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Chitosan pretreatment for cotton dyeing with black tea

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Abstract: Chitosan is used in a wide range of applications due to its intrinsic properties. Chitosan is a biopolymer obtained from chitin and among their most important aspects highlights its bonding with cotton and its antibacterial properties. In this study two different molecular weight chitosan are used in the dyeing process of cotton with black tea to evaluate its influence. In order to evaluate the effect of the pretreatment with chitosan, DSC and reflection spectrophotometer analysis are performed. The curing temperature is evaluated by the DSC analysis of cotton fabric treated with 15 g/L of chitosan, whilst the enhancement of the dyeing is evaluated by the colorimetric coordinates and the K/S value obtained spectrophotometrically. This study shows the extent of improvement of the pretreatment with chitosan in dyeing with natural products as black tea.

1. Introduction
Chitosan is an N-deacetylated derivative biopolymer of chitin (2-acetamido-2-deoxy-β-D-glucose through a β (1-4) linkage). The deacetylation of chitin is never completed and there is no specified nomenclature that describes the degree of deacetylation [1, 2]. Chitin can be easily acquired from crab or shrimp shells. Its N-deacetylation is performed under alkali environment as shown in figure 1. The chitin that has been formed from the shells is deacetylated in 40% sodium hydroxide at 120°C for 1-3h. This produces 70% deacetylated chitosan. Most natural polysaccharides are neutral or acidic, but chitin and chitosan are highly basic polysaccharides [3]. The bond between chitosan and cotton is a difficult bond because of the likeness of the two polymers and it has to be dissolved in an acid to improve the bond. This is only possible as result of the highly basic nature of chitosan.

![Figure 1. N-deacetylation of chitin to chitosan](image_url)
The bonding of chitosan with cotton happens after the cotton is oxidised [4]. Figure 2 shows how the cotton (I) is oxidized (II) and its reaction place with chitosan (III).

![Figure 2. Oxidisation of cotton (a) and reaction with chitosan (b) [4]](image)

Chitosan has a wide range of applications. It is most known for its use in wound dressing [5, 6] but it has however a lot of other uses. It can be used in photography, cosmetics, as artificial skin, as contact lens, heavy metal capturing in polluted water, colour removal in textile mills, paper finishing, drug delivery system, etc. But is most important feather might be the fact that is an antibacterial agent [7].

2. Objective
The main objective of this work is to study the influence of the chitosan molecular weight and its concentration in dyeing with black tea and the curing temperature of the cotton treated with two different molecular mass chitosan, low and medium.

As the curing is necessary for a good bond between cotton and chitosan, the cotton gets dried at 60 °C and cured at different temperatures.

3. Materials and methods
In the present paper, we used chitosan as a natural mordent. One has low molecular weight (XL), and the other one medium molecular weight (XM). Both types of chitosan were commercial products, supplied by Sigma-Aldrich. Different kinds of concentration were used, 5 g/L and 15 g/L of both types of chitosan. As a natural dye, black tea was used by boiling it in water for 2 hours using 2 g/L of concentration.

The fabric used was a cotton twill fabric with 210 g/m² which had been chemically bleached in an industrial process. After the chitosan treatments, cotton samples were dried at 80°C in a screen printing engineering TD-20. After drying, treated samples were cured at different temperatures: 80, 140 and 200°C in a WTC Binder 030.

Dyeing experiments were performed using M:L (material to liquor) ratio of 1:40 with manual agitation using 50% dye concentration. Dye baths temperatures were raised to 90-95°C for 1 h.

The influence of curing temperature was performed on a DSC with the aim of determining the change in behaviour of the chitosan after treatment on cotton. The test was performed on a Metler Toledo DSC 1 Stare System with Stare software by heating 20°C/min and a range from 30°C to 400°C. In order to evaluate and compare objectively the influence of pre-treatment of cotton with chitosan, the
dyed samples were analyzed in a reflection spectrophotometer MINOLTA S.A CM-3600d model with standard 10° observer and illuminant D65, whereby the chromatic coordinates in the CIELAB space and the colour strength (K/S) were obtained according to the Kubelka-Munk equation.

4. Results and discussion
First of all, the DSC results obtained, show the difference between two chitosan’s molecular weight. There is a common peak around 100°C caused by the loss of water, while the peak at 320°C gives the temperature of decomposition of amine (GlcN) units with correspondent exothermic peak at 295 °C [8].

![Figure 3: DSC of the low and medium chitosan molecular weight](image)

In figure 4, 5 and 6 the results of DSC analyses of the cotton fabric treated with both types of chitosan and untreated fabric are shown. The concentration of chitosan used is 15g/L in order to maximize the effect of the chitosan on the cotton surface fabric. Figure 4 shows the results of treated and dried fabrics using chitosan low and medium.

![Figure 4. DSC of untreated fabric and cotton treated chitosan 15g/L and cured at 80 degrees](image)

The thermogram found, reported in Figure 4, is quite comparable to those related to cotton material, reported in literatura. The DSC curve of the untreated and treated fabrics show the same
thermal behaviour, seeing the loss of water at 90 °C and an endothermic curve at 380 °C approximately, due to the cellulose depolymerization [9].

As can be seen in figure 5 and 6 samples dried at 80°C and cured at 140 and 200°C, respectively show the same endothermic curve, not being able to observe any significant difference.

Unfortunately the exothermic peak related to the decomposition of amine (GlcN) units of chitosan, which is observed in figure 3, disappears analysing treated fabrics, being completely hidden by the substrates decomposition peaks, so quantitative considerations cannot be done. In a second step, the effect of using low chitosan or medium chitosan as a mordant in the dyeing process was studied in more details in terms of color strength, quantified by calculating the staining level K/S values from reflectance measurements on the dyed fabrics. The K/S results show that pre-treated cotton with chitosan as a mordant has more colour strength than untreated cotton dyed, so this suggests that the treatment with chitosan enhances the linkage between the black tea dye and the cellulose. Furthermore, there is a significant difference between the K/S values of the fabric pretreated with chitosan low and medium, being this value higher when medium chitosan is used as mordant.
5. Conclusions
In this work the influence of pre-treatment with chitosan in natural dyeing has been verified using black tea as a natural dye. It has been tested in an exhaustion dyeing bath and the results show that fabrics pre-treated with a natural mordant have better colour strength than fabrics which have not been pre-treated. The medium molecular weight chitosan shows better K/S value than the dyeing with pre-treated cotton with low molecular weight chitosan.

On the other hand, it hasn’t been possible to study the curing temperature of pre-treatment by DSC results because there is no difference after comparing the results of each treated sample with the untreated fabric results.

As result it is possible to say that a concentration of 5g/L of chitosan medium is enough to get good dyeing results with natural dyes, without damaging the cotton fabric. However, the use of different experimental techniques to know the optimum curing temperature is necessary.

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