

# Multifunctionalization of cotton with onion skin extract

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**Abstract** The present study aimed to develop a dyeing process of cotton fabrics with natural onion skin extracts in order to obtain dyed fabrics with antimicrobial and anti-UV properties. The extract was characterized by LC-ESI-MS/MS and the antimicrobial activity of the extract was also evaluated. The dyeing process was optimized considering the influence of the temperature, pH and electrolytes. The effect of cotton pre-treatment with chitosan in the dye uptake was also evaluated. The dyed fabrics were characterized according to antimicrobial activity, anti-UV protection and fastness properties.

**Keywords**— Cotton, natural dyes, onion skin, UV protection, antimicrobial, chitosan

## I. INTRODUCTION

IN recent years, the textile industry has been severely criticized for their contribution to environmental pollution. Therefore, ecological and economic restrictions have been established, including the prohibition of certain synthetic dyes and toxic finishing agents. All these factors led to a greater motivation for the use of natural products, improving sustainability of dyeing and finishing textile processes [1,2]. Moreover, it is possible to extract natural dyes from byproducts such as food, wood and agricultural waste at lower costs. Additionally, these extracts have other interesting properties that allow the functionalization of textiles with UV protection [3] and antimicrobial activity [4]. Among the natural extracts, those obtained from onion skin, mainly composed by quercetin, seem to be interesting for textile applications [5]. The skin, as well as the non-edible apical dry parts of the onion bulbs, are removed prior to processing, constituting an abundant, cheap and readily available agricultural byproduct. Such residues have been used for textile dyeing, since quercetin is a natural colorant that provides several brown hues to natural fibers [5].

In present investigation, the main objective was to develop a dyeing process of cotton fabrics with natural onion skin extracts in order to obtain dyed fabrics with antimicrobial

and anti-UV properties.

## II. EXPERIMENTAL SECTION

### A. Materials and methods

Bleached cotton fabrics (225 gm<sup>-2</sup>) were used in this study. The onion skin extract was obtained in aqueous medium. The mass spectrometry analysis was performed using a Waters pump model 1525 $\mu$  (Milford, USA) using a Waters Symmetry® C18 (4.6 x 75 mm x 3.6  $\mu$ m) column, along with Quattro micro API Waters (Beverly, EUA) triple-quadrupole mass spectrometer with electrospray as ionization source. The optimization of the dyeing process was performed in an Ahiba Texomat Turbo Color. The dyed samples were evaluated through their color strength (K/S) and color intensity (I) using a Datacolor 550 spectrophotometer. Washing fastness tests were performed according to ISO 105-C06:2010 standard test in a Linitest. The rubbing fastness tests were carried out according to ISO 105-X12:2016 standard method using a Crockmeter. The UPF was measured using a SDL-M350 spectrophotometer, according to the standard procedure AS/NZS 4399:1996. The antimicrobial activity of fabrics was performed according to a non-standard qualitative method as described by Magalhães et al. [6].

### III. RESULTS AND DISCUSSION

#### A. Optimization of the extraction process

The UV-Vis spectra of onion skins extracts obtained at different extraction temperatures are shown in Figure 1. It was observed that the spectra of onion skin extract change with the temperature, as it can be seen in Figure 1a).

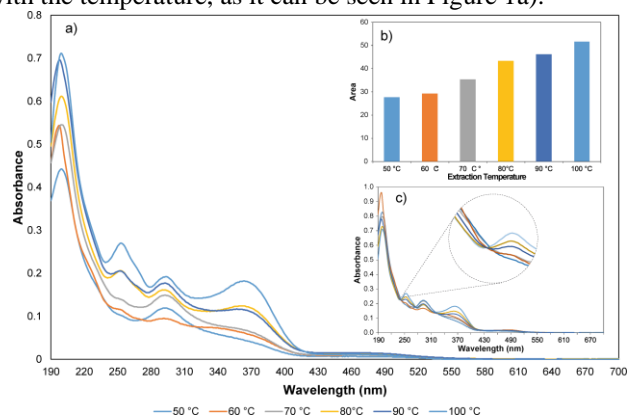


Figure 1. (a) UV-Vis absorption spectrum of the onion skin extract at different extraction temperatures (b) Spectral area of the solutions obtained at different temperatures and (c) Normalized spectra of extracts of onion skin obtained at different temperatures.

For all extraction temperatures, the maximum absorption peak was found at 199 nm. However, at temperatures under 80 °C, the spectra present lower definition for peaks above 199 nm. This possibly indicates that the extraction may not be complete under this temperature. Also, the extracts of onion skin showed an intense brown coloration at pH 4.

Figure 1b) shows the areas of the spectra of solutions obtained at different extraction temperatures. It was observed that increasing temperature favored a higher absorbance of the onion skin extract. Therefore, at higher temperatures there is a higher concentration of extracted compounds and, consequently, a greater efficiency of the extraction process. The normalized spectra of the different solutions (Figure 1c) present three isobestic points. This means that the qualitative composition of the extract remains unchanged regardless of the extraction temperature used. The samples are characterized by the presence of the same compounds but in different proportions [7].

It is also verified that the onion skin extract is able to absorb radiation in the UVA (315-400 nm) and UVB (280-315 nm) regions. Thus, it can be expected that their absorption by textile fabrics can increase the protection level conferred to harmful UV radiations.

#### B. Chemical characterization of the extract

In the mass spectra of onion skin extract were identified five characteristic ions of phenolic compounds. Their identities were confirmed through the analysis of ion fragments of the molecules and the data was compared to those provided in the literature.

The compounds identified in the onion skin extract using HPLC-MS/MS is described in Table 1, in addition to its retention time, observed mass  $[M-H]^-$ , ion fragmentation profile and the consulted literature. It has been found that among the five compounds identified in the extract, four are quercetins, in free or glycosylated form. In fact, quercetin is the most abundant flavonoid found in many onion species [8], and it can be used as a natural dye that offers different shades of brown in textile materials produced with natural fibers [5].

#### C. Antimicrobial properties of the extract

Antimicrobial activity against Gram-positive and Gram-negative bacteria and *C. albicans* was evaluated using the plate microdilution method. The results showed that the *S. aureus* was relatively sensitive to onion extract, whereas *E. coli* was very resistant until the maximum concentration tested. The fungus showed complete resistance [9].

#### D. Dyeing process

By analyzing the results presented in Fig. 2 it is possible to observe that the increase of the dyeing temperature favored the exhaustion of the dye extract in the fiber. This can be seen by the color intensity of samples. The best results were obtained at 100 °C. This behavior can be assigned to the higher kinetic energy of the dye molecules and consequently, to their increasing migration ability at higher temperatures [10-11], which favors the multiplication of the number of colored molecules that interact with the active sites on the surface of the fabrics [12].

TABLE I.  
CHEMICAL COMPOSITION OF ONION SKIN EXTRACT AND CORRESPONDING FRAGMENTATION PROFILE. IDENTIFICATION ACCOMPLISHED BY MS/MS SPECTRA COMPARISON WITH LITERATURE

Number	$T_R$ (min)	Compound name	$[M-H]^-$ (m/z)	MS/MS	Reference
1	7.08	Protocatechuic acid	153	109	[13]
2	7.56	Quercetin diglycoside	625	463, 301	[14]
3	7.93	Quercetin diglycoside	625	463, 301	[14]
4	8.66	Quercetin-hexoside	463	301, 300, 271, 254, 179, 151	[15]
5	11.07	Quercetin	301	273, 257, 229, 179, 151, 107	[16]

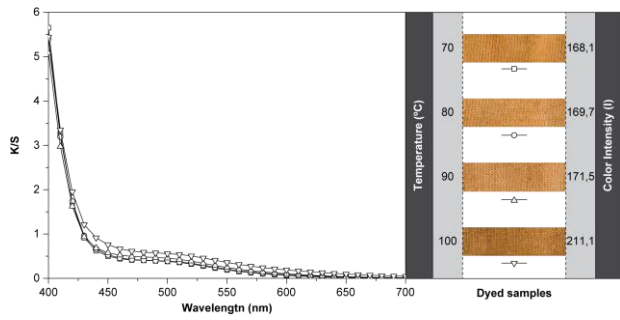


Figure 2. Dyeing of cotton with onion skin extract - K/S curves, Color intensity and samples dyed at different temperatures tested.

The study of the influence of pH on the dyeing of cotton with the onion skin extract shows that the color intensity decreases with the pH of the dyeing solution (Figure 3). The best results were obtained at pH 4.0.

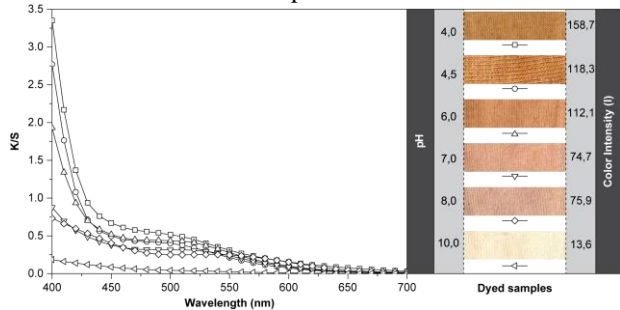


Figure 3. Dyeing of cotton with onion skin extract - K/S curves, Color intensity and samples dyed at different pH values tested.

The effect of the dyebath pH on the dyeing process yield is related with the ionic interactions between ions in solution and chemical groups on surface of cotton [4]. Some of the hydroxymethyl (-CH<sub>2</sub>OH) groups presented in the cotton fibers are naturally oxidized to carboxylic groups during growth and subsequent processes. Consequently, cellulosic fibers generally exhibit a slightly negative charge when immersed in aqueous dyeing solutions. If the pH of the solution is increased above 8, some of the hydroxyl groups present on the hydroxymethyl side chains may also ionize, increasing significantly the negative charge. This negative electric potential at the surface of the cellulose fibers contributes to repel anions at higher pH values. At pH below 4, the carboxyl and hydroxyl groups along the polymer chain of cellulosic fibers are poorly ionized, which considerably reduces the negative surface electrical potential of the fiber. As a result, it reduces the repulsive action on the dyebath anions. In this context, the dye molecules can easily reach the surface of the cotton fibers and interact with them throughout the formation of hydrogen bonds, along with some ion-dipole interactions. Therefore, the negative charge on the adsorbent surface of the cellulose clearly creates an adverse situation for the adsorption of the onion skin extract at alkaline pH. For this reason, the best results were obtained under acidic conditions [17].

The addition of salt to the dyebath increased the color

intensity of dyed cotton fabrics (Figure 4). This behavior can be attributed to the neutralization of the negative surface charge by the sodium ions in the dyeing solution, which favors the absorption of colored compounds [11].

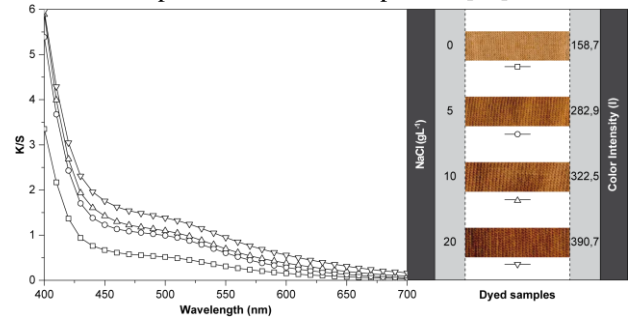


Figure 4. Dyeing of cotton with onion skin extract - K/S curves, Color intensity and samples dyed with different concentrations of NaCl.

Pre-treatment of cotton with an aqueous solution of chitosan (1.5% w/v) showed a significant increase in the color strength of dyed samples (Figure 5). As can be seen, the color intensity of the pre-treated chitosan sample is considerably higher than that of the bleached samples dyed with and without NaCl. Therefore, it can be concluded that chitosan pre-treatment increases the dye uptake due to the interaction between the cationized surface and colored natural compounds.

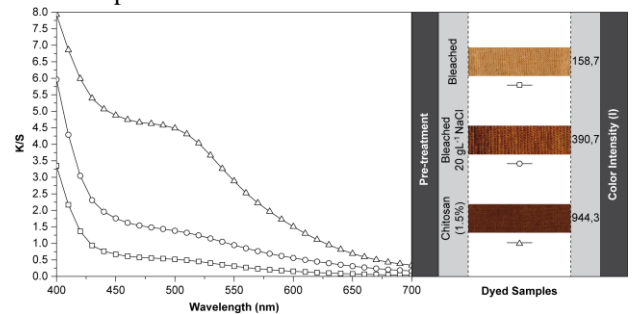


Figure 5. Dyeing of cotton with onion skin extract - K/S curves, Color intensity and samples with and without pre-treatment with chitosan dyed in the presence and absence of NaCl.

#### E. UV protection factor of dyed materials

The UPF results of dyed cotton fabrics with onion skin extract are shown in Figure 6.

In general, samples dyed without pre-treatment with chitosan showed a statistically significant increase of the average UPF index when compared to the bleached samples (A1).

However, the differences between the UPF mean values of the samples dyed with extract concentrations higher than 30 gL<sup>-1</sup> (A4 to A6) are not statistically significant according to the Tukey test at a significance level  $\alpha = 0.05$ . Based on these results, dyed samples with extract concentration of 10 gL<sup>-1</sup> have a UPF index that can be classified as very good, while dyed samples with extract concentrations equal to or higher than 20 gL<sup>-1</sup> can be classified as having excellent protection against UV radiation.

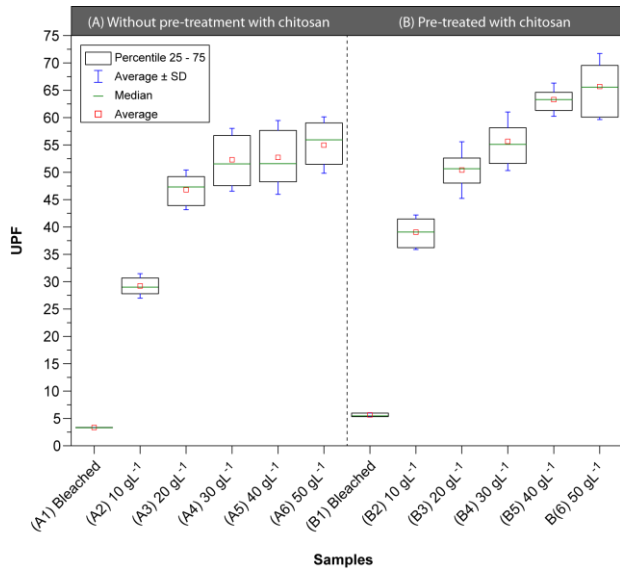


Figure 6. Boxplot from de UPF values of samples with and without previous treatment with chitosan, after dyeing with onion skin extract at different concentrations

Similarly, samples dyed after the pre-treatment with chitosan showed a statistically significant increase of their UPF index average when compared to the bleached samples pre-treated with chitosan (B1).

It was also observed that the UPF index undergoes a statistically significant increase when the concentration of the extract used in the dyeing increases to 40 gL<sup>-1</sup>. Thus, the materials pre-treated with chitosan and subsequently dyed had UPF indexes that ranged from very good, for samples

dyed with 10 gL<sup>-1</sup> extract (B2), to excellent in the case of samples dyed with extracts of concentration equal or higher than 20 gL<sup>-1</sup> (B3 to B6).

#### F. Evaluation of antimicrobial activity of dyed materials

Table 2 presents the results of the antimicrobial evaluation of cotton samples.

In samples subjected to sterility control no growth of microorganisms was observed, confirming their sterility. On the other hand, in the samples used as negative control there was growth, as expected, for all the microorganisms.

All dyed samples showed activity only against *S. aureus*. whereas, against *E. coli* and *C. albicans*, no sample showed inhibitory effect.

Comparing the bioactivity results of the pre-treated chitosan samples with those without pre-treatment, it is possible to suppose that the application of chitosan provided higher diffusion of antimicrobials, since the zone of inhibition formed was significantly larger.

#### G. Evaluation of washing and rubbing fastness properties of dyed materials

The washing and rubbing fastness properties were evaluated. The washing fastness of bleached dyed fabrics was 2-3. However, the pre-treatment with chitosan promoted an improvement in the washing fastness level, especially regarding to the color change of the dyed substrate. In turn, the rubbing fastness obtained was good, ranging from 3-4 to 5 and it was slightly improved in the samples pre-treated with chitosan.

TABLE II.  
ANTIMICROBIAL ACTIVITY OF COTTON FABRICS DYED WITH ONION SKIN EXTRACT

Sample	Microorganisms		
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
Dyed (30 gL <sup>-1</sup> )	(+)	(-)	(+)
Dyed (50 gL <sup>-1</sup> )	(+)	(-)	(+)
Pre-treated with chitosan (1.5%) and dyed (30 gL <sup>-1</sup> )	(+)	(-)	(+)
Pre-treated with chitosan (1.5%) and dyed (50 gL <sup>-1</sup> )	(+)	(-)	(+)
Pre-treated with chitosan (1.5%)	(+)	(-)	(+)
Bleached	(+)	(+)	(+)

(+): Growth of the microorganism in the textile; (-): Absence of growth of the microorganism in the textile

#### IV. CONCLUSIONS

The results showed that it is possible to dye cotton fabrics with natural extracts of onion skins, obtaining acceptable levels of fastness and antimicrobial and anti-UV properties. The best color intensity was obtained by adding 20 gL<sup>-1</sup> of NaCl to dyebath and carrying out the dyeing at 100 °C and pH 4.0. However, the chitosan cotton pre-treatment proved to be more effective, since it allowed increased dye uptake compared to electrolyte use. In this context, chitosan could successfully replace the application of large amounts of salt in the dyeing process, making them more sustainable.

The pre-treatment with chitosan increases UPF values in all cases, due to the increase of dye exhaustion.

The onion skin extract showed antimicrobial activity only against *S. aureus*.

The fabrics pre-treated with chitosan showed better washing and rubbing fastness indexes.

To sum up, the developed dyeing and finishing process allows us to obtain sustainable dyed and multifunctional cotton materials as they are produced with low environmental impact and using only natural based products.

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