ELECTROKINETIC PROPERTIES OF WOOL AND COTTON FABRICS DYED WITH THE FLOWER EXTRACT OF SPANISH BROOM PLANT

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Abstract: *The use of natural dyes derived from natural plant sources for textiles dyeing has increased in recent years as consumers increasingly desire to replace synthetic chemicals with natural compounds. A natural dye from Spanish broom was produced by aqueous extraction. Wool and cotton fabrics were dyed in acidic medium. The electrokinetic properties of the dyed textiles were analysed as well as laundering durability and the colour fastness. The results showed that 5 washing cycles had no effect on the colour intensity of the dyed wool fabrics, suggesting that the pigments extracted from the flowers of Spanish broom have a high potential as a source of natural dyes, for protein rather than cellulosic fibres.*
Keywords: *natural dye, Spanish broom, electrokinetic properties, zeta potential, wool, cotton.*

1. Introduction

High demands are made everywhere in the world towards renewability and sustainability. Main goal of this research is to follow the principles of circular economy, minimizing waste and carbon emissions in production processes, while making continuous use of all the resources involved.

For this research extract of Spanish broom (*Spartium junceum* L.) plant was applied. This plant was chosen due to its wide availability in the Mediterranean region. Additionally, it can be found in other tropical, subtropical and temperate areas of the world. Although throughout history it has proven to be a plant with many interesting uses, such as production of fibers, yarns, fabrics, ropes, baskets, pigments, oils, perfumes etc. Today, it is considered an invasive, even noxious, weed [1], so the attempts are made to eradicate in the USA, the Canary Islands, the Azores, Argentina, Bolivia, Peru, Uruguay, South Africa, and the Dominican Republic [2,3].

Natural dyes from plant, animal, and mineral sources are being re-examined to test their environmental and health hazards. It is possible to produce them without contaminating the environment due to their biodegradable properties. In this way their decomposition does not produce hazardous waste in the environment [4]. Widely available biomass was used for the production of natural dyes applied for wool and cotton fabric in this work.

The surface properties of selected fabrics were characterized by zeta potential (ZP). ZP is an indicator for changes in the surface charge of textile fabrics influenced by the adsorption of dyestuff molecules. In general, cotton surface is rich in acidic functional groups and its isoelectric point (IEP) occurs at low pH (~2). IEP is an important parameter for chemical fabric treatment which indicates that fabric surface is neutral when the pH is at isoelectric point. Wool's surface is amphoteric and has many carboxyl and amino groups and according to literature [5] shows IEP around pH 5. When the pH is below the isoelectric point, the amino groups on the wool surface are protonated and the wool surface becomes positive. When the pH is above the isoelectric point, the carboxyl groups on the wool surface are ionized and it becomes negatively charged. Additionally, color fastness during the washing was performed to test natural dye durability.

2. Experimental

2.1 Materials

Two different already pre-treated (scoured, bleached and cleaned for stains) textile fabrics were used for the experiment: cotton (C) and wool fabric (W). The cotton fabric was woven in plain weave with a warp yarn density of 26 cm^{-1} and a weft yarn density of 25 cm^{-1}, having mass per unit area 191.45 g/m^2. The cotton fabric was manufactured by Čateks, d.o.o., Čakovec, Croatia.

The wool fabric was woven in plain weave with a warp and weft yarn density of 22 cm^{-1}, having mass per unit area 118.16 g/m^2. The fabric was supplied by Tekstilpromet, d.d., Zagreb, Croatia. The flowers of Spanish broom were collected near the town of Šibenik and air-dried before the aqueous extraction. Aluminum sulfate dodecahydrate ($KAl(SO_4)_2$ x12 H_2O) from Sigma Aldrich, UK was used as mordant.

2.2 Methods

The experimental work was carried out in 3 stages: Extraction of dyes from the flower, pre-mordanting and dyeing. The mordanted and dyed fabrics were washed afterwards and their surface properties were studied.

2.2.1 Extraction of natural dyes

The flowers, Figure 1a., were extracted by boiling for one hour in distilled water at a material-liquid ratio (MLR) of 1:2.7. After the first extraction procedure, the solution was cooled and filtered, Figures 1b. and c.

a. b. c.

Figure 1: Extraction process in water: a. Spanish broom flowers; b. flowers after filtration; and c. an aqueous extract of Spanish broom flowers.

2.2.2 Pre-mordanting

Cotton and wool fabrics were mordanted with potassium aluminum sulfate dodecahydrate $KAl(SO_4)_2 \times 12\ H_2O$ (alum). Fabrics were treated in Turbomat P4502 laboratory dyeing machine, Mathis, Switzerland, at 50 °C for 30 min at LR 1:40 with a mordant concentration of 3% owf (over weight of fabric). After mordanting, the fabrics were air dried and dyed.

2.2.3 Dyeing

Initial and mordanted cotton and wool fabrics were dyed in an aqueous extract of Spanish broom flowers in an acidic medium (pH 5) in the Turbomat P4502 laboratory dyeing machine, Mathis, Switzerland, at 90 °C for 60 min at LR 1:40. Subsequently, the fabrics were thoroughly washed in cold water, followed by hot soaping with Kemopon 30, Kemo, Zagreb, Croatia and cold rinsing.

2.2.4 Washing process

Washing was performed with 2.5 g/L ECE-2 colour fastness test detergent (ISO105-C08/C09) in Turbomat P4502 machine, Mathis, Switzerland, at pH 10 and 60 °C for 30 min with LR of 1:20 for 5 washing cycles. After the washing cycle, the textiles were rinsed and dried 5 times and air dried before starting a new washing cycle.

The labelling of all samples is shown in Table 1:

Table 1: Labels description

Label	Description
C	cotton fabric
W	wool fabric
1E	1st extraction of dye solution
3%Al	alum mordant in concentration of 3% owf
5x	number of washing cycles (5 cycles)

2.2.5 Zeta potential

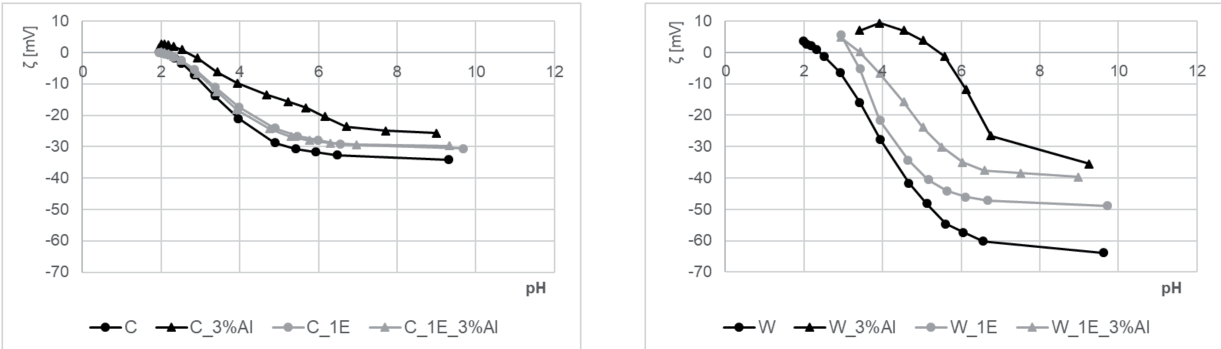
Surface properties of initial, mordanted and dyed wool and cotton fabrics before and after washing cycles were characterized by zeta potential (ζ) determined by streaming potential method using electrokinetic analyser SurPASS, Anton Paar GmbH, Graz, Austria.

2.2.6 Colour fastness

The colour coordinates of the dyes were determined using the Datacolor 850 spectrophotometer, Switzerland, at illuminant D65 and geometry d/10°. The coordinates used to determine the 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 the hue angle in the range from 0° to 360°.

3. Results

Zeta potentials of initial, mordanted and dyed cotton and wool fabric in variation of pH of an electrolyte solution are presented in Figure 2. IEP values of initial and treated cotton fabrics are in accordance with literature [5, 6] thereby confirming its surface is rich in carboxyl and hydroxyl groups. ZP plateau value in alkaline region is -34.2 mV thus suggesting that cotton fabric has undergone a pre-treatment of scouring and bleaching. On the contrary, the IEP of the initial wool fabric shows a significantly lower value (IEP= 2.4), which is a consequence of the aging and chemical bleaching of the material where additional anionic groups are formed on the surface due to the oxidation of impurities deposited on the fiber surface and oxidation of the cysteine residues of the keratin [7]. Therefore, in this work, the emphasis was on the dyeing and washing processes that were carried out in acidic environment at pH 5 and alkaline environment at pH 10, respectively.



a. b.

Figure 2: Zeta potential of initial, mordanted and dyed fabrics: a. cotton and b. wool vs. pH of 1mmol/L KCl

The results presented in Figure 2a. show that the zeta potential values of the dyed cotton fabrics (C_1E and C_1E_3%Al) are similar regardless of the use of mordants. The negative charge of the cotton fabric rising from hydroxyl groups and the anionic character of the dye used [8]. The zeta potential of initial, mordanted and dyed wool fabrics is shown in Figure 2b. The alum mordant concentration used in this study was 3%, which was sufficient to cover the surface of the wool fabric, as shown in the results presented in Table 2. The zeta potential of the wool fabric (W_3%Al) treated with mordant before dyeing is positive (3.8 mV) at pH 5. The positive surface charge is influenced by the interaction of the mordant with the negatively charged wool fabric [9]. A similar but less pronounced effect is characteristic of wool fabric dyed with mordant (W_1E_3%Al) compared to dyed wool fabric (W_1E). The surface properties of cotton and wool fabrics characterized by zeta potential at pH 5 and pH 9 are shown in Table 2. These pH values were chosen due to the acidic nature of the dye bath (pH 5) and the alkaline starting point in the measurement of the zeta potential (pH 9).

Table 2: Zeta potential of initial and mordanted cotton and wool fabrics at pH 5 and pH 9

	ζ (mv)	
Fabric	pH 5	pH 9
C	-29.2	-34.2
C_3%Al	-15.7	-25.7
W	-48.2	-63.8
W_3%Al	3.8	-35.6

Table 2 shows the zeta potential of initial and mordanted cotton and wool fabrics at pH 9 and pH 5. The zeta potential values of initial (C) and mordanted cotton fabrics (C_3%Al) at pH 5 and pH 9 are different. The decrease in negative zeta potential of mordanted fabric, especially at pH 5, indicates the deposition of a relatively small amount of mordant on the fabric surface. This result affected the poor dyeing of cotton fabrics, as described in more detail in a previous study [8]. The electrokinetic behaviour of initial wool fabrics and mordant wool fabrics depended much more on the pH of an electrolyte solution. Mordanting caused a reduction of the zeta potential of the wool fabrics, so that the values were less negative at pH 9 and positive at pH 5.

Results of the zeta potential are compared with the CIE Lab coordinates of tested fabrics, Figure 3.

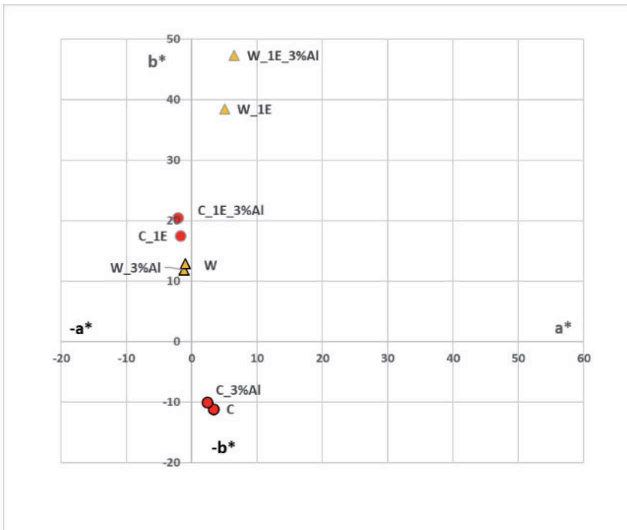
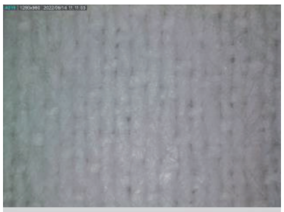


Figure 3: CIELAB coordinates of initial, mordanted and dyed fabrics: a. cotton and b. wool

Cotton fabrics have no affinity for the anionic dye and show a light yellow colour compared to wool fabrics (W_1E and W_1E_3%Al), which have a higher colour intensity. The colour value for the initial wool is C* W = 12.87, for the dyed wool C* W_1E = 38.74 and C* W_1E_3%Al = 47.31. The influence of the mordant on the colour intensity is visible in Figure 3. A change in the surface charge of the fabric affects the coloration and morphological properties, as shown in Figure 3 and Table 3. Table 3 shows digital images of cotton and wool fabrics at 50x magnification. The change in structural variables is determined as a function of treatment.

Table 3: Surface of initial and dyed cotton and wool fabric under magnification of 50x


C


C_3%Al


C_1E


C_1E_3%Al


W


W_3%Al


W_1E


W_1E_3%Al

The second part of the study deals with the influence of the washing process on the color fastness of the fabric surface. Figure 4 shows the results of zeta potential of dyed fabrics and effect of 5 washing cycles on zeta potential of undyed and dyed cotton and wool fabrics before and after mordanting.

It is obvious that the zeta potential of the washed samples is more negative compared to the cotton fabrics before washing. Moreover, there are no significant differences in the zeta potential of undyed and dyed cotton fabrics after they were exposed to the washing process (Figure 4a.). Compared to the unwashed samples shown in Figure 2, there is a slight increase in negative charge, which can be attributed to the influence of the washing process and structural changes in the cotton fabrics [10]. In the case of wool (Figure 4b.), the largest differences are observed in the initial (W) and dyed and mordanted (W_1E_3%Al) fabrics after the washing process. The alkaline medium affected the hydrolysis of the wool, the possible cleavage of the cysteine bond and the formation of sulfamide and methylene imide bonds, which affected the change in surface charge [6, 11]. Additionally, dyed and mordanted wool after washing shows higher hydrophilicity due to the more open and swollen fiber structure while the maximum of ZP is caused by the decrease of fibre swelling in the range of pH 4-6 [6, 12].

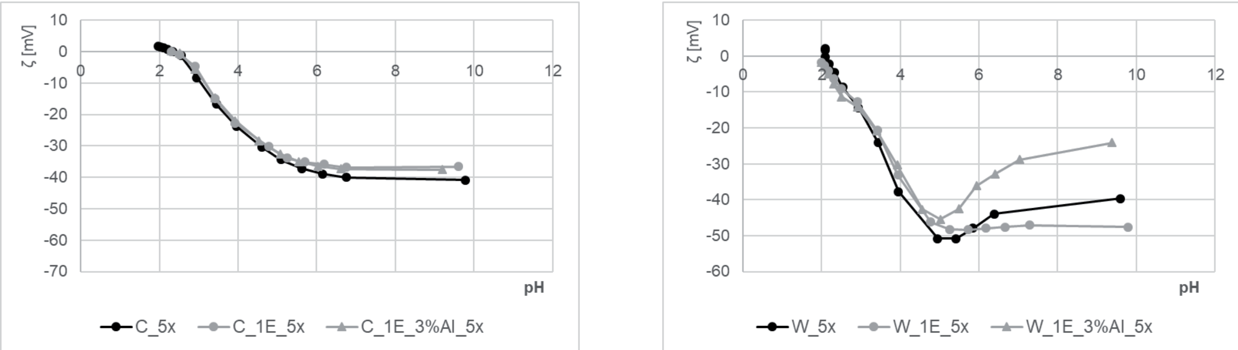


Figure 4: Zeta potential of 5 times washed initial, dyed and dyed mordant fabrics: a. cotton and b. wool vs. pH of 1mmol/L KCl

The equalization of the isoelectric points (IEP) of all wool fabrics also indicates a change in the chemical properties of wool.

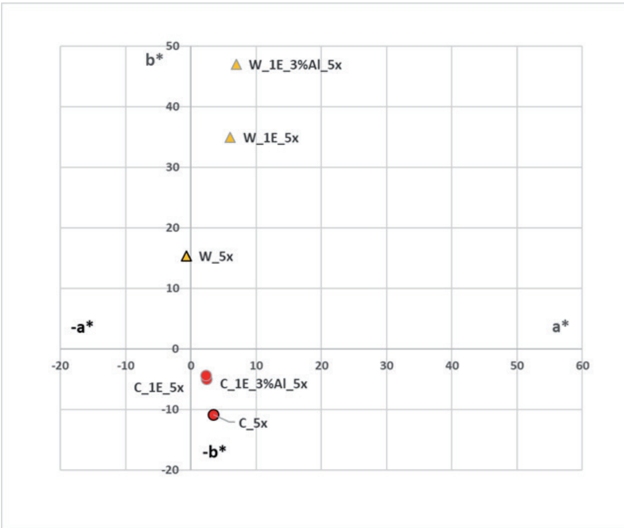
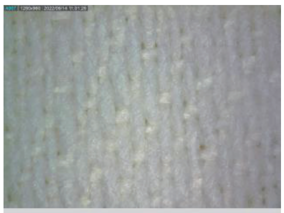
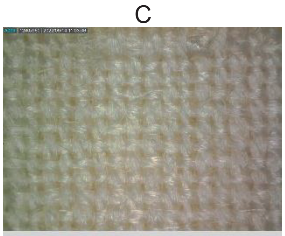
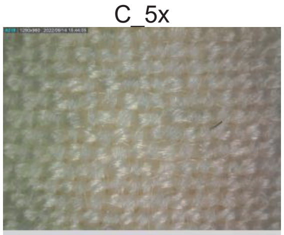
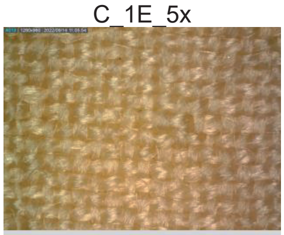
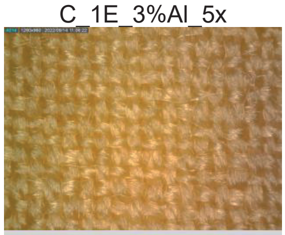


Figure 5: CIELAB coordinates of cotton and wool dyed fabrics after 5 washing cycles

Dyed wool fabrics without alum mordant (W_1E and W_1E_5x) show no significant differences in ZP values within the pH 6-10, indicating that washing had no significant effect on ionic bonding between the dye and the fibre and on colour intensity (Figure 5). Table 4 shows images of the washed fabrics under 50x magnification.

Table 4: Surface of virgin and dye cotton and wool fabric under 50x magnification

			
C	C_5x	C_1E_5x	C_1E_3%Al_5x
			
W	W_5x	W_1E_5x	W_1E_3%Al_5x

4. Conclusion

In accordance with the zero-waste model, this study focuses on the total utilisation of Spanish broom. Most of the use of Spanish broom has been successfully processed in previous research. Natural dyes show better dyeing ability for wool fibres. They also show excellent colour fastness at 5 wash cycles, especially when using a low concentration of alum mordant. In the world market, wool represents only 1% of textile fibre production, but it successfully presents itself as a superior product in terms of its environmental values and human health benefits. The positive results obtained by the more environmentally friendly use of natural dyes from Spanish broom make it possible to meet the strict requirements of various EU regulations. Regardless of various directives and regulations, the use of natural dyes is a return to our natural heritage with an emphasis on strategic thinking and the welfare of the surrounding nature.

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