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LABORATORY STUDIES ON NATURAL FABRICS TEXTILE PRINTING WITH *SPIRULINA PLATENSIS* SOURCED PHYCOCYANIN

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Abstract:*Naturally sourced elements represent a sustainable alternative solution for the textile finishing industry, in the context of intense use of contamined, fossil-based raw materials. This study focuses on the exploration of an alternative naturally sourced blue colorant matter solution, by validating the possibility of the employment of Spirulina platensis sourced phycocyanin in natural fabrics coloration through the pigment printing technique. The experiments involved the laboratory-scale exploratory studies of the application of this blue colorant matter on cotton and wool textile substrates, using commercial synthetic printing mother paste. The influence of five different mordants(Cream of tartar, Alum, Tartaric acid, Tanic acid and Aluminum triformate), though pre-mordanting treatment and the printing mother paste were analyzed by measuring the chromatic coordinates and calculating the color strength (K/S), together with the measurement of VIS absorbance spectrum. The color characterization revealed good compatibility of wool -phycocyanin – synthetic paste. Results on cotton were not as good as expected. They conclusions evidence reduced affinity between the fibres and the phycocyanin. In terms of color improvements, Tannic acid revealed the most promising results, for both cotton and wool experiments. The validation of the finishing process was obtained through a fair behavior in laundering fastness, showing low response when analyzed against light degrading external factors.*

Key words: *phycocyanin, blue, microalgae, wool, cotton, pigment printing*

1. INTRODUCTION

The negative environmental impacts, complemented with hazardous health issues, as toxicity, carcinogenic character, allergies producers, of the synthetic dyes have lead to search forsustainable solutions [1][2][3]. Various experiments of textile printing on natural fibers, using natural vegetal colorant matter, have been performed. Due to the fact that natural dyes do not present fiber affinity, as their synthetic alternatives, various mordants were employed for this purpose, as aluminum, stannous chloride, magnesium sul phate, tannic acid, myrobalan, etc.[4][3][5].

One emerging sector able to providea sustainable solution to several industries is represented bymicroalgae and macroalgae exploitation, owning developed cultivation technologies [6], and various commercial application sectors [7].Similar to plants, algae produce highly bioactive compounds, primary and secondary metabolites, as lipids, proteins, carotenoids, phycobiliproteins, phenolic compounds, with valuable prospects for industrial applications [8].The blue-green microalga *Spirulina platensis* is a source of phycocyanin, a naturally occurring blue colorant matter, representing a secondary metabolite. Phycocyanin is a water-soluble protein, pertaining to the phycobiliproteins family, characterized by covalent attachments of open chain tetrapyrroles. This protein may reach up to 20% of the weight of the cell protein, being used already in various industries as food, cosmetics, the therapeutic agent in oxidative diseases treatment, and biomedical research as a fluorescent marker, etc.[9]. Nevertheless, the potential of this colorant matter is not mentioned in the research destined to the textile industry, but very few applications of natural colorants are considered for pigment printing [10].The aim of the present work is to evaluate the viability of the textile application of a algal sourced natural alternative for the blue color, phycocyanin, on natural fibers of cotton and wool, through the printingfinishing process. Synthetic commercial printing paste was tested for process efficiency identification.

2. MATERIALS AND METHODS

2.1 Materials

Commercial undyed, bleached 200 g/m^2 cotton fabrics, EMPA221 (supplied by Intexter UPC, Spain) and bleached wool fabric (supplied by James Heal, England), both complying with ISO 105-F01 were used as printing textile substrates. 5 mordants were applied for the study of their influence in color uptake: Cream of tartar (6% w.o.f) and Alum (10% w.o.f) (supplied Gran velada), Tartaric acid (6% w.o.f), Tannic acid (2% w.o.f) and Aluminum triformate (10% w.o.f) (supplied Sigma Aldrich). Phycocyanin-rich liquid extract, obtained from *Spirulina platensis*, (procured from Banco Español de Algas (BEA), Spain) was employed as a natural dye in all the experiments.

2.2 Methods

2.2.1 Phycocyanin quantification

The phycocyanin-rich liquid solution was subjected to UV VIS spectral absorbance (UV, Thermoscientific Evolution 60S) and the amount of mg/ml of phycocyanin in solution was obtained based on the equation established by Bennett and Bogorad,(1973) [11]with extinction coefficients defined by Bryant et al (1979)[12].

2.2.2Pretreatment of fabrics and pigment printing

Wool bleaching involved the treatment of the fabric for 60 minutes at 55^{o}C, in a Rb=1/15 solution of decalcified water containing 2g/L of Pyrophosphate tetrasodium (Sigma Aldrich), 10 -20 ml/L of Hydrogen peroxide 30% (Fisher Scientific), 2g/L of nonionic Clarite detergent (Huntsman), adjusting the pH at 8,5-9 with Ammonia 25% (PanReac). The fabric is further rinsed and dried at ambient temperature.The bleached wool and the cotton were subjected to a mordant solution, according to the concentrations defined in section 2.1., for 45 minutes at a temperature of 85^{o}C.

A conventional commercial printing stock paste was prepared with the following ingredients, supplied from Color Center, Spain: Color center BC (binder),Color center MC-LF (fixer), Color center H35 (thickener), with 2% dye concentration proportional to the printing paste weight.The binder and fixer were mixed through intense blending, together with the corresponding quantity of water, and the phycocyanin rich solution. Further , the thickener was gradually added, forming the printing paste.The curing step was performed during 3 minutes at 150^{o}C, and the drying step involved ventilation at 40^{o}C, in a laboratory-type drying oven (by Memmert, Germany).Conventional manual printing screen and scraper were used for the application of the colored printing paste onthe fabrics. The scraper was passed over the fabric with three repetitions, applying uniform pressure.

2.2.3 Printed fabrics characterization and analysis

The chromatic coordinates of the printed samples were measured with Datacolor DC 650 (Datacolor, Spain) according to the indications defined in standard UNE-EN ISO 105-J01:2000.

The reflectance spectrum was determined via measurements with UV-VIS spectrophotometer Lambda 950 (Perkin Elmer, Spain). Color relative dye uptake, K/S was calculated with the Kubelka-Munk equation, given in Equation 1.

$$K/S=((1-R^2))/2R \quad \textbf{(1)}$$

where K is the absorption coefficient, S is the scattering coefficient and R reflectance at maximum wavelength [13].

Color fastnessfor laundering and light degradation was determined following the European standardized protocols. As UNE-EN ISO 105-C06:2010. (laundering fastness), involvingthe immersion of the tested fabric into a canister containing 150 mL of water and 0,6 gr of standardized detergent, together with 10 steel balls, during a washing cycle of 45 minutes at 25ºC into a Gyrowash apparatus (James Heal, UK). And UNE-EN ISO B02:2014(light fastness) where samples are pretreated by spraying with water, before the subjection to Xenon arc fading lamp for 16 hours.

3. RESULTS AND DISCUSSIONS

Mild blue tones were obtained through the printing process involving phycocyanin as colorant matter embedded in synthetic printing paste.

In order to analyze the influence of mordants on the resulting blueish printed cotton, it can be identified, as per ΔE values, in Table 1, that a slight total color difference, is facilitated by the use of mordants, in comparison with the printed non-mordanted cotton fabric. The most accentuated color difference, is obtained by the use of Tannic acid, most probably due to the additional influence of the intrinsic natural color of the auxiliary. Nevertheless, this is followed by Alum, justified by a bonding creation between the textile substrate and colorant. The bluer shade is conferred by the Tannic acid (Δb), followed by less intense bluer shades, attributed to the use of Alum, Cream of tartar, Tartaric acid, and Aluminium triformiate.

Table 1:*Color coordinates of phycocyanin printed cotton fabrics with synthetic paste*

Sample	Color coordinates and color strength							
	L	**a**	**B**	**ΔL**	**Δa**	**Δb**	**ΔE**	**K/S**
No mordant	89,56	-1,12	2,42	-	-	-	-	37,27
Cream of tartar	89,47	-1,28	2,68	0,09	0,16	-0,26	0,32	36,10
Alum	91,31	-0,7	2,93	-1,75	-0,42	-0,51	1,87	34,85
Tartaric acid	90,53	-1,03	2,66	-0,97	-0,09	-0,24	1,00	36,57
Aluminium Triformate	90,11	-0,51	2,61	-0,55	-0,61	-0,19	0,84	35,42
Tannic acid	88,64	-0,37	4,03	0,92	-0,75	-1,61	2,00	23,70

On the other hand, the color characterization assumptions are supported by the analysis of VIS spectrum, in terms of color absorbance, as presented in Figure 1. Therefore, the VIS spectrum, reveals color difference between the analyzed fabrics, and confirms the slight influence of the used mordants in final color intensity, thus positive impact in color absorbance in this finishing process employed.

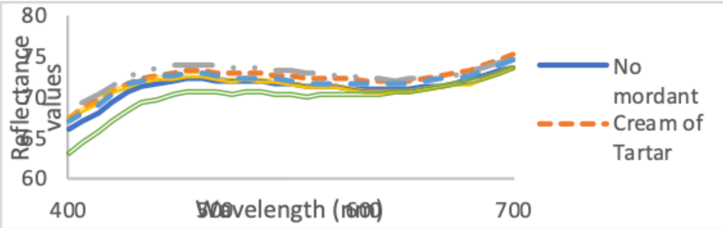

***Fig. 1**. VIS spectrum of phycocyanin printed cotton (synthetic paste), and influence of various mordants*

The color analysis of the wool printed fabrics focuses on the differences between the non-mordanted printed fabric and the ones treated with various mordants. According to **Error! Reference source not found.**Table 2, significant color difference is observed with respect to the non-mordanted fabric, to all the applied mordants. The general conclusion is that the color lightness difference (ΔL) shows darker colors with the use of Tannic acid, followed by far by the rest of mordants. In the same time, all finished wool textiles show a yellower (Δb) tone, when compared with the non-mordanted one. Considering the whole sets of experiments, wool printing process revealed more intense blue shades, confirming higher affinity between wool, phycocyanin and printing paste.

***Table2.** Color coordinates of phycocyanin printed wool fabrics with synthetic paste*

Sample	**Color coordinates and color strength**							
	L	**a**	**b**	**ΔL**	**Δa**	**Δb**	**ΔE**	**K/S**
No mordant	82,01	-2,98	10,55	-	-	-	-	23,98
Cream of tartar	82,59	-7,7	2,83	-0,58	4,72	7,72	9,07	28,06
Alum	82,05	-5,62	2,73	-0,04	2,64	7,82	8,25	27,82
Aluminium Triformate	81,15	-7,95	2,69	0,86	4,97	7,86	9,34	28,16
Tartaric acid	81,5	-6,98	2,82	0,51	4	7,73	8,72	27,59
Tannic acid	74,06	-3,43	6,68	7,95	0,45	3,87	8,85	26,14

The similarity in color shades between all the printed wool fabrics, prepared in this study, is clearly reflected in Fig 2., with the exception of the case where Tannic acid is employed, justified by higher color absorbance and also the intrinsic color shade of the mordant.

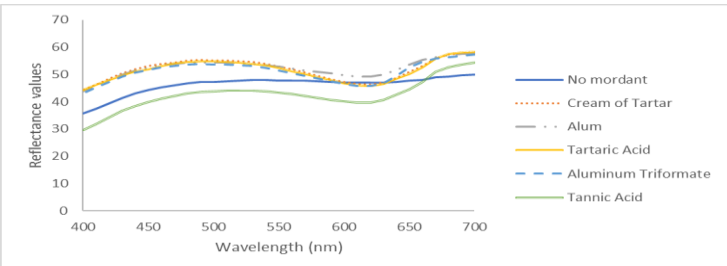

***Fig. 2**. VIS spectrum of phycocyanin printed wool (synthetic paste), and influence of various mordants*

A comparative analysis, in terms of influence over color strength, of pre-mordanting of cotton andwool textile substrates has been performed on the printed fabrics. The K/S values in cotton and wool dyeing were calculated for determining the influence of the pre-mordanting process. In the case of the cotton experiments, it can be observed slightly higher values for the not mordanted reference case, which indicates not significant benefits in pre-mordanting the fabric substrate when pigment printing with phycocyanin. Nevertheless, in the case of wool applications, overall the results are confirming to the expected output of the printing process and application of pre-mordanting of wool textile substrates is beneficial with respect to improved color strength values.

Laundering and light fastness tests were performed on the cotton and wool fabrics (Table 3), revealing fair behavior in terms of discharge, at laundering tests and very poor behavior against light agents. Improvements in light fastness, in printing of cotton, were not observed, due to the lack of effect of the pre-mordanting treatment.

Table3. *Fastness results of mordanted cotton printed with synthetic paste*

Cotton Samples	**Discharge**						**Light fastness**
	Wool	***Acrilic***	***Polyester***	***Poliamide***	***Cotton***	***Acetate***	
No mordant	4-5	4-5	4-5	4-5	4-5	4-5	3
Cream of tartar	4-5	4-5	4-5	4-5	4-5	4-5	1
Alum	4-5	4-5	4-5	4-5	4-5	4-5	1
Tartaric acid	4-5	4-5	4-5	4-5	4-5	4-5	1
Aluminium Triformate	4-5	4-5	4-5	4-5	4-5	4-5	1
Tannic acid	4-5	4-5	4-5	4-5	4-5	4-5	1
Wool samples							
No mordant	4-5	4-5	4-5	4-5	4-5	4-5	1
Cream of tartar	4-5	4-5	4-5	4-5	4-5	4-5	1
Alum	4-5	4-5	4-5	4-5	4-5	4-5	1
Tartaric acid	4-5	4-5	4-5	4-5	4-5	4-5	1
Tannic acid	4-5	4-5	4-5	4-5	4-5	4-5	1

On the other hand, wool light fastness did not show improvements, with the application of various mordants. This could be explained also by the liquid state of the phycocyanin extract, generating the need for experimenting with powder phycocyanin.

5. CONCLUSIONS

Laboratory experiments based on printing of natural fibers, as cotton and wool, with algae sourced blue colorant material, showed good manipulation properties, in the exploratory experimental set of application with synthetic printing paste.Light blue shades of printed fabrics were obtained, in all experimental cases, and this is due to the nature of the phycocyanin extract, tailored liquid extract, revealing the need of further experimenting with commercial phycocyanin.Color strength, K/S, values indicated no benefits when cotton fabrics were pre-mordanted, and revealing the contrary conclusions for the wool case, with validated improvements when the textile substrates were treated.The individual analysis of each experimental case revealed slight influence of the used mordants in final color intensity, when referring to cotton fabrics printed with synthetic printing paste. These finished fabrics showed fair behavior in terms of discharge, in laundering tests.Printed wool with synthetic printing paste, definitely revealed more intense blue colors, highlighting a better compatibility between the fabric, printing paste and phycocyanin. Even, mordant application presented differences when used Cream of tartar and Alum, and specifically the Tannic acid. The fair behavior at laundering fastness appears, and poor behavior against light agents.

The results of the experiments developed in this study, represent the first step in demonstrating the behavioral characteristics of this sustainable colorant matter, validating the possibility of use of this chromoprotein in the textile industry. Considering the liquid state of the phycocyanin extract, and the tailored production, it is fair to assume the need of a more general experimenting with commercial phycocyanin, in powder state.

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CONTENTS

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