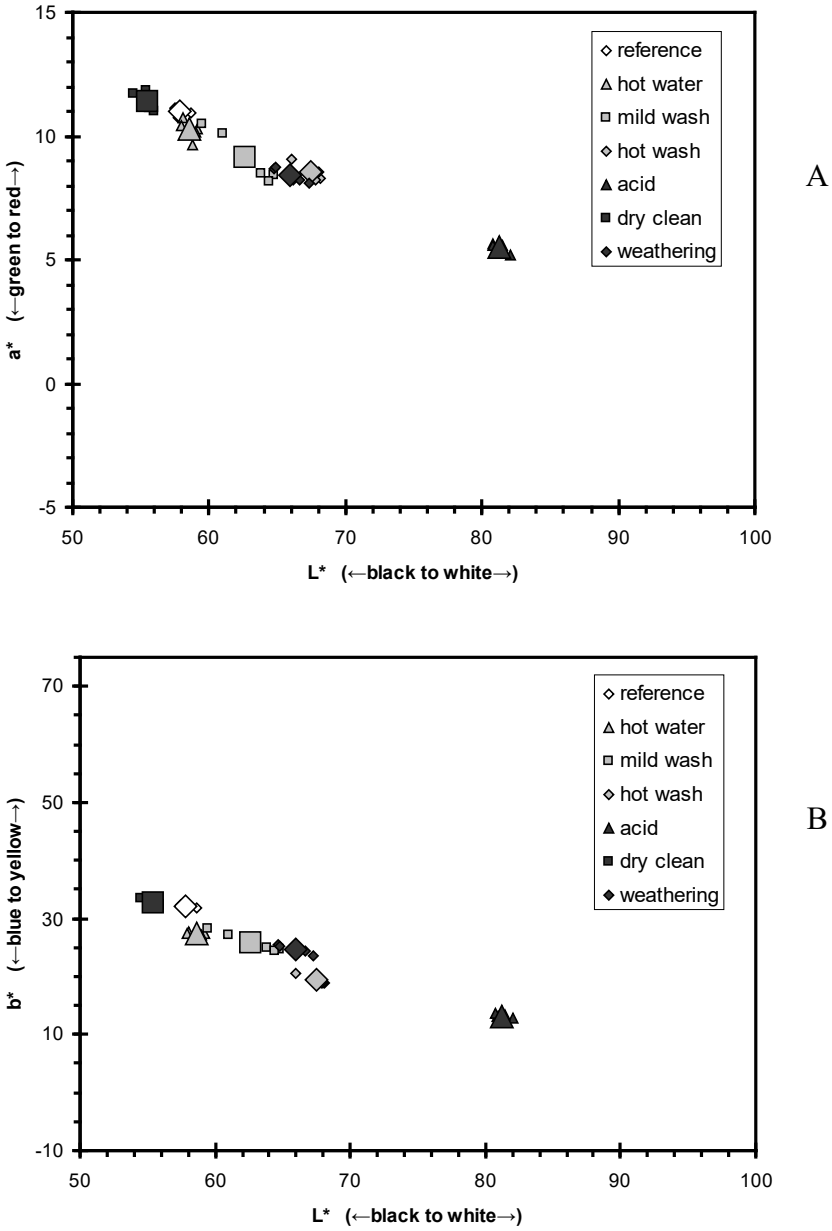


Figure 7. Color fastness for copper sulfate treated fabrics in L*-a* (A) and L*-b* (B) coordinate systems

CONCLUSIONS

The substances in the bark of the apple tree make it possible to obtain interesting cotton colors of various shades of yellow, from very light to intense dark yellow, and in the case of using modifiers, even brown and khaki. Mordants based on organic acids are not effective as dye binding agents.

The biggest disadvantage of dyes derived from apple tree bark is very poor resistance to sunlight, practically excluding the possibility of external use (except for the colors obtained on the iron and copper mortar, which are more resistant). All the obtained samples were not resistant to acids, which is consistent with the observation of dyeing with the use of oxalic acid mordant. The samples turned out to be relatively good resistant to mild wash and worse to hot wash. At the same time, the samples turned out to be quite poorly resistant to hot water. In the case of iron, the samples were less resistant to both hot wash and hot water than to mild wash, which proves that the greatest influence on them was not the detergent, but high temperature. By far the best color fastness was demonstrated for samples subjected to dry

clean washing. No significant loss of color was found in any of the cases, and in some cases even a slight increase in its intensity.

Low UV resistance is sufficient reason why apple tree bark never came into widespread use as a source of dye. At the same time, it is also an indication why artificial dyes obtained from the 19th century were widely used. Taking into account the interesting colors obtained, the application of apple bark in some specific use may be considered. In interior conditions, not exposed to sunlight, it is worth investigating the possibility of using UV stabilizers for improving color fastness. In case of positive results, apple tree bark can be a natural and eco-friendly alternative source of dyes.

REFERENCES

1. ABDEL-KAREEM O., 2012: History of Dyes Used in Different Historical Periods of Egypt. Research Journal of Textile and Apparel 16; 79-92, DOI: 10.1108/RJTA-16-04-2012-B009.
2. ADAMCOVÁ A., HORNA A., ŠATÍNSKÝ D., 2022: Determination of Phloridzin and Other Phenolic Compounds in Apple Tree Leaves, Bark, and Buds Using Liquid Chromatography with Multilayered Column Technology and Evaluation of the Total Antioxidant Activity. Pharmaceuticals (Basel, Switzerland), 15(2); 244. DOI: 10.3390/ph15020244
3. ALI N.F., El-MOHAMEDY R.S.R., 2011: Eco-friendly and protective natural dye from red prickly pear (*Opuntia Lasiacantha* Pfeiffer) plant, Journal of Saudi Chemical Society 15; 257-261, DOI: 10.1016/j.jscs.2010.10.001
4. CLARK M. (ed.), 2011: Handbook of Textile and Industrial Dyeing, Principles, Processes and Types of Dyes, Woodhead Publishing, Oxford, ISBN 978-1-84569-695-5
5. El-NAGAR Kh., SANAD S.H., MOHAMED A.S., RAMADAN A., 2005: Mechanical Properties and Stability to Light Exposure for Dyed Egyptian Cotton Fabric with Natural and Synthetic Dyes, Polymer-Plastics Technology and Engineering 44 (7); 1269-1279, DOI: 10.1080/03602550500207816
6. LECONTE N., LECLERE J., 2013: Use of an apple tree bark extract in a cosmetic anti-ageing composition, European Patent Office EP2811978B1
7. NIINIMÄKI K., PETERS G., DAHLBO H., PERRY P., RISSANEN T., GWILT A., 2020: The environmental price of fast fashion, Nature Reviews Earth & Environment 1; 189-200, DOI: 10.1038/s43017-020-0039-9.
8. SAMANTA A.K., AGARWAL P., 2009: Application of natural dyes on textiles, Indian Journalof Fibre and Textile Research 34 (04); 384-399
9. SAMANTA A.K., KONAR A., 2011: Dyeing of Textiles with Natural Dyes, in Kumbasar E.P.A. (ed.), Natural Dyes, IntechOpen, London, DOI: 10.5772/21341
10. SAXENA S. & RAJA A., 2014: Natural Dyes: Sources, Chemistry, Application and Sustainability Issues. in: Muthu S. (eds.), Roadmap to Sustainable Textiles and Clothing. Textile Science and Clothing Technology, Springer, Singapore, 37-80, DOI: 10.1007/978-981-287-065-0_2
11. SINGH H.B., BHARATI K.A., 2014: Handbook of natural dyes and pigments. Woodhead Publishing India Pvt. Ltd., New Delhi, ISBN 978-93-80308-54-8, DOI: 10.1016/C2014-0-02803-1
12. ŠVARC-GAJIĆ J., CERDÀ V., DELERUE-MATOS C., MASKOVIC P., CLAVIJO S., SUÁREZ R., CVETANOVIC A., RAMALHOSA M., BARROSO M.F., MOREIRA M., MORAIS S., WITHOUCK H., BOEYKENS A., 2021: Chemical

Characterization and In Vitro Bioactivity of Apple Bark Extracts Obtained by Subcritical Water. Waste and Biomass Valorization. 12. 10.1007/s12649-021-01477-z.
13. TÁBORSKÝ J., SUS J., LACHMAN J., ŠEBKOVÁ B., ADAMCOVÁ A., ŠATÍNSKÝ D., 2021: Dynamics of Phloridzin and Related Compounds in Four Cultivars of Apple Trees during the Vegetation Period. Molecules (Basel, Switzerland), 26(13); 3816. DOI: 10.3390/molecules26133816
14. WANGATIA L.M., TADESSE K., MOYO S., 2015: Mango bark mordant for dyeing cotton with natural dye fully eco-friendly natural dyeing, International Journal of Textile Science 4 (2); 36-41, DOI: 10.5923/j.textile.20150402.02

Streszczenie: *Przydatność kory jabłoni jako naturalnego surowca do barwienia bawełny*. Przeprowadzono badanie barwienia tkaniny bawełnianej ekstraktem z kory jabłoni z zastosowaniem zapraw - soli nieorganicznych glinu, cyny, żelaza i miedzi, ponadto kwasu szczawiowego oraz bez zaprawy. Barwa tkaniny oznaczana była w systemie CIE L*a*b*. Uzyskano żółte zabarwienie o różnym odcieniu, od cytrynowego do ciepłej, intensywnej żółtej. W przypadku żelaza i miedzi uzyskano zdecydowanie odmienną barwę, ciemny khaki i rdzawo brązowy odpowiednio. Przeprowadzono testy trwałości barwy stosując gorącą wodę, kwas mineralny, łagodne i gorące pranie, czyszczenie na sucho oraz naturalną ekspozycję na światło słoneczne. Stwierdzono znakomitą odporność na czyszczenie na sucho oraz dobrą na łagodne pranie. Najsłabszą odporność barwiona tkanina wykazywała na działanie światła słonecznego oraz kwasu mineralnego.

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