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Cotton Fabric Bleached with Seawater: Mechanical and Coloristic Properties

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The textile industry needs a high volume of water to carry out its processes, which among them; textile chemical finishing is the main responsible for high water expenditure. However, nowadays there is a worldwide concern regarding the scarcity of fresh water. This research aims to study the use of seawater in the cotton bleaching process and compare the results obtained with the bleaching process made with distilled water. The characterization of the substrates was performed through the following analyses: reflectance spectrophotometry, white degree (ºBerger), wettability, tensile strength, elongation, scanning electron microscopy and dispersive energy spectroscopy. The bleaching with seawater presented good whiteness index, high tensile strength values and excellent hydrophilicity, which suggest that it may be possible to perform this process in cotton fabric using seawater.

Keywords: *Textile bleaching, seawater, whiteness, cotton.*

1. Introduction

Currently, the global water crisis is a much discussed subject among study groups, institutes of technology and development and governments[1,2]. This concern is due to the fact that water has fundamental importance for the life of all species, is the universal solvent, and supplies a large part of the industries[3,4].

The textile segment is one of the industrial sectors with the highest water footprints. Among the textile chain, the sector which is responsible for the greatest water demand is chemical textile finishing, which consist of a set of processes applied to textile materials in order to transform them, from the raw state, into white, dyed, printed and finished substrates[5]. There are several factors that directly influence the parameters of each process executed in the finishing area, such as the type of feedstock to be processed and its properties, the sensitivity it presents to the action of chemical products and the susceptibility of the fiber to chemical modifications[6].

Among the main textile finishing is the bleaching process, which aims to remove natural pigments from the fibers, make the substrate white, and leave it apt to undergo further chemical processes, such as dyeing and printing[7,8]. There is a large literature on the use of different chemical agents for textile bleaching processes, including researches on the use of peracetic acid[5,9], enzymes [7,10] and process activators[11]. However, scientific work on the use of seawater as solvent in the bleaching process has not been found in current literature. Considering the imminent shortage of fresh water in Brazil and around in the world, and the need to save this precious resource, the application of seawater in textile bleaching processes may be innovative due to its great availability (more than 97% of the Earth's total water supply[4]) and the fact that it has not been evaluated yet.

Therefore, there is an enormous potential for the development and execution of chemical bleaching with seawater, which is explored on this work through studying the bleaching process with seawater of a 100% cotton substrate, analyzing aspects such as: tensile strength, elongation, white degree, colorimetric coordinate, morphology, chemical composition and hydrophilicity, comparing the results obtained with samples processed with distilled water.

2. Materials and Methods

2.1 Textile substrate

For this study, a 100% cotton plain weave fabric with approximately 137 g/m² was used. Figure 1 shows the fabric used.

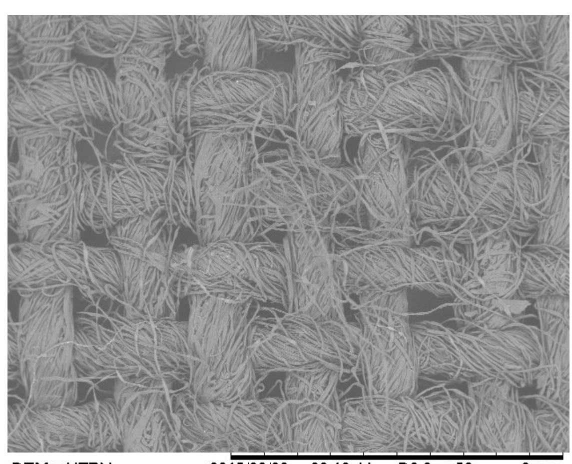

Figure 1. Image of the fabric used with 50x magnification.

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2.2 Solvents

Distilled water and seawater from Ponta Negra beach, located in Natal, Rio Grande do Norte (RN), Brazil were employed in the bleaching processes.

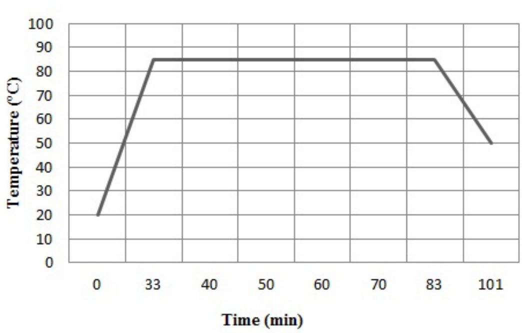
2.3 Bleaching process

The procedures were performed on the Mathis® Alt-B Touch 35 machine according to the formulation described in Table 1:

Table 1. Formulation of bleaching process.

Reagent	Concentration
Hydrogen peroxide [30%]	20.0 mL/L
Phosphorous-based nonsilicate stabilizer	2.0 g/L
Sodium hydroxide 36ºBe	12.0 g/L
Detergent/Humectant	2.0 g/L

The bleaching process started at room temperature, approximately 20°C. It was then heated to the temperature of 85°C with a gradient of 2 °C/min and remained at this temperature for 50 minutes. The process is shown in Graphic 1. After bleaching, all samples were washed for 20 minutes at 80°C, using the same equipment, only with "conventional" water. Subsequently, the samples were dried at room temperature. The bleaching was performed using both distilled water and seawater.



Graphic 1. Procedure of bleaching process.

2.4 Characterization of solvents (waters)

In order to evaluate the solvents used in the work, physical-chemical analyzes were performed in the Aquanalous Laboratory (Natal, RN, Brazil). Experiments were carried out according to the latest version of *Standard Methods for Exaination of Water & Wasterwater 22nd 2012* (SMWW). The methodologies used were:

- pH: electrometric method;
- Electrical conductivity: potentiometric method (electrometric);
- Salinity: electrometric method;
- Total alkalinity: titration with the aid of indicators;
- Total hardness: titration with the aid of indicators (by EDTA);
- Calcium: titration with the aid of indicators (by EDTA);
- Magnesium: titration with the aid of indicators (by EDTA).

2.5 Mechanical characterization

Tensile strength and elongation of the samples before and after bleaching process were measured on the TENSOLAB 3000 MESDAN® dynamometer, following the standard ASTM D 5034, with ambient conditions of 20ºC ± 1 and 65% ± 2 relative humidity.

Five samples were performed for each condition (treated with seawater, treated distilled water and raw fabric). The results were compared in the weft and warp directions.

2.6 Colorimetric characterization and Whiteness degree

Color coordinates and whiteness index (ºBerger) of the bleached fabrics were measured by using a Konica Minolta, Model CM-2600D spectrophotometer with D65 illuminant and observer at 10°, over the range of 390–700 nm. The average of ten reflectance measurements, taken from different positions of the bleached fabrics, was adopted.

2.7 Chemical and morphological characterization

2.7.1 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

SEM analysis was used to study the morphology of the bleached fabrics. Images were obtained with the Hitachi TM-3000 scanning electron microscope. Chemical analyze was performed by EDS technique using an EDAX Si (Li) detector with an acceleration voltage of 15 kV.

2.8 Wettability

In order to evaluate qualitatively the fabrics' wettability before and after bleaching processes, a dye solution drop (reactive dye – 2g/L) was applied, verifying the time of complete absorption. The hydrophilicity of the samples was tested according to the BS 4554:1970 method, known as the drop test, in which a drop of 100.0 μL of water is placed on the surface of the specimen. The time required for the droplet to completely penetrate the fabric was measured by means of a stopwatch in triplicate.

3. Results and Discussion

3.1 Water characterization

Table 2 shows the results obtained for physico-chemical analyses performed for the seawater and distilled water used for the bleaching processes.

Table 2. Solvents characterization (Results of physico-chemical properties).

Parameters	Seawater	Distilled water
Ph	7.00	7.36
Electrical conductivity [µS/cm at 25ºC]	56,700.00	<0.01
Total alkalinity [mg/L of $CaCO_3$]	116.28	6.30
Total hardness [mg/L]	7,045.06	2.00
Calcium [mg/L of Ca]	463.61	<0.01
Magnesium [mg/L of Mg]	1,423.78	0.48
Salinity [%]	37.80	0.00

Seawater's characteristics are similar to fresh water, with some noticeable differences due to the presence of salts dissolved in the water. One of its important aspects is salinity, which is defined as the concentration of dissolved inorganic solids in the water[12]. For this parameter can be observe a considerable difference when compared the seawater (37.80%) and distilled water (0.00%). Seawater is a complex solution containing the majority of the known elements. Some of the its most abundant components, as percent of total mass of dissolved material, are chlorine (55.0%), sulfate (7.7%), sodium (30.7%), magnesium (3.6%), calcium (1.2%) and potassium ions (1.1%)[13,14].

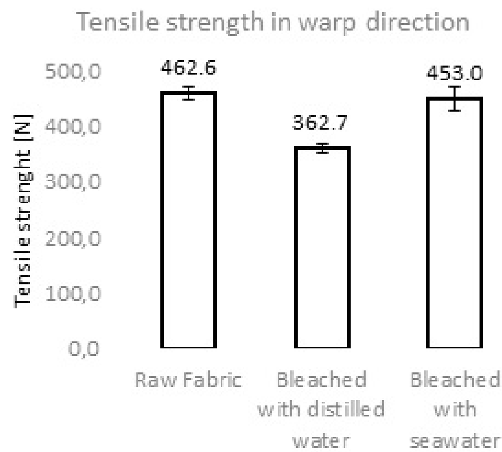
The main difference between freshwater and seawater is the amount and types of dissolved salts in its composition[15]. This difference influences considerably other parameters such as temperature, heat, salinity and conductivity, density among others[13]. With the results obtained, it was verified that the electrical conductivity, total alkalinity, total hardness and salinity indices present considerably higher values for seawater than for distilled water, as demonstrated in Table 2.

The solution called seawater has its composition defined by a series of flows of inputs and outputs of elements, largely transported by fluvial enviroment[16,17]. But, in general terms, the composition of seawater is almost uniform, with just some slight variation from ocean to ocean and from surface to bottom. The relative proportion of the elements is maintained due to the fact that the processes in the ocean are cyclical, so, the input and output rate of the elements are equivalent[15]. This "law" of constant proportions was first proposed by Dittmar (1884), based on 77 samples of seawater collected from several places around the world[18].

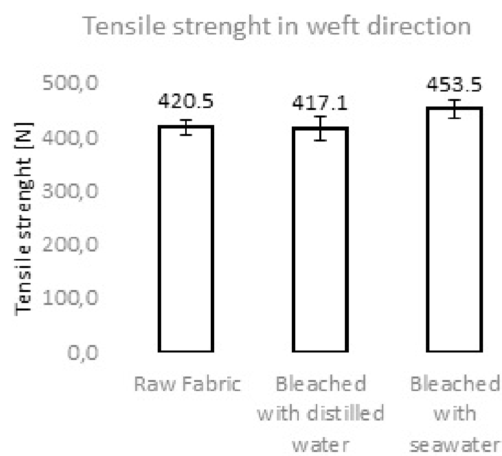
3.2 Mechanical behavior

Graphics 2, 3, 4 and 5 show the tensile and elongation tests of the samples while raw, processed with distilled water and processed with seawater, all analyzed in the weft and warp directions.

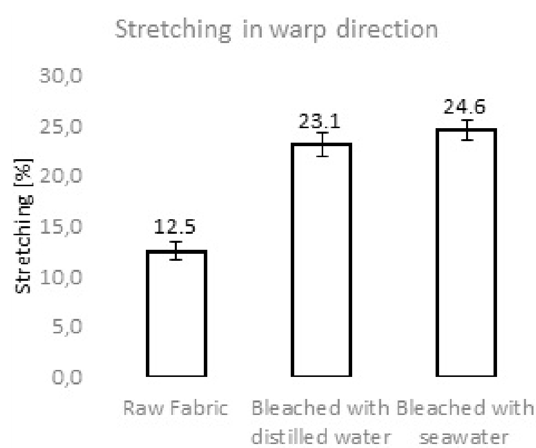
In regard to tensile strength values, samples bleached with seawater presented, in both directions, superior performance than those processed with distilled water, being notably similar to raw fabric in the warp direction.



Graphic 2. Values of tensile strength in the warp direction.

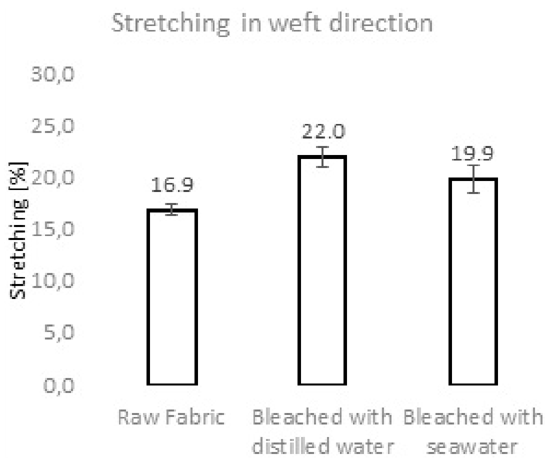


Graphic 3. Values of tensile strength in the weft direction.



Graphic 4. Results of elongation in warp direction.

In the raw fabric, the warp yarns are starched in order to present greater resistance to the weaving process. After bleaching, the resistance in the warp direction tends to decrease, due to desizing and the action of chemical agents such as H_2O_2 and NaOH on the fiber[8], which did not occur effectively in the fabric processed with seawater.



Graphic 5. Results of elongation in the weft direction.

This behavior may be related to the presence of chemical elements in seawater, probably decreasing these agents' potential of acting on fibers during the process. Despite the removal of the gum from the warp yarns, the number of constituent elements in seawater chemistry as ions Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} may be responsible to inhibit the total decomposition of peroxide, decreasing its effect to eliminate the gum present in the warp yarns and to degrade the cotton fiber, maintaining the substrate's resistance property (compared with raw cotton). As seen in Table 2 results, in the seawater composition has Ca^{2+}, Mg^{2+} ions in large quantities.

According to the results obtained, the samples bleached with seawater presented elongation property values similar to those bleached with distilled water. This indicates that using seawater for the bleaching process does not impair the mechanical properties of cotton fabrics.

3.3 Colorimetric characterization

After bleaching, the samples were analyzed colorimetrically with reflectance spectrophotometry. The average of the colorimetric coordinate results (L*, a*, b*) obtained are presented in the Table 3.

Colorimetric coordinates relate to points in the spectral space CIEL*a*b*. For the bleached sample, the most important of those is the L index, which indicates brightness and varies in a clarity scale from 0 to 100, where the minimum value is black, and maximum, white. The increase in the L coordinate indicates that the objective of lightening the samples was successfully carried out for both the samples bleached with seawater and distilled water. According to the CIEL*a*b* index, the luminosity level of the samples improved around 8% when compared with the raw fabric. It was also verified that the raw fabric at the b+ coordinate is much more intense, indicating that the substrate is more yellowish. Figure 2 demonstrates that the color differences of the samples are remarkable.

3.3.1 Whiteness Degree (ºBerger)

Cellulose and most other fibers forming natural polymers are white in their natural state. However, pigmented impurities in fibers may absorb light, causing the fibers to have a creamy, yellowed or dull appearance, masking their natural whiteness. Bleaching, through the use of oxidizing agents such as H_2O_2, aims to decolorize these impurities. These processes must be controlled closely, so that color in the fibers is destroyed with minimal damage to the fibrous material. Two mechanisms have been proposed for bleaching, the ionic and the free radical mechanism.

Table 3 . CIEL*a*b* colorimetric coordinates of raw fabric samples and after bleaching process.

CIEL*a*b* colorimetric coordinates						
	L*		**a***		**b***	
Sample	**Average**	**Standard deviation**	**Average**	**Standard deviation**	**Average**	**Standard deviation**
Raw fabric	85.62	0.27	2.14	0.07	13.17	0.09
Distilled water	93.54	0.33	0.10	0.28	4.71	0.36
Seawater	92.75	0.35	0.09	0.02	4.85	0.23

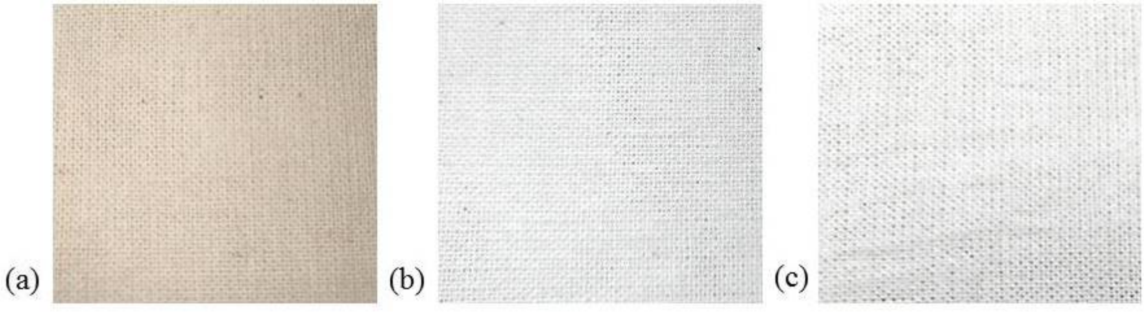


Figure 2. Sample images: (a) Raw fabric, (b) Fabric bleached with distilled water and (c) Fabric bleached with seawater.

Berger's equation (1) is commonly used for some types of illuminants and observers[19].

$$W = 0.333Y + 1.060Z - 1.277X \quad (1)$$

Where: X, Y and Z are the tristimulus values of the measured sample. There are other mathematical equations for the quantification of whiteness[20], but for this work the Berger's equation was used. The results obtained for Berger degree are presented in Table 4.

Table 4. Results of Berger scale.

	Average ºBerger	Standard deviation ºBerger
Raw fabric	11.52	1.12
Bleached with distilled water	61.13	2.16
Bleached with seawater	59.05	1.61

According to the results, the level of whiteness obtained after bleaching was similar for both types of water, with a slight difference of approximately 2.0%. According to this, it can be stated than the use of seawater does not have a significant influence on the aforementioned property, indicating that this solvent could be used to bleach cotton fibers.

3.4 Scanning Electron Microscopy (SEM)

The structure of raw fabric submitted to the bleaching processes was visually compared by using scanning electron microscopy. Images were captured at four magnification levels (100x, 200x, 500x, 1000x) in order to provide a high clarity of the sample structure. Figures 3, 4 and 5 illustrate, respectively, the structures of the fabric while raw, bleached with seawater, and bleached with distilled water.

According to the microscopy images, the contraction of the fabric structure after the bleaching processes was notorious. This occurs due to the removal of the gum from warp yarns, which eliminates impurities from the substrate and increases the hydrophilicity of the cotton fibers. Therefore, without the gum and the high water absorption, there was a relaxation in the yarn structure, and consequently, the contraction can be seen in the sample (Figure 4 and Figure 5). It was also possible to observe, as shown in Figure 4, that in the sample processed with seawater, there is a deposition of some impregnated compounds on the fibers.

3.5 Energy Dispersive Spectroscopy (EDS)

X-ray energy dispersive spectroscopy (EDS) analysis was performed in order to qualify the chemical compounds

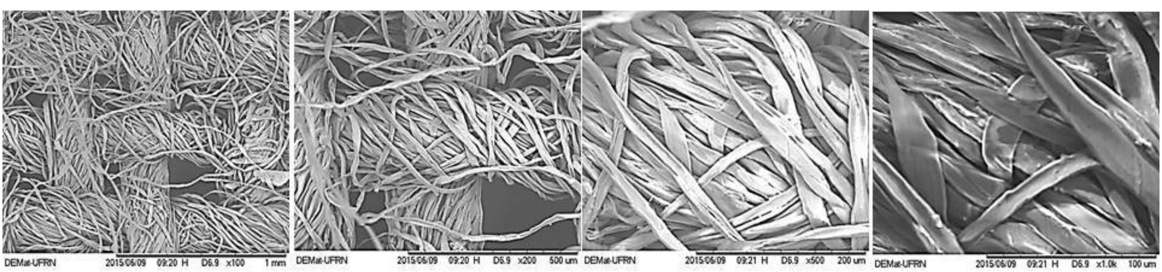


Figure 3. SEM images of raw fabric (magnification of 100x, 200x, 500x e 1000x)

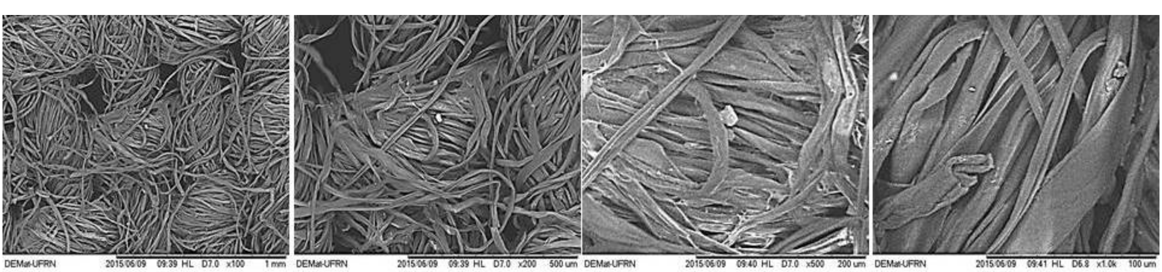


Figure 4. SEM images of fabric bleached with seawater (magnification of 100x, 200x, 500x e 1000x)

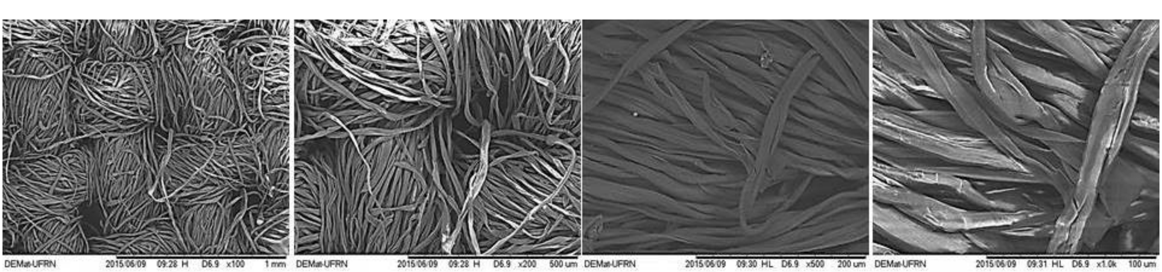


Figure 5. SEM images of fabric bleached with distilled water (magnification of 100x, 200x, 500x e 1000x)

found in the substrates, verifying, in the samples processed with seawater, the presence of magnesium, calcium, phosphorus, potassium and sodium atoms. On the other hand, on the samples treated with distilled water, there was no identification of any of the compounds aforementioned.

The elements identified in the sample bleached with seawater are abundantly present in the water that was used in the process. This indicates that, in alkaline conditions, precipitations, mainly of salts of calcium and magnesium, would have occurred.

Figure 6 shows the SEM image (magnification 500x) of the fabric after bleaching process with seawater. It is possible to observe some impurities in the surface of the fabrics. The EDS shows the presence of elements as Mg, Mn and Ca.

Even though the mechanical and color properties of the substrate with seawater are practically unchanged (compared to bleaching with distilled water), this deposition of elements must be studied to understand its influence in subsequent dyeing and printing processes.

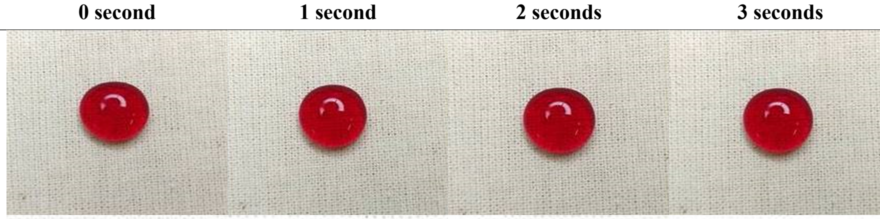
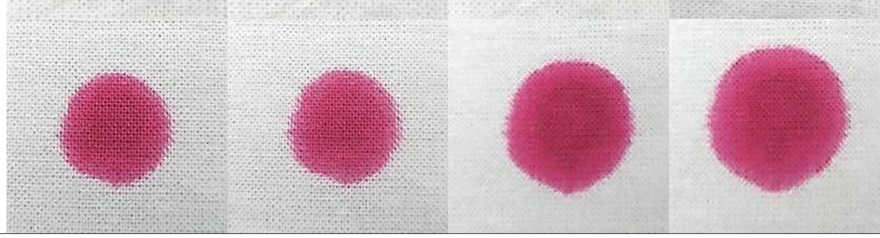
3.6 Wettability

All the samples were tested by dye solution absorption test. Samples treated with seawater showed complete drop absorption in 3 seconds, while for those bleached with distilled water initial and instantaneous wetting is easily obtained. This result proves the effectiveness of the processes in eliminating the waxes, oils and impurities that make the fabric hydrophobic, improving the hydrophilicity of the textile substrate, leaving the cotton fabric prepared for the subsequent finishing processes. Table 5 illustrates the difference in the absorption time of the samples.

The samples processed with seawater have some difference in the wettability property when compared with the samples bleached with distilled water. The outermost layer is a decisive factor on wettability and the presence of some impurities as verified in the SEM images can be responsible to create a kind of layer/barrier that decrease the time of total drop dye solution absorption, as can be observed in Table 6. The time to total drop dye solution absorption for the raw cotton is very higher (more than 7 minutes), which prove that the bleaching process used improve considerably the wettability of the samples.

It is important to relate that although the samples bleached with seawater to delay to completely absorb a drop. The fabric is prepared for the next finishing process. Because most of the subsequent processes have a contact time between solution and fabric much higher than three seconds (time to complete drop absorption).

Table 5. Absorption time of dye solution drop.

Samples	**Absorption time**			
	0 second	**1 second**	**2 seconds**	**3 seconds**
Raw fabric				
Bleached with seawater				
Bleached with distilled water				

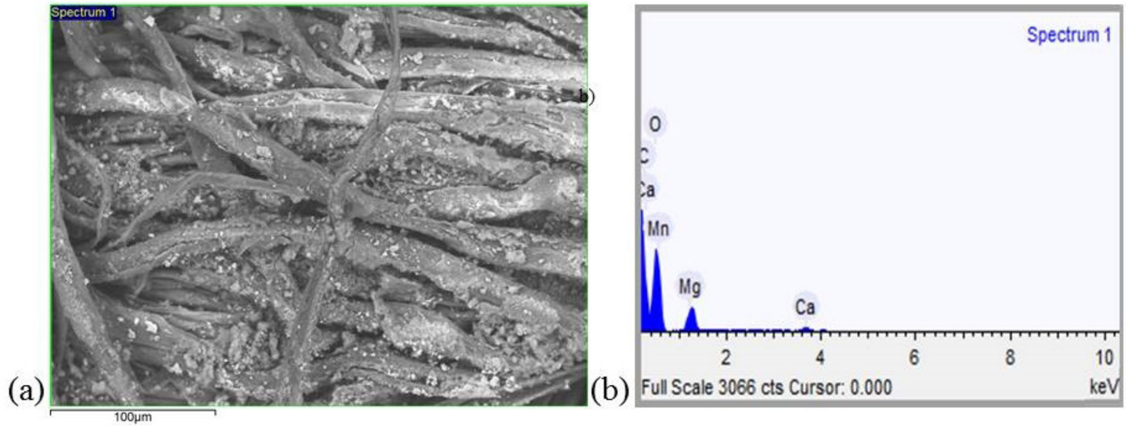


Figure 6. SEM image of the fabric bleached with seawater (a) and EDS spectrum (b).

Table 6. Wettability test results. Time (seconds) for total absorption of the drop dye solution

Samples	Test 01	Test 02	Test 03	Average	Standard Deviation
Raw fabric	448 s	430 s	475 s	451s	22.6 s
Bleached with seawater	2.5 s	3.1 s	2.9 s	2.8 s	0.3 s
Bleached with distilled water	<0.1 s	<0.1 s	<0.1 s	<0.1 s	-
	Instantaneous	Instantaneous	Instantaneous	Instantaneous	Instantaneous

4. Conclusions

This research shows that the use of seawater has potential of application in chemical bleaching processes in the textile industries. With the results of mechanical behavior, it was verified that the cotton fabrics bleached with seawater presented tensile strength and elongation similar to those processed with distilled water.

When evaluating the results of the colorimetric analysis, it was verified that the bleaching with seawater resulted in similar properties to those of the process with distilled water. Given that one of bleaching's main objectives is to leave the substrate white for subsequent processes, it is possible to say that the use of seawater does not negatively interfere in the levels of whiteness obtained in the samples.

It was observed, through scanning electron microcopy that the structure of the fabrics contract after both bleaching processes. Furthermore, agglomerate depositions were observed on the samples bleached with seawater. Those were investigated through the EDS technique, and presented mainly calcium and magnesium.

Finally, the wettability resultant from the both bleaching processes demonstrated that they were effective for the removal of impurities, waxes, oils and gums, leaving the cotton hydrophilic. This result was evident due to the immediate absorption of a drop of water in the samples targeted with distilled and, in only 3 seconds in the case of seawater. When evaluating all results obtained in this research and studying the properties and objectives of the textile bleaching process, it is possible to conclude that the use of seawater in this type of processing in cotton fabric can be developed for industrial scale.

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