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Article

Colorimetric Analysis of Cotton Textile Bleaching through H_2O_2 Activated by UV Light

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The bleaching process is one of the steps of cotton fabric manufacture. Traditionally, the most common bleaching procedure is based on the use of a hydrogen peroxide (H_2O_2) solution in alkali pH associated with high temperature. In this study, we investigated the possibility of applying a photolysis technique, combining ultraviolet (UV) light and H_2O_2 in acidic pH to promote raw cotton fabric bleaching, without adding heat and stabilizers to the process. A colorimetric analysis was performed to assess the bleaching procedure in the samples. The experiment consisted in moistening cotton fabric samples with H_2O_2 and then illuminating them with UV light with different doses, ranging from 0.6 to 36 J cm^{-2}. Our findings have shown that it is important to balance the hydrogen peroxide and the amount of delivered UV light to the cotton fabric in order to achieve a satisfactory whiteness without compromising the fabric mechanical properties.

Keywords: photolysis, cotton fabric, hydrogen peroxide, UV light, photobleaching

Introduction

From the field to the consumer, cotton fiber undergoes several processes, such as: weaving or knitting, desizing, scouring, bleaching, dyeing and goods preparation. Like all natural fibers, cotton presents some natural pigments that lead it to have a yellowish brown color. This coloration may also come from environmental factors like soil, dust, insects and others. The bleaching process is responsible for removing these pigments in order to make the cotton whiter.[1-3]

Bleaching agents are used to oxidize or reduce the coloring matter, which is washed out to obtain permanent whiteness. Optical brighteners are also added to the process in order to achieve higher whiteness levels.

Hydrogen peroxide (H_2O_2) has been used for industrial cotton bleaching for decades. One of the most common methods combines hydrogen peroxide, caustic soda, sodium silicate, temperature (95-98 °C) and pH around 10 and 11. However, it consumes high amount of energy and may chemically damage the cotton fibers.[3,4] The process is usually performed in alkaline conditions, however, the mechanism of removing non cellulosic materials is unknown for alkaline bleaching, it has been assumed that perhydroxyl ions dissociate from hydrogen peroxide according to the reactions described in equations 1 and 2.[2,5]

$$H_2O_2 \overset{\Delta}{\leftrightarrow} H^+ + HOO^- \quad (1)$$

$$2H_2O_2 \overset{\Delta}{\leftrightarrow} 2H_2O + O_2 \quad (2)$$

Under acid or neutral pH conditions, the formation of perhydroxyl ions is very low, thus it is usually added an alkali to promote dissociation of the perhydroxyl ions from the H_2O_2 (equation 3). Cotton fabrics have a relatively small damage of the raw cotton by perhydroxyl ions, due to the electrical repulsion between the charged cotton and the ions.[3,4]

$$H_2O_2 + OH^- \overset{\Delta}{\leftrightarrow} H_2O + HOO^- \quad (3)$$

Currently, research on cotton bleaching aims to decrease the necessity of using extra chemical substances in the traditional process. An example is the use of enzymatic processes alternatively to hydrogen peroxide (H_2O_2) reactions, which could be produced *in situ* by enzyme-fragmenting waxes.[6] Montazer and Morshedi[7] proposed a "nano-photo bleaching" on wool. They showed that protease pretreated wool fabric enhanced the adsorption of TiO_2 nanoparticles along with citric acid and, after exposure

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to the daylight (sunlight), the technique led to a whiter wool with enhanced hydrophylicity. Using hydrogen peroxide associated with ultrasonic methods is also an explored method that reduce the long time required for bleaching.[7]

Photolysis of H_2O_2/UV has been studied for dyes discoloration and waste treatment because it is a very oxidative process of organic pollutants in industrial wastewater. Ultraviolet irradiation conjugated with hydrogen peroxide has stronger molar absorption and the highest quantum yields at 254 nm and accelerated hydroxyl that generates the radicals.[8]

It is shown in the literature[9-11] the application of H_2O_2/UV to oxidize organic matter in the UV-C spectral range. This process is related to the production of reactive oxygen species, mainly hydroxyl radicals, for which there are simultaneous reaction to direct photocatalysis of the H_2O_2 under UV light.[9,12,13]

Another important issue in the conventional method for cotton bleaching is the enormous amount of water required for the entire process; from 200 to 270 tons of water are used for each ton of raw cotton. About 90% of this amount of water is used to eliminate chemical compounds used during the bleaching process.[14]

As chemical bleaching is an expensive and wasteful process, the present study aims to evaluate, through colorimetry and tensile test, cotton fabric whitening when hydrogen peroxide in acidic pH is photoactivated by UV light around 254 nm.

Experimental

Cotton samples were obtained from Cedro Textil SA (Minas Gerais, Brazil) in three different conditions: raw cotton fabric (RCF, not submitted to bleaching process and pre-treatment); chemically bleached cotton fabric (CBCF, traditional bleaching method); and optically bleached cotton fabric (OBCF, traditional bleaching). The bleaching tests with H_2O_2/UV were performed in RCF samples.

To evaluate and quantify the cotton fabric bleaching, we used a handheld colorimeter (TCS USB Black, Pocket Spec Technologies Inc., Denver, USA). This device emits a white light pulse from a high intensity light emitting diode (LED) and collects the backscattered light from the sample with spectral width 400-700 nm.[15]

The colorimeter provided the results in RGB (red, green, blue) color space, with values varying from 0 to 255 for each component, and the measurements were calibrated to a standard white, 255/255/255. A first series of measurements were performed on samples of RCF, CBCF and OBCF (standard white cotton fabric sample). Five measurements were acquired from each cotton sample.

To better quantify the whiteness, the RGB color components were converted to L*a*b* (Commission Internationale de l'Eclairage, CIELab). The CIELab system space provides a three-dimensional representation for color perception and indicate a position in the international space color, so the relative perceptual differences between any two colors in L*a*b* can be approximated by treating each color as a point in a three-dimensional space (with three components: L*, a*, b*).[16-19]

In CIELab, L is the luminance which represents the difference between light (L* = 100) and dark (L* = 0); a and b are variables which represent the color values on the red-green axis and blue-yellow axis, respectively.[20,21] After converting RGB to L*a*b* (for practical and convenience reasons, the conversion was performed online),[16] the Euclidean distance (ΔE) between "perfect white" and measured value was calculated as follows:

$$\Delta E = \sqrt{\left(L_1^* - L_2^*\right)^2 + \left(a_1^* - a_2^*\right)^2 + \left(b_1^* - b_2^*\right)^2} \quad (4)$$

where (L_1^*, a_1^*, b_1^* = 100, 0.005, –0.01) corresponds to the calibration white (RGB = 255,255,255) and (L_2^*, a_2^*, b_2^*) corresponds to the measured sample coordinates. Figure 1 presents a schematic of the 3 dimensional Lab color space with the definition of ΔE, that is the straight-line distance between two points.

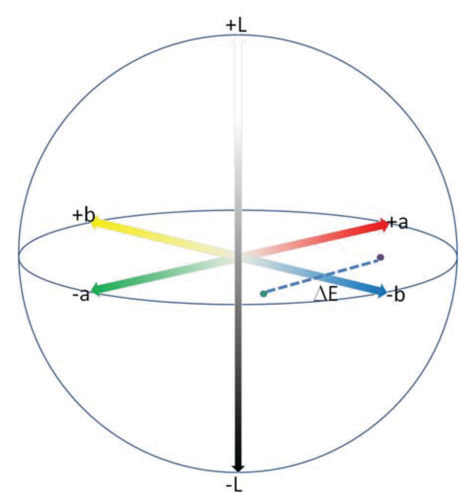

Figure 1. Representation of the 3D CIE-Lab color space. L: brightness; a: hue; b: chroma. ΔE is the so-called Euclidean distance between two points in the space.

For photolysis, a UV lamp (electric power 4 W, Phillips TUV FAM, Amsterdam, Netherlands) was used, and according to the manufacturer, it emits UV-C radiation around 254 nm with 9 W of optic power. The lamp was placed in a homemade closed box to protect people from the UV radiation during the experiments.[9,22]

The irradiation intensity was 1 mW cm^{-2} and it was used an optical fiber based spectral radiometer (Ocean Optics USB 200+UV+VIS) to quantify. To calculate the light dose (D) delivered to the samples, it was used seven different light doses (D) ranging from 0.6 to 36 J cm^{-2} (Table 1) used in the experiments.

$$D = I_0 \times t \quad (5)$$

where I_0 is the light irradiance (in mW cm^{-2}) emitted by the lamp and t is the irradiation time in seconds.

Table 1. Radiation intensity applied to the raw cotton fabric and light dose delivered to the samples

Intensity (I_0) / (mW cm^{-2})	Dose on the sample (D) / (J cm^{-2})						
1	0.6	1.2	1.8	3.6	5.4	22	36

The solution of hydrogen peroxide (H_2O_2) used in the present study was acquired from a local compound drugstore at 40% (v/v) with pH = 1.4.[23]

The experimental protocol for cotton bleaching was carried out as follows: samples were individually moistened in hydrogen peroxide solution through submersion for about 3 to 5 s; each sample was placed at a time within the box to receive the light dose (D); after irradiation, the samples were washed with clean water (at room temperature) and let naturally dry for further analysis. It is important to notice that in our process, no pre-treatment and heat was applied to the raw cotton and during the bleaching. The colorimetric measurements were performed with the dry samples.

To assess if the cotton could be mechanically damaged by the photobleaching process, it was utilized a sample of the UV irradiation + H_2O_2 in 40% (v/v) with dose variation of 0.6-36 J cm^{-2}, and compared with raw cotton fabric (RCF) and chemically bleached cotton fabric (CBCF), a tensile test was conducted in a universal testing machine, EMIC DL-1000 (EMIC, São José dos Pinhais, PR, Brazil).

Results and Discussion

This study aimed to explore the possibility of using a photonic technique in which hydrogen peroxide in acid pH is photoactivated by different doses of UV to promote raw cotton fabric bleaching. First, a colorimetric assessment of cotton fabric was performed and the results of the three different cotton samples acquired from factory (no procedure was performed on these samples in our laboratory) are presented in Table 2.

Table 2. RGB color components of measurements on cotton fabric

Type of raw cotton	R (red)	G (green)	B (blue)
RCF	223 ± 2	225 ± 2	187 ± 1
CBCF	246 ± 2	247 ± 2	232 ± 1
OBCF	240 ± 1	241 ± 0.6	238 ± 0.3

RCF: raw cotton fabric; CBCF: chemically bleached cotton fabric; OBCF: optically bleached cotton fabric.

In order to better evaluate the whiteness, the RGB coordinates were converted into CIELab color space and the results are presented in Table 3.

Table 3. Evaluation of the color as CIElab and Euclidean distance (ΔE) between measurement and calibration white

Type of raw cotton	L*	a*	b*	ΔE
RCF	88.5 ± 0.6	–7.1 ± 0.2	18.3 ± 0.2	22.7 ± 0.3
CBCF	96.9 ± 0.7	–3.2 ± 0.2	7.4 ± 0.2	8.7 ± 0.2
OBCF	94.9 ± 0.2	–0.8 ± 0.2	1.2 ± 0.3	5.3 ± 0.2

RCF: raw cotton fabric; CBCF: chemically bleached cotton fabric; OBCF: optically bleached cotton fabric.

From the data of ΔE in Table 3, the graph of Figure 2 was plotted in order to better compare the cotton and it is possible to observe, as expected, that after converting to L*a*b*, the calculated Euclidean distances (ΔE) showed that the OBCF was the most similar sample to the perfect white; followed by CBCF, and then by RCF. According to the manufactory, CBCF is a fabric that was subject to the traditional bleaching process, and the OBCF is a CBFC that was subjected to a dyeing process with white dye, which confers it a high quality of whiteness.

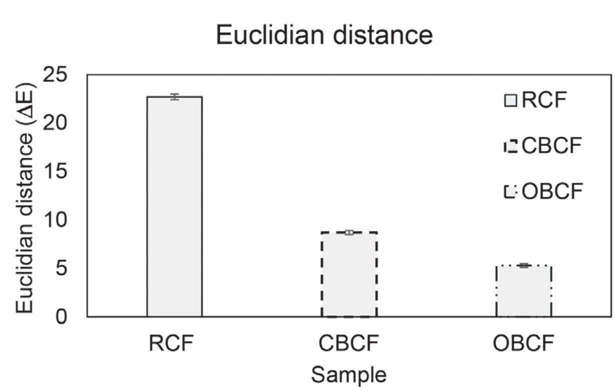

Figure 2. Euclidian distance (ΔE) between calibration white and raw cotton fabric (RCF), chemically bleached cotton fabric (CBCF); optically bleached cotton fabric (OBCF).

Using intensity of 1 mW cm^{-2} UV light in H_2O_2 at 40% (v/v), the bleaching was monitored from 0.6 to 36 J cm^{-2}.

From the graph of Figure 3, one can observe that as the delivered light dose increases, the Euclidean distance decreases, approaching to the ΔE corresponding to OBCF. It means that the UV mediated photolysis of H_2O_2 is, indeed, promoting the degradation of the non-cellulosic materials present in the fabric.

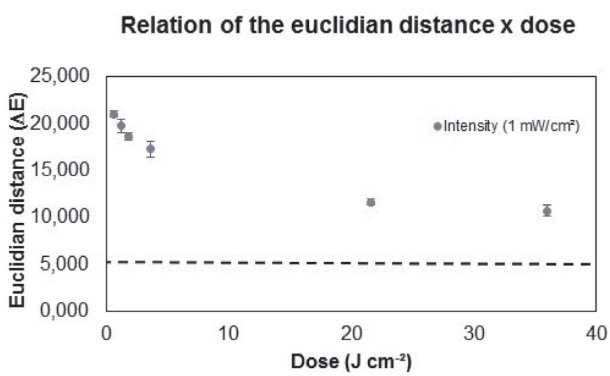

Figure 3. Euclidean distance (ΔE) as a function of delivered light dose (D) for cotton fabric samples treated with H_2O_2 40% and UV light at 1 mW cm^{-2}. The dashed line at ΔE = 5.3 corresponds to the OBCF.

From this result, it was made an experiment in the laboratory, with light intensity variation, solution concentration variation, analyzing the variation of time. It was possible to verify that the cotton was damaged when light intensity was high (data not shown). In the literature, the current process described with a photobleaching, and also with UV/H_2O_2, is known as the advanced oxidative process (AOP).

In the literature, the mechanism of the reaction when the pH decreaes is not perfectly described, however, it uses the equation system as shown below:

$$H_2O_2 + h\nu \rightarrow HO^{\bullet} + HO^{\bullet} \quad (6)$$
$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (7)$$
$$H_2O_2 + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (8)$$
$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (9)$$
$$HO^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (10)$$
$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (11)$$
$$HO^{\bullet} + R \rightarrow ? \quad (12)$$

In the system with UV light being absorbed by hydrogen peroxide and splitting the molecule in two radicals (equation 6), after this rate-limiting step, radicals will rapidly undergo non-selective reactions with organic compounds or other substance present in the solution system, leading to new radical (equations 7-9), and termination reactions (equations 10-11). Finally, the next step (equation 12) is used to denote R as an organic compound. Therefore, it is shown the mechanism applied in the decomposition of the organic compounds present in the raw cotton.[24-26]

To have these results, it was made a preliminary experiment in laboratory (not shown on this paper), varying the dose delivery during a time. The above result (Figure 3) was one of the best results, because when the intensity is increased together with the dose,[24-26] it causes a damage to the cotton.

After the experiment, we observed that the sample, which received the highest UV light dose, was fragile. The simple stretching with hands were able to cause fibers rupture.

The combination of a high concentration of H_2O_2 in acid pH with higher levels of UV light on the raw cotton probably induced the cotton fibers degradation, leading to a lower mechanical resistance, which is an undesired effect.

Since the high fragility was observed in the sample receiving H_2O_2 40% with 20 mW cm^{-2} UV light, a mechanical evaluation of the samples after the procedure was important. Thus, a tensile test was performed in order to evaluate how the photochemical process was inducing fragility to the samples. The results of the tensile test performed on RCF, CBCF and photobleached RCF (RFP) are presented in Figure 4.

It is possible to observe that strain *versus* load curves, between 1 and 2 mm, present an accommodation of the cotton fibers, due to the interaction of the machine and the samples. Highest value of each curve corresponds to the point of ultimate strength, and the graph shows that the maximum load applied (435.98 N) occurred for the chemical bleached cotton fabric (CBCF), which is a traditional process applied in textile industrial, followed by the raw cotton fabric (RCF) with 206.9 N, whose sample is a fabric without bleaching treatment, and the lowest value was 81.67 N for the sample treated with UV (36 J cm^{-2}) and H_2O_2 (RCP). These results indicate that the hydrogen peroxide bleaching process mediated by UV light in acid pH and 36 J cm^{-2} decreased the mechanical resistance of the cotton fabric after photobleaching process. To have an ideal irradiation without compromising the mechanical resistance, it is necessary to optimize the relation of light intensity and hydrogen peroxide concentration.

Our results corroborate with the literature reports showing that cellulose is susceptible to oxidation damage, reducing the tensile strength of raw cotton fabric, as using acidic process causes shrinkage of the fabric and changes its physical-mechanical properties.[3,6]

Conclusions

This study showed the viability of the photonic technique applied to hydrogen peroxide in raw cotton samples and a UV light intensity in photobleaching process

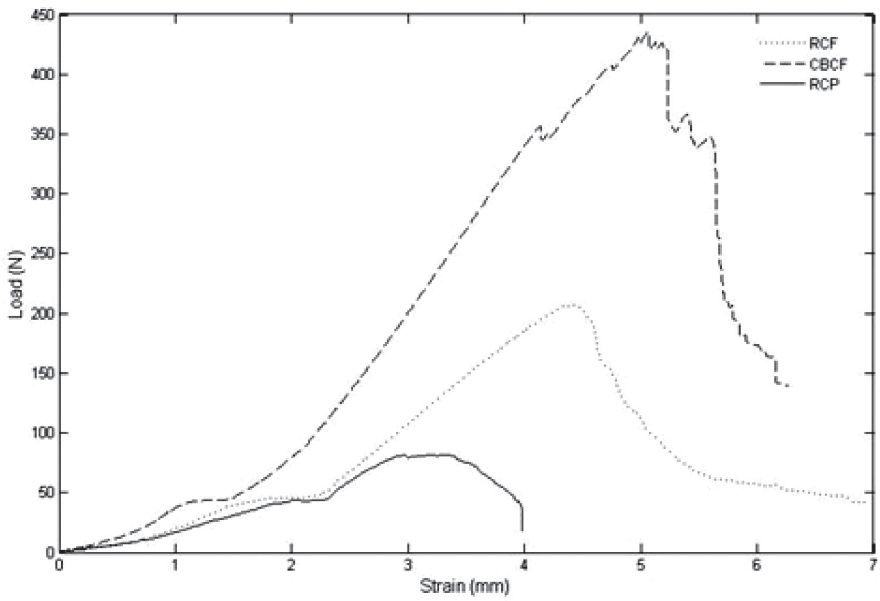

Figure 4. Tensile test in raw cotton with load as a function of strain. Raw cotton fabric (RCF) corresponds to the dotted line, chemically bleached cotton fabric (CBCF) corresponds to the dashed line and photobleached cotton fabric (RCP) corresponds to the continuous line.

was also evaluated, and increased bleaching is observed with the increase in UV intensity.

Tensile tests showed that cotton fabric becomes more fragile after a photolysis process in high intensity conjugated to hydrogen peroxide in 40% (v/v), which must be overcome by future approaches.[4,27] This is a preliminary result of the use of acidic hydrogen peroxide combined with UV light around 254 nm.

Our preliminary results indicate that the combination of acidic H_2O_2 and UV light has the potential of being used in textile industries as a suitable method for raw cotton bleaching. Future studies including a wider range of peroxide concentrations and UV light intensities would be necessary to verify our present findings.

Finally, this study shows that when UV light is applied to cotton fabric samples moistened in hydrogen peroxide solution, it results in chemical bond breaking of the non-cellulosic materials present in the raw cotton. This work already resulted in the application of a patent in Brazil (patent No. BR10201601426).

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