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NATURAL COTTON PRINTING WITH RED MACROALGAE BIOMASS OF *GRACILARIA GRACILIS AND GRACILARIA CORNEA*

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Abstract: *Environmental protection is gaining popularity in our society due to the accentuated and irresponsible use of natural resources. Consequently, measures need to be taken in all of the demanding industries, including the textile one, as more sustainable alternatives to the actually employed synthetic dyes. One of the solutions can be represented by the utilization of algal biomass as colorant matter. Therefore, this research work aimed the validation of the employment of lyophilized algal biomass in a conventional pigment-printing process. Two different Gracilaria genus species were employed for the comparison of color efficiency and printing suitability, Gracilaria cornea and Gracilaria gracilis. The printing process results revealed brown-red and pink uniformly printed cotton substrates, with good color strength (K/S=11,66 and 23,7 respectively) and good to excellent behavior (analyzed according to greyscale) to rubbing and laundering fastness. Both printed cotton fabrics proffer a special pattern generated by the algal biomass. In conclusion, lyophilized red algal biomass can be employed in the conventional printing process on cotton substrates with no need for previous pigment extraction treatments. This study can serve as a research line opener for further investigation in the application of algae in the textile finishing process.*

Key words: *algae, lyophilized biomass, textile, natural pigments, sustainability*

1. INTRODUCTION

Consumption and the consequently availability of natural resources have become a concerning issue in the societal and industrial development, due to the dramatic expansion of their usage in the last 40 years and the correlation with general environmental degradation [1]. When referring to one of the most demanding and polluting industry, the textile industry, the consumers tend to focus their demands on eco-fashion [2] and sustainability [3].

Taken into consideration that approximately 30 million of tons of textiles are consumed globally per annum and need 700000 tons of synthetic dyes for coloration. Enormous quantities, from which a high amount remains in the environment, accelerating its degradation [4]. This is forcing a continuous search for more sustainable alternatives, which could mitigate the harmful consequences generated by the synthetic dyes. Recent studies have centered the attention on the employment of algae, based on their relevant chemical constituents content, in industries as food [5], cosmetic and pharma [6], agriculture and animal feed [7].

The term algae refer to the photosynthetic organisms which are characterized as being prokaryotic and may be unicellular (microalgae) or pluricellular (macroalgae). By means of pigment content, they are divided into three kingdoms: Rhodophyta (red algae), Phaeophyta (brown algae) and Chlorophyta (green algae) [7]. Red algae is one of the algal phyla with high potential in coloration industries due to the visible tint of the biomass [8]. *Gracilaria genus* is a representative grouping of red seaweeds, with an important content of phycoerythrin (red pigment), generated as secondary metabolite and actually highly prized for its agar content for food and cosmetics industry [9].

Algal application in the textile industry has not been yet documented, neither in dyeing nor printing processes. Even though, research on pigment content and extraction methods have gathered important interest nowadays [10],[11],[12]. In function of the algae type, several added value products can be extracted, such as fatty acids, fats, oil, natural dyes, sugars pigments, antioxidants, etc.[13].

This research was focused on the demonstration and validation of the cotton printing process at laboratory level, involving lyophilized red macroalgal biomass. The aim of the research was to compare the printing processes involving two different algae species pertaining to the same genus, *Gracilaria.* The printing results showed uniformly printed fabrics, which were color characterized, observing the color strength values (K/S) of 11 and 24 respectively. The laundering and rubbing fastness measurements defined the color behavior to external physical agents, analyzed with the greyscale method, as *good* to *excellent*.

2. MATERIALS AND METHODS

2.1. Algal biomass cultivation and colorant matter preparation

Gracilaria gracilis is a cartilaginous, cylindrical red macroalgae, marine species, generally distributed on rocks and stones. It is considered a traditional source of agar. *Gracilaria cornea* also known as *Hydropuntia cornea*, is characterized by being a marine agarophyte, currently used in commerce as source of hydrocolloids [9].

Red algal biomass was employed as colorant matter and was supplied by Algaplus, Portugal. The two Gracilaria genus species, *Gracilaria cornea*, and *Gracilaria gracilis* were cultivated in an open-system culture, in industrial-scale cultivation tanks. The colorant matter applied in the printing process was obtained through a lyophilization process of the fresh biomass, resulting in the algal biomass powder, which was added to the mother printing paste, as described in table 1.

2.2. Textile printing process

In this research work, 200g/m^2 cotton fabrics (supplied by Intexter UPC, Spain) were used as textile substrates for the pigment-printing process, where the natural lyophilized products, were used as coloring matter. The conventional printing paste elaborated is presented in table 1.

Table 1: *Printing paste recipe*

Paste element	Mother paste	
Binder	Resin STK-100*	250 gr
Fixer	Color Center MC-LF*	25 gr
Thickener	Clear HC-35*	20 gr
Pigment	Lyophilized algal biomass	30% (reported to the total weight of the paste)
Water		703 gr
Total		1000 gr

*supplied by Color-Center, Spain

The printing process, carried out at laboratory scale, simulated a conventional industrial printing process, with a printing screen and scraper, and a uniformly applied pressure. According to the binder curing requirements, the printed fabrics were dried in a laboratory drying oven (supplied by Memmert, Germany) at 80ºC for 10 minutes and then further subjected to a curing stage at 110ºC for 2 minutes.

2.3. Printed fabrics characterization

2.3.1. Chromatic coordinates measurement and color characterization

In order to validate the color characteristics of the printed fabrics, the chromatic coordinates, CIELab values were measured with a Datacolor DC 650 (supplied by Datacolor, Spain), employing the requirements of the European accepted standard for textiles characterization (UNE-EN ISO 105-J01:2000). The main characteristics of the apparatus are illuminant D65, observant angle 10º, and a diffuse measuring geometry.

2.3.2. Color strength calculation

Dye uptake or *K/S* value represents a method for the fabric color strength calculation based on the measurement of the reflectance of the fabric at the maximum absorbance lengthwave. This measurement was done using a UV-VIS spectrophotometer Lambda 950 (supplied by Perkin Elmer, Spain) and the color strength was calculated by applying the formula developed by Kubelka and Munk [14]:

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

Where,
K is the coefficient of adsorption,
S is the coefficient of scattering,
R is the reflectance value of the fabric at λ_{max}

The resulting value is directly proportional to the amount of dye present in the material.

2.3.3. Laundering and rubbing fastness

The color fastness to domestic and commercial laundering (UNE-EN ISO 105-C06:2010) was established by submitting samples of cotton of 10×4 cm to the Gyrowash apparatus (Supplied by James Heal, United Kingdom), in a canister together with 150 ml of water, 0.6g of detergent and 10 steel balls for 45 minutes at 25ºC.

The rubbing fastness followed the requirement of the standard UNE-EN ISO 105-X12:2003, which implies the employment of the Crockmeter apparatus (supplied by Atlas, Spain), where printed cotton samples of 14×5 cm are tested for dry and wet rubbing fastness. The rubbing is exercised on the fabric at 1 cycle per second meanwhile applying a force of 9 N, at a temperature of 20ºC. The wet rubbing involves an additional pretreatment of the fabric samples by impregnation until 95-100%.

3. RESULTS AND DISSCUSION

3.1. Color characterization

For the realization of the printing process *Gracilaria cornea* powder biomass was used to provide pink colors; meanwhile, *Gracilaria gracilis* was used to provide brown colors.

Table 2. confirms the colors obtained through the measurement of the chromatic

coordinates, which objectively place the color shades in the pink and respectively brown color sphere.

Table 2: *Chromatic coordinates values of printed cotton*

	Gracilaria gracilis	*Gracilaria cornea*
L*	76,55	72,08
a*	10,62	5,45
b*	9,27	21,37
(C*)	14,1	22,05
(hº)	41,11	75,7

*C=Chroma, hº=Hue angle

Fig. 1: *Fresh biomass and printed cotton with Gracilaria gracilis (left) and Gracilaria cornea (right)*

The color difference between the two Gracilaria species was calculated based on the chromatic coordinates measurements, in terms of ΔL* (19,9), as color lightness and ΔE* (13,89), as a parameter for color difference. The results show that the cotton fabric printed with *Gracilaria gracilis* presents lighter shades, and the **ΔE*** presents a significant nuance difference between the two strains employed in the experiments, even though they belong to the same algal genus.

Color efficiency was determined based on the reflectance strength of the printed fabrics, as shown in fig 2. through the fabrics spectrum.

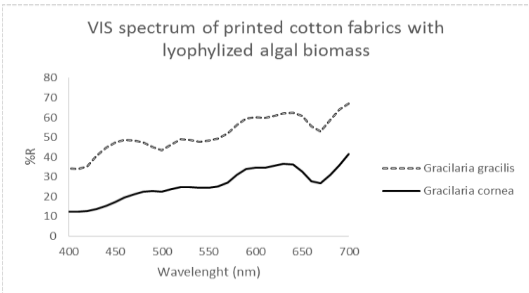

Fig. 2: *VIS spectrum of printed cotton fabrics with lyophilized algal biomass, no pigment extraction realized*

According to the principle of reflection, 100% of reflection corresponds to a white fabric (total light reflection), meanwhile, 0% of reflection corresponds to the black color, which absorbs all the emitted light fascile. In consequence, it can be observed that, according to the reflectance values, the biomass *Gracilaria gracilis* generates lighter colors, when compared with the cotton fabrics printed with the lyophilized biomass corresponding to *Gracilaria cornea*. It can also be confirmed that the two strains of algae employed in the experiments are pertaining to the same algae genus, based on the similar peaks of the color spectrums obtained.

The color efficiency of red macroalgae *Gracilaria gracilis* is characterized by a value of 23,70 which shows to be approximately double, than the one provided by *Gracilaria cornea* 11,66. Both values, when compared with scientific literature centered on dyeing or printing with red/pink natural colorants, show a good level of dye uptake [15].

3.2. Rubbing and laundering fastness

The results of the fastness of the printed cotton fabrics with lyophilized red macroalgae biomass belonging to the *Gracilaria genus* are presented in table 4.

Table 3: *Printed cotton substrates with lyophilized algal biomass rubbing and laundering fastness values*

Laundering fastness at 25ºC		*Gracilaria gracilis*	*Gracilaria cornea*
Change in color		3-4	3-4
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	4
	Dry staining	4-5	4-5

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

In terms of color fastness to rubbing and laundering, both species show similar results when reported to the grayscale, characterized as *good* to *excellent*. When compared with natural colorants, which come from other sources, it can be affirmed that the printing process with lyophilized algal biomass, originating from red macroalgae is viable and applicable on cotton substrates [15],[16].

4. CONCLUSION

The application of lyophilized algal biomass, as colorant matter, obtained from two red macroalgae belonging to the *Gracilaria genus*, in a conventional textile pigment-printing process, at laboratory scale, was demonstrated and validated successfully through this research work.

Taking into account that the application of a mordanting process is required in the majority of the dyeing processes which involve natural colorants [15] the actual study does not employ this process auxiliary. So, it can be affirmed that the color depends exclusively on the colorant matter, binder and fiber.

Textile characterization results show uniformly printed fabrics with variations of red color. Even though the two types of algal biomass appertain to the same genus, differences between the color shade and brightness were observed. The color efficiency and the textile spectrum show more intense and darker color generated by *Gracilaria cornea.*

The textile application validation is sustained by the rubbing and laundering fastness measured according to European standards, mandatory to be applied to the textile industry products. These results characterize the color behavior as *good* to *excellent* in terms of color fading when the fabrics were subjected to a laundering process, and when tested the rubbing staining on a white reference fabric.

In order to obtain a fully sustainable printing process, further experiments must be realized, to find natural alternatives, not only to the colorant matter but also to the auxiliary products employed in the process as resins, binders, and thickeners.

In conclusion, when placed in the environmental protection context, generated by resource scarcity and pollution emission by the industrial activities, finding more sustainable raw materials represents a great accomplishment and a first step in the mitigation process of the environmental degradation. As the textile industry is one of the most demanded and pollution generating industry, sustainable sources of colorant matter represent a way to make a positive change to a more aware society.

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