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UV Protection on Cotton Dyed with Tea due to Polyphenols Presence

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Abstract. Recently, natural dyes are becoming more important because they are considered environmentally friendly. However, the reduction in pollution is not only the main aspect that makes them interesting. New properties such antibacterial, flame retardancy, etc., can be added to the material dyed with them. In this work we consider different teas, the red one, the black and the green tea. Tea is commonly known all over the world ant they are considerably appreciated by their antioxidant properties. In this work the antioxidant effect of tea extracts has been determined and cotton fabrics were dyed. Previously, fabrics were treated with chitosan as a natural and not pollutant mordant. The effectiveness of dyeing cotton with tea extracts has been objectively studied by the K/S value and the chromatic values CIELab. Furthermore, the ultraviolet (UV) protection has been determined as the Ultraviolet Protection Factor (UPF). Having dyed cotton with the tea extracts and analysing the results, no relationship was found between antioxidant effect and the dyeing yield nor the UPF. The same kind of tea offered fabrics with different colours depending on the extraction method. Some samples showed reddish hue and others a greenish one but it was not directly related to red or green tea. We could conclude that the final colour is more influenced by the way the extraction has been performed than by the kind of tea used. Regarding the UPF, it has been demonstrated that the effectiveness depends on the method used and the level of protection is considerably increased although there are two kinds of tea which show higher results.

INTRODUCTION

In recent years concern about ultraviolet radiation (UVR) has increased exponentially. UVR is one of the types of radiation emitted by the sun that is not completely absorbed by the atmosphere and reaches the earth and the people who lives in it. That radiation is a kind of an electromagnetic radiation with a wavelength shorter than visible light and greater than weak X rays. The range of ultraviolet radiation is also subdivided into UVA (400-315nm), UVB (315-280nm) and UVC (<280nm) and the most dangerous radiation for the humans is UVB followed by UVA [1, 2]. In fact, 99% of the UVR that reaches the earth's surface is UVA radiation, but UVB radiation is more energetic so the effects are more dangerous. One of the problems that nowadays the human population is facing is the decrease in the thickness of the ozone layer, because it is causing an increase of the amount of UVB radiation that reaches the Earth's surface. It is estimated that a 1% decrease in the ozone layer will cause an increase in solar radiation at the earth's surface that could increase the number of cases of skin cancer by up to 2.3%. [3]. That is why the World Health Organization (WHO) have recently recommend the use of textiles with high protection factors (World Health Organization. Data access: 27/02/2013).

Have been demonstrated that textiles can provide protection against UV radiation but the parameters of them have to be choose in a correct way because in many cases the protection they provide is not enough. Recent studies have provided information regarding the characteristics that textiles must have in order to offer very good UV protection [4, 5]. The Ultraviolet Protection Factor (UPF) is used to assign a textile's degree of protection and the methodology used is described in EN 13758-1 standard (EN 13758-1). The most important plain fabrics parameters, in order to obtain the best UV protection are the structural parameters such as ligation coefficient, weight/sqm., the ligament, or warp and weft density [6]. Light fabrics which structural parameters has low values are most used on spring and

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summer seasons where the radiation on Earth's surface is more intense. It has been also studied that in light fabrics the UPF can be increased using some finishing products or some specific fibres with high UVR absorption [7].

In this aspect the natural animal and vegetables origin finishings, are beginning to be used taking in advantage its functional properties. There are studies in which different natural products are used in order to improve the properties of the fabric. Specifically, chitosan [8, 9], keratin, and different types of teas have been used to increase the protection against ultraviolet radiation of the fabrics [10]. In other papers the use of coffee, Rubia Tinctoria, Curcuma Tinctoria, Alium Cepa, Lawsone, Cistus, Altea, Eucalyptus leaves, Seaweed, Orange peel, or Broccoli is studied [10-13]. All of these studies shows very good results, so the use of other natural extracts can be studied being the prospect of success very high.

The use of natural dyes on textiles is carried out with the aim of acquiring properties that it does not inherently possess. So, through the dyeing of fabrics with natural dyes, functional fabrics are obtained with properties such as antimicrobials, antifungals and protection against ultraviolet radiation [14, 15]. The majority of these products used to increase the protection against ultraviolet radiation have a high content of polyphenols that will be conferred to the fabric [16]. One of the most interesting natural products is tea liquor, because polyphenols represent more than 36% of chemical composition of dry tea leaves [17]. Polyphenols are subdivided into flavonoids that are among nature's most potent antioxidant compounds [18, 19].

Scalbert et al. in their paper "Dietary polyphenols and the prevention of diseases" estate that the consumption of food rich in polyphenols is highly related to a lower incidence of diseases [20] due to its antioxidant activity [21]. There are studies, still performed in animals, which show that the consumption of green tea may decrease the appearance of tumours [22]. It is therefore believed, that these polyphenols acquired by the fabric have protective properties against ultraviolet radiation.

In order to make suitable dyes with natural extracts on textile substrates such as cotton, it is necessary to pre-treat the fabric to increase the affinity between both. Following the principles of environmentally friendly dyeing, Chemat proposes the use of products, mordants and systems for extracting liquor which are respectful of the environment [23]. There are many natural products used as mordants such as E. acuminata DC var euprista Karth [24]. Chitosan, is also widely used as a bio-mordanting agent [25, 26] as it offers many advantages and the results of the mentioned studies show that chitosan can be perfectly used as a substitute for metal-based mordants [27].

In Punrattanasin's work, the ultraviolet protection provided by cotton stained with green tea is established [28] but Perva-Uzunalic et al. work is especially interesting because show that there is a greater degradation of the catechins at high temperatures and long processing times [29], so this work will be taken into account for the liquor extraction process.

The aim of this study is to evaluate the tea polyphenols influence on the ultraviolet protection factor of cotton fabric. The procedure consisted on mordanting the cotton with medium molecular weight chitosan to improve the affinity of cotton fabric with the tea extracts. The absorption on UV-Vis region and the quantity of polyphenols of tea extracts, the colour strength of dyed samples, and the UV protection were studied.

EXPERIMENTAL

Materials

The fabric used, previously bleached, was a 100% cotton twill fabric with 210g/m^2.

Chitosan medium molecular weight powder, viscosity 200.000 cps, CAS 9012-76-4) was purchased from Sigma Aldrich Chemical. Glacial acetic acid (98%) was supplied by Akralab.

As a natural dyes commercial samples of black, green, white and red tea were used.

Methods

Extract Preparation

The method used to obtain the aqueous extractions of each tea is by boiling. The procedure used to get different extract with four types of tea was without temperature and heating the mixture to boiling point. Tea powder added to

100 ml distilled water was stirred, heated to 100 ºC for 2 hours, allowed to stand for 15 minutes and then filtered with filter paper.

Tea Extracts Absorption in the UV-Visible Region

UV-visible spectrometry refers to techniques that measure the amount of light of a particular wavelength emitted that is absorbed by a sample. As it is known, the colour of a sample can be often correlated with the presence of a particular chemical structure (Dean et al 1990). The UV-VIS 1000 CECIL Spectrophotometer was used to carry out the tea extractions measurements in the UV-visible region comprised between 200 and 700 nm. This technique is intended to know exactly the tea extracts absorbance in the ultraviolet region between 200 and 400 nm.

Extracts Characterization

In the high performance liquid chromatography (HPLC) technique, the compound passes through the stationary phase placed in the chromatographic column. The sample to be analysed is introduced by pressure pumping in small quantities and its components are delayed differentially depending on the chemical and physical interactions with the stationary phase [30].

This technique is used to determine the polyphenols present in the extracts of the different teas. The equipment used was the AB SCIEX TripleTOF™ 5600 LC/MS/MS and the automated calibration was performed using an external Calibration Delivery System (CDS) that infuses calibration solution previously to sample introduction. The column used is a Phenomenex C18.5 µm (4.6 x 250 mm) column with an accumulation time of 100ms.

Cotton Pre-Treatment with Chitosan and Dyeing

To dissolve the chitosan 3 g/L of acetic acid was needed. A 5 g/L solution of chitosan was prepared. Cotton fabrics were treated by padding (80-85% pick-up) with a 1 bar roller pressure and a speed of 1m/min. After this time, the treated fabrics were dried at 60 ºC in a Screen Printing Engineering TD-20 horizontal drier and then cured at 120 °C for 3 min in a forced air convection heater (WTC Binder 030).

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Cotton Dyeing

The dyeing process with natural extracts has been carried out by exhaustion process with a bath ratio of 1/40. The dye bath was prepared with 50% of the resulting extraction and 50% of distilled water. The textile samples were immersed in the exhaustion bath for 1 hour at 90-95ºC.

Colour Fabric Measurement

The determination of samples colour was carried out by the following standard procedure. The equipment Minolta CM-3600d UV-visible spectrophotometer used as a illuminant D65/10° observer, in terms of CIELAB values (L*, a*, b*, c*, h).

The Kubelka–Munk equation [31] where K is the coefficient of absorption; S is the coefficient of scattering and R is the reflectance, was used in order to obtain the relative colour strength (K/S) of the different dyed fabrics using the light reflectance technique.

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

The method used to evaluate the ultraviolet protection factor was composed of an UV-lamp, a digital detector of UV radiation and an opaque box.

A total of 60 measurements of each sample were taken, because the photodetector takes a measurement in a 5 seconds interval in a total measurement time of 300 seconds.

The emission source emits ultraviolet radiation at two specific wavelengths, 312nm and 365nm, which correspond to UVB radiation and UVA radiation respectively. These two emission sources were chosen because they represent the ultraviolet radiation and are available in the market easily.

In according with European Standard EN 13758-1, the UPF of fabric is determined from the total spectral transmittance as follows:

$$UPF = \frac{E(312)\cdot\varepsilon(312)\cdot\Delta(\lambda)+E(365)\cdot\varepsilon(365)\cdot\Delta(\lambda)}{E(312)\cdot\varepsilon(312)\cdot T(312)\cdot\Delta(\lambda)+E(365)\cdot\varepsilon(365)\cdot T(365)\cdot\Delta(\lambda)} \quad (2)$$

The samples are prepared and conditioned according to the ISO 139:2005 standard. All of them were extracted from the center of the fabric at an exact distance of 125 0mm from the selvage. The second sample of the same reference was extracted from a distance of 1cm from the first sample. The standardized size of each sample is 10x10cm because covers the photodetector completely [32].

RESULTS AND DISCUSSION

Tea Extracts Absorption on UV-Vis Region

The absorption spectrum is a graphical representation that indicates the amount of light absorbed at different values of wavelength (λ). Therefore, of each tea extract diluted in a solution, whose maximum absorbance is within the measurement range of 200 to 700nm, the absorbance value can be obtained in comparison with a white solution containing the solvent of the solution under study, in this case distilled water. The chemical structure of a chromophore molecule affects directly to the absorption spectrum.

The absorption spectrum of the tea extracts obtained by the boiling technique are shown below. That process is made in order to characterize the extracts. In addition, the ability to absorb ultraviolet radiation of the samples is glimpsed, and thus to obtain a relationship between the UPF acquired by the fabrics dyed with natural tea extracts.

While the visible spectrum region shows very low absorption, in the ultraviolet region the values are very high, so it is supposed that the extracts, conveniently applied on fabrics can confer a high ultraviolet protection factor (UPF). The absorption spectrum of green, red, black and white tea extracts between 200 and 700 nm is shown in **FIGURE 1**.

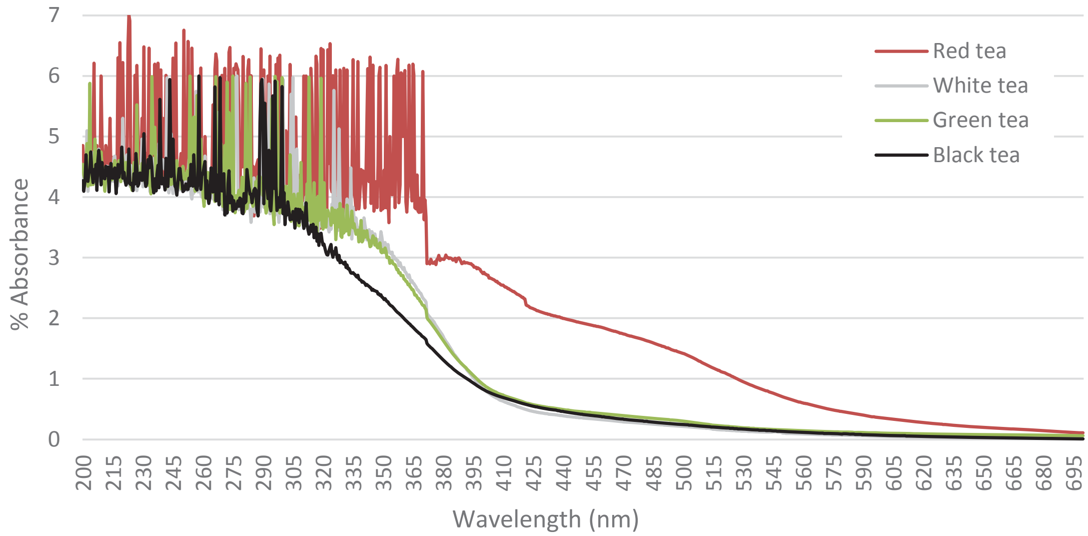

FIGURE 1. Tea extracts absorption spectrum between 200 and 700nm.

The extract obtained by boiling that show the highest absorption is red tea extract with a high extent compared to the other extracts. Black, green and white tea extracts present similar values to each other. It is expected that the cotton fabric dyed with red tea extract will provide the highest protection against ultraviolet radiation, so that fabric will obtain the highest UPF values.

Extractions Characterization (HPLC)

The tea extracts analysis and characterization have been carried out using high performance liquid chromatography (HPLC). The HPLC technique separates of the components of the extracts based on chemical interactions between the analysed substance and the chromatographic column. Some polyphenols have been obtained from each tea extract. The technique offers the measurement intensity and the measurement error, in parts per million (ppm). All tea extracts' polyphenols taken into account are those whose intensity is higher than 5E + 05 and the measurement error is between 2 and -2 ppm, in **TABLE 1** results are shown.

TABLE 1. Red tea extracts' polyphenols obtained.

Polyphenol	Intensity	Measurement error (ppm)
(-)-Epigallocatechin	1,25E+06	-1,6
(+)-Gallocatechin	3,00E+06	-1,6

Tea Extracts Colorimetric Properties

The dyeing of cotton fabrics has been carried out following the procedure described, being previously treated with medium molecular weight chitosan as a mordanting process.

Chitosan has been chosen as a bio-mordant for the functionalization of cotton fabrics and to improve the adhesion of natural tea extracts as a dyes, following the principles of "green extraction" being environmentally respectful. Medium molecular weight chitosan (XM) in a concentration of 5 g/L. has been used adding 6mL of acetic acid in order to obtain a slightly acidic pH to promote the dissolution of chitosan. To ensure that the chitosan is completely dissolved, the solution is kept under stirring for 24 hours as described in Gupta's et al. work [31]. Studying the colour strength value (K/S) according to the wavelength in the visible region of the UVR (400 to 700 nm), an objective comparison is obtained by using different types of teas as a dyes.

The K/S spectrum of the pre-treated cotton fabric with medium molecular weight chitosan and without pre-treating and dyed with the tea extracts is presented in **FIGURE 2**. Red and black tea extracts applied on the cotton fabric, offer greater colour strength than white and green tea extracts. The samples which have suffer a bio-mordanting process present higher K/S values than the samples without have being mordanted.

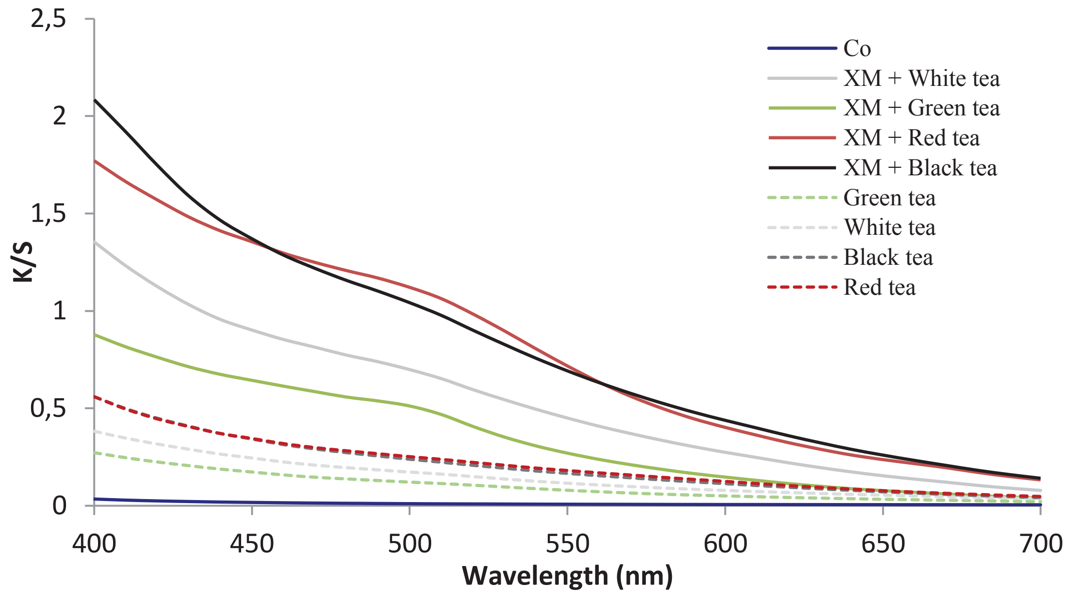

FIGURE 2. Tea extracts dyeing colour strength (K/S) spectrum. Comparison of chitosan mordanted and non-mordanted fabrics.

In order to obtain the maximum value showed for each tea extract, the maximum K/S value offered by each dyeing specie and the wavelength at which it is reached are observed. Can be seen on **TABLE 2**, that black tea and red tea present the highest K/S value at 400nm and have a very similar spectrum. Can also be observed that the mordanted and non-mordanted fabrics show the maximum K/S value at 400nm with the difference that the non-mordanted textiles offer considerably lower K/S values. Regarding the maximum K/S value, the pre-mordanted fabrics show an increase of more than 300% compared to the non-mordanted ones.

TABLE 2. Maximum K/S value of mordanted and non-mordanted tea extracts dyed fabrics.

Sample	**K/S (λ=400 nm)**
XM + White tea	1,355
XM + Green tea	0,878
XM + Red tea	1,771
XM + Black tea	2,085
White tea	0,383
Green tea	0,273
Red tea	0,560
Black tea	0,559

The percentage of reflectance that the mordanted and dyed fabrics shows can be seen in **FIGURE 3,** and the values are similar to the K/S values. Red tea and black tea dyeings show a very similar reflectance spectrum while green tea and white tea have higher percentage of reflectance values. It is interesting to note that at 400nm, the percentage of reflectance difference between red and black tea is slightly significant whilst the maximum K/S value difference is significant.

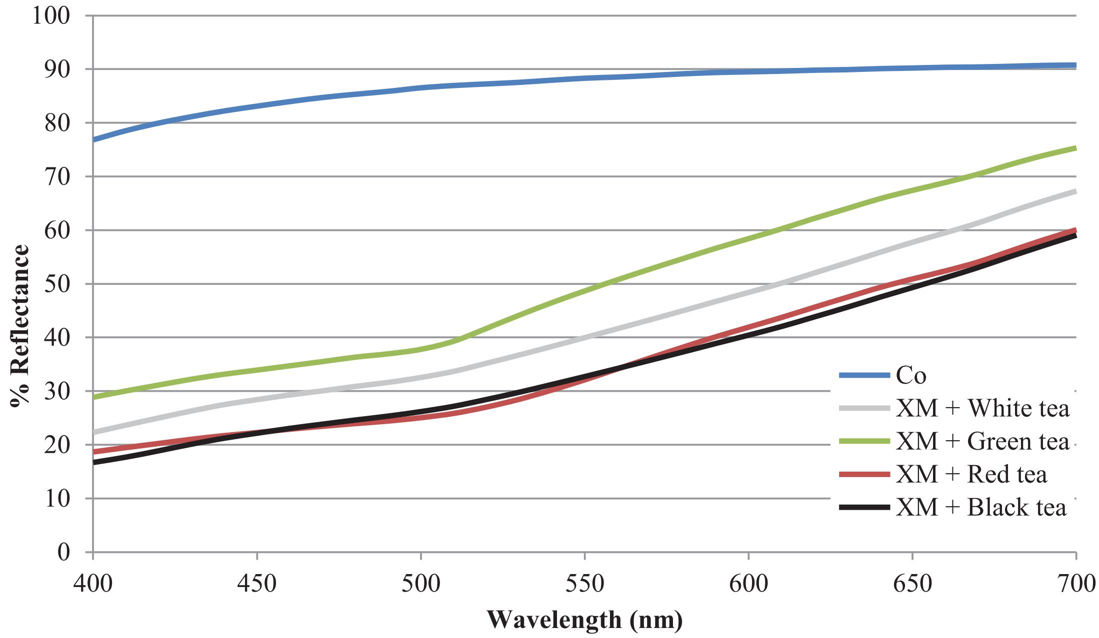

FIGURE 3. Dyed fabrics percentage of reflectance spectrum.

UV Protection

Can be observed in **FIGURE 4** that dyeing the cotton fabric with any type of tea extract, improve the UPF value of them. That UPF value indicates that the UVR protection is considerable so all the teas extracts offer an important improvement of the UPF. All tea extracts noticeably improve the undyed fabric exceeding the UPF value of 50, which means that the protection achieved is classified as "Very good" according to the European standard EN 13758-2.

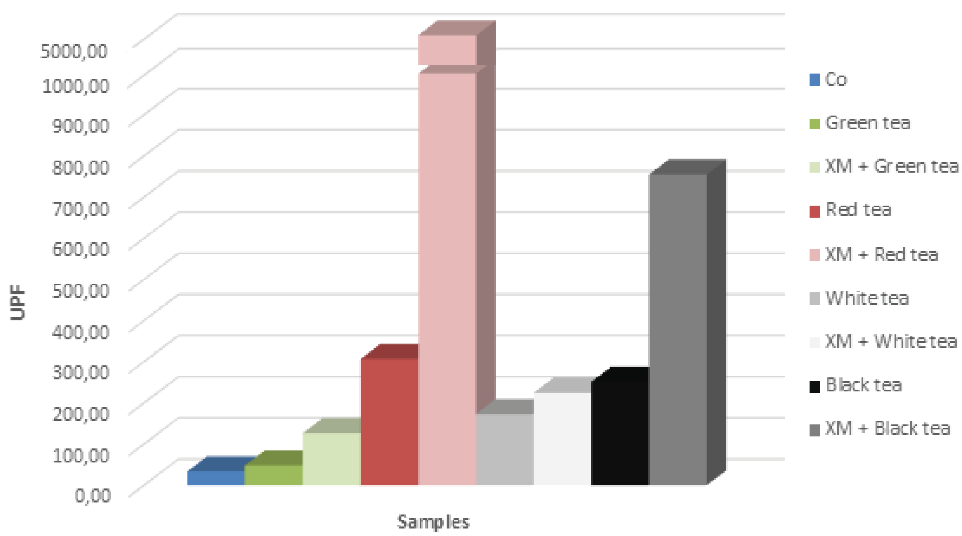

FIGURE 4. UPF dyed fabrics value. Sample comparison with different tea extracts on pre-treated cotton with medium molecular weight chitosan.

On one hand it should be noted that red tea and black tea offer higher UPF values than green tea and white tea dyeing. Exceptional is the ultraviolet protection factor offered by red tea as it exceeds UPF value of 5.000 while the black tea extract rounds values of 755, so the red tea is the extract that best protects against ultraviolet radiation. On the other hand, it is confirmed that those extracts applied to cotton fabric with a pre-treatment with a natural origin mordant such as medium molecular weight chitosan improves the UPF compared to dyeing without pre-treatment with mordants.

Finally, the **FIGURE 5** shows a summary of the results obtained. A diamond graphic has been created to show the absorbance and the polyphenols obtained from tea extractions, and the fabrics UPF and colour strength. On the figure below, each colour line represents each tea extract.

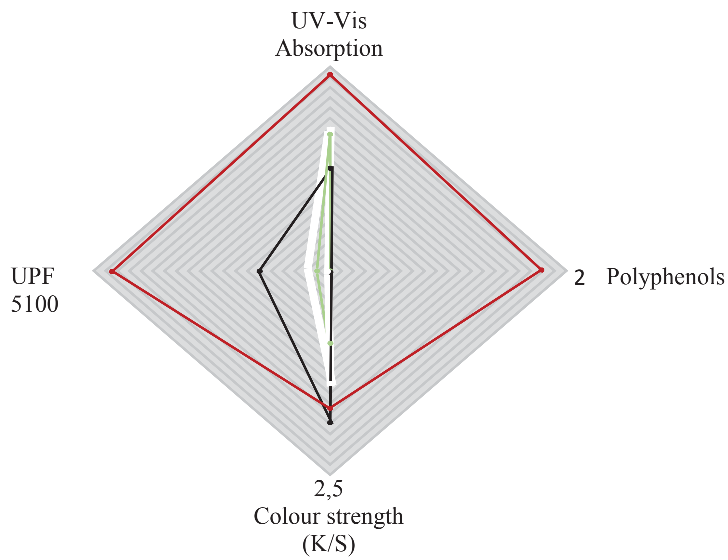

FIGURE 5. Comparison of red tea, black tea, green tea and white tea extracts, UV-Vis absorption, UPF, polyphenols, and colour strength.

As can be seen, the red tea is the extract that shows higher UPF, polyphenols and absorbance on the UV-Vis region. It is important to notice that the black tea extract shows better colour strength but do not show any polyphenol and that is the reason why red tea extract have higher UPF values.

CONCLUSIONS

The results obtained on the present paper show that the absorption of the extracts in the ultraviolet region is considerably higher than in the visible region of the electromagnetic spectrum. This absorption is closely (intimately) linked with the UV protection of dyed cotton fabrics, as the UPF value is very high. The tea extract with the highest absorption, as well as the highest UPF, is red tea, although the rest of tea extracts also show very good values. It is very interesting to note that red tea is the only extract that offers polyphenols included between the established limits, being these (-)-Epigallocatechin and (+)-Gallocatechin. It can be affirmed that the influence of polyphenols compared to UPF is very strong. The red tea, which is the only extract that presents polyphenols, offers a UPF value six times greater than the black tea, which is the following extract with the highest UPF value. A previous bio-mordanting of cotton maximizes dyeing properties as well as protection against UVR in dyestuffs with natural dyes.

In addition, it can be ruled out that the increase of fabrics' UPF value is due to colour acquired. Comparing the dyed cotton colour strength with natural dyes and direct dyes, the UPF of natural dyed cotton offers much higher values than those shown by direct dyed cotton.

To sum up, a high relationship can be observed between the UPF and the polyphenols presents on the dyed fabrics with natural tea extracts. What has been demonstrated is that the UPF of cotton fabrics can be enhanced with natural tea extracts used as a dye and it is more influenced by the polyphenols presents in the extraction than by the colour acquired by the fabric.

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