IOP Conf. Series: Materials Science and Engineering **254** (2017) 192011 doi:10.1088/1757-899X/254/19/192011

Printing of cotton with eco-friendly, red algal pigment from *Gracilaria sp.*

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Abstract. Natural dyes represent an emerging trend in the textile industry and eco-fashion due to the increasing awareness of the sustainability concept, which must be applied to the surrounding environment. In the light of the stated problem, the search for alternative sources of dyes, revealed the new, eco-friendly, biodegradable, non-carcinogenic and sustainable colorant matter, the algal biomass. In the present work, the suitability and viability of printing cotton fabrics with pigments obtained from the red macroalgae *Gracilaria sp.*, has been investigated. For this aim, phycoerythrin, the red pigment, was extracted from fresh algal biomass, and used in a laboratory pigment-printing process, employing a natural and synthetic printing paste, for process efficiency comparison. The color values and the rubbing and laundering fastness of the printed substrates were evaluated. Results show that a light pink color can be obtained when applying both tested printing processes, and in terms of color fastness, both printing pastes show *good* behavior. In conclusion, the algal pigments show a high printing capacity on cotton substrates, either when employing the synthetic conventional paste and; moreover, when applying the more sustainable and eco-friendly natural paste.

1. Introduction

The growing popularity of the sustainability and greening concepts generates an increase in the awareness of the need to protect the environment. When applying these concepts to one of the most demanded industries, the textile industry, research studies exposed the necessity of exploration for more sustainable alternatives to the synthetic products, which are pollution generating. A solution to these needs can be represented by the focus on the reutilization of natural dyes, although they were used for the coloration of goods from ancient times. Nevertheless, dyes originating from vegetable sources are interesting due to the very low dyes´ toxicity[1].
Natural dyes are pigments derived from mineral, animal or plant sources[2], and can be obtained from any part of the plant, such as leaves, fruits, seeds, flowers, bark root, etc[3]. The two biggest disadvantages of plant pigments production are represented by the need of a wide arable land for their cultivation and the CO_2 emissions[4].

Regardless of the source, these products, which may be categorized as ´green´ dyes, are in essence, secondary metabolites produced by the organism[5]. The unique characteristic of secondary metabolites generation presents a scientific and technological challenge.

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Taking into consideration the difficulties and inconvenients imposed by the ´conventional´ natural dyes, this investigation work puts in light another source of natural pigments, namely, the algal biomass, which surpasses the previously mentioned impediments.

In recent years, significant interest has been developed in the commercial utilization of algae, based on their valuable chemical constituents, taking into account the multiple bioactive compounds content with applications in the food, cosmetic, agri- and horticultural sectors and in human health. The main compounds, which present special interest, include pigments, lipids and fatty acids, proteins, polysaccharides and phenolic[6]. Macroalgae contain phycoerythrins and carotenoids, which represent valuable pigments for the textile finishing industry. Phycoerythrin, is a water-soluble, light harvesting protein, which is specialized in the energy transfer chain[7].

There is an increasing interest on the employment of natural dyes in textile processes. Although dyeing with natural dyes is widespread through scientific research, papers on the printing via natural colorants are limited.

Pigment printing is considered the easiest printing method[8], and it is defined as the process of fixing insoluble pigments, which have no affinity to the fiber on the textile with binding agents. It is considered the most economical printing process and can be applied to all substrates[9].

This study was focused on the validation of pigment printing of natural dyes, originating from red macro algae, on cotton substrates. To this purpose, phycoerythrin, the red pigment extracted from Gracilaria sp., was used in a laboratory pigment-printing process employing a natural and synthetic printing paste, with the aim of comparing the process efficiency. The color values and the rubbing and laundering fastness of the printed substrates were evaluated and revealed good to excellent color behavior when applied on cotton substrates.

2. Materials and methods

2.1. Pigment cultivation and extraction

Phycoerythrin, red pigment, was extracted from the red macroalgae *Gracilaria sp*., obtained from Algaplus, Portugal. The fresh algal biomass was collected from large-scale cultivation tanks, in an open-system; and was subjected to one freeze (-20 ºC) - thaw (4 ºC) cycle, in order to obtain the pigment. The extracts were obtained in distilled water at pH=7, after magnetic stirring for 5 hours, under dimmed light. In the extraction process, Ammonium Sulphate (supplied by Sigma-Aldrich, Spain for protein stabilization was added) in a concentration of 20 %, with respect to the biomass weight for protein stabilization. The resulting extract was a solution, which was employed as obtained in the printing process, by adding it to the mother pastes described in table 1.

2.2. Textile finishing process on cotton fabrics

2.2.1. Cotton pretreatment.

A mordanting pre-treatment was applied to cotton fabrics in order to increase the affinity dye-cellulosic-fiber, by immersing the fabric substrate in a solution containing 6 % (reported to the dry fabric weight) Cream of Tartar (supplied by Sigma-Aldrich, Spain), for 45 minutes, at 85 ºC.

2.2.2. *Printing process.*

In this study, cotton fabrics (supplied by Intexter UPC, Spain) weighing 200 gr/m^2, were used for the application of pigment printing process and the natural sources extracts were used directly as dyestuff in the natural and synthetic printing pastes, as shown in table 1.

Table 1. Printing paste recipe (synthetic paste<left> and natural paste <right>).

Paste element	Synthetic mother paste		Natural mother paste	
Binder	Resin STK-100*	250 gr	Resin AC-60*	270 gr
Fixer	Color Center MC-LF*	25 gr	Color Center MC-LF*	40 gr
Thickener	Clear HC-35*	20 gr	CMC**	10 gr
Pigment	Phycoerythrin (red)	2 gr	Phycoerythrin (red)	2 gr
Water		703 gr	Water	678 gr
Total		1000 gr		1000 gr

*supplied by Color-Center, Spain
**supplied by Sigma-Aldrich, Spain

The fabrics were printed at laboratory scale, using a manual method including a printing screen and scraper; passing the scraper over the cotton fabrics for three times, applying a uniform pressure. The fabrics printed with the synthetic paste were dried in a laboratory type drying oven (supplied by Memmert, Germany) at 80 ºC for 10 minutes and cured at 110 ºC for 2 minutes. On the other hand, the fabrics printed with the natural paste were dried and cured at room temperature for 24 hours, due to the fact that the binder used in the printing process is self-crosslinking at approximately 20 ºC.

2.3. Fabric characterization

2.3.1. Color characterization.

In order to realize the objective color characterization of the printed cotton fabrics, the chromatic coordinates, CIELa*b* values, were determined according to the European standard (UNE-EN ISO 105-J01:2000) with the DATACOLOR DC 650 (supplied by DATACOLOR, Spain) apparatus with an illuminant D65 and an observant at an angle of 10º and a diffuse measuring geometry.

2.3.2. Fastness to laundering and rubbing measurements

2.3.2.1. Color fastness to domestic and commercial laundering.

The European standard (UNE-EN ISO 105-C06:2010), was employed for the analysis of the color resistance to laundering, by testing cotton samples of 10×4 cm with the Gyrowash apparatus (supplied by James Heal, United Kingdom). The working conditions were the following: temperature=25 ºC, time of work= 45 minutes, 150 ml of water, 0.6 gr of detergent and 10 steel balls. All of the components were added into a canister together with the sample fabrics. At the end of the test, the samples were dried in forced-air circulation dryer.

2.3.2.2. Color fastness to rubbing.

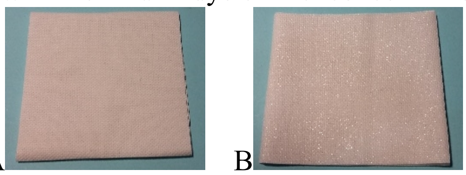
The resistance of the printed fabrics to rubbing was measured and analyzed according to the European standard, UNE-EN ISO 105-X12:2003, which requires the subjection of the cotton samples of about 14×5 cm to the Crockmeter apparatus (supplied by Atlas, Spain) at a temperature of 20 ºC with an applied force of 9 N.

Two types of color fastness to rubbing were tested: in dry conditions, where the rubbing was made at 1 cycle per second exercising the rubbing on the fabric and in the same time applying the mentioned force. The wet rubbing was realized in the same manner as the dry method, but with the addition of a previous conditioning phase, in which the fabric was immersed in distilled water until it was reached an impregnation level comprised between 95 % and 100 %.

3. Results and discussions

3.1. Printing process

During the printing process, the algal pigment was used to provide a light red color, as seen in figure 1. The color shades only related with the natural dye extract concentration, binder and fiber type.



A B

Figure 1. Printed cotton fabrics, A. synthetic paste and B. natural paste

3.2. Color characterization and printing efficiency

During the printing process, the phycoerythrin obtained from *Gracilaria sp.* was used to provide a light red color (pink). As presented in **Table 1**. the color shades only related with the natural dye extract concentration, binder and fiber type.

Table 2. shows that in cotton printing there is a favorable circumstance in the use of natural dyestuff. As known, the L* value represents the lightness of the color (L*, L*= 0 refers to black and L*= 100 refers to white). In the employment of the synthetic paste, it can be observed a slightly lighter color than in the case where the natural paste was employed. In addition, it can be mentioned that the light color obtained was due to the low concentration of colorant employed in the process. Regarding the color area, both types of the printed fabrics are found in the red –yellow area (a*, b*). From the color analysis of the phycoerythrin, it can be stated that a light red color can be obtained with this kind of natural dye and that the intensity of the color depends on the amount of colorant added to the mother paste, in both synthetic and natural printing processes.

Table 2. Color values of the printed cotton

	PE with synthetic paste	PE with natural paste
L*	92,99	92,5
a*	2,61	2,73
b*	3,91	2,71
Chroma (C*)	4,7	3,85
Hue angle (h°)	56,31	44,75

Table 3. Color intensity and lightness differences between the synthetic paste printed cotton fabrics and the ones printed with the natural paste

	Cotton synthetic vs. natural paste
ΔL*	0.49
ΔE*	1.30

The significance of ΔE*, by being characterized by a positive value, confirms that exists a difference of color between the samples printed with synthetic paste and the ones printed with natural paste. Meanwhile, the value of ΔL* indicates a slightly lighter color in the case where it was employed the synthetic printing paste, due to the fact that the sample was subjected to high temperatures in the binder curing phase.

3.3. Fastness of prints

The characterization of the printed cotton through laundering and rubbing fastness can be seen in **Table 4**. The fastness results indicate similar values for both types of printed fabrics and confirm the applicability of this natural pigment in the natural and synthetic printing processes. The washing fastness, in terms of staining, revealed the same value for both tested cases, 4-5, which means relatively no staining. Meanwhile, the change in color parameter exposes a difference between the printing processes, with a higher resistance to laundering of the cotton printed with the synthetic paste. The rubbing fastness results reveal *good* to *excellent* behavior of the cotton printed fabrics.

Table 4. Fastness properties of cotton printed fabrics with synthetic and natural paste

Laundering fastness at 25 ºC		PE with synthetic paste	PE with natural paste
Change in color		4	2
Staining	Wool	4-5	4-5
	Acrylic	4-5	4-5
	Polyester	4-5	4-5
	Polyamide	4-5	4-5
	Cotton	4-5	4-5
	Acetate	4-5	4-5
Rubbing fastness	Wet staining	4-5	5
	Dry staining	4-5	5

1-Very poor 2-Poor·3-Moderate 4- Good 5- Excellent

4. Conclusions

Having as a starting point the hypothesis that the natural dyes are not common to be used in a printing process, this study aimed to validate the employment of algal pigments in the mentioned process, by applying natural and synthetic printing processes.

The printing process results are visualized as pink color fixed uniformly on one side of the cotton fabrics, in both synthetic and natural processes analyzed.

The coloring tests highlighted the applicability of the phycoerythrin in the printing process, without being dependent on the nature of the paste components, natural or synthetic. The resulting colors were defined as light pink colors due to the low pigment concentration employed in the textile finishing process, so it can be affirmed that the algal colorant concentration added to the mother paste, is directly proportional to the intensity of the resulting color. In terms of the printed fabrics brightness, it was observed that the curing temperature of the binder employed in the synthetic paste composition generates a slight decrease in color intensity.

The laundering and rubbing fastness revealed good to excellent results in the printing of cotton with pigments obtained from algal biomass, in both analyzed cases, natural and synthetic printing pastes.

As algal biomass represents one of the resources with the highest availability in nature, and the cultivation process for industrial purposes does not generate the pollutants emitted by the production and employment of the synthetic colorants. Hence, it can be affirmed that the sustainability and durability concept, in terms of environmental protection, is applied. Nonetheless, by employing algal sourced pigments, the final textile product is charged with the added value necessary in an eco-aware society.

Acknowledgements

This work was supported by the European research project ¨SEACOLORS¨ (Demonstration of new natural dyes from algae as substitution of synthetic dyes actually used by textile industries) within the LIFE 2013 ¨Environment Policy and Governance project application¨ program.

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