NOVEL APPLICATION OF β-CYCLODEXTRINS IN TEXTILE DYEING PROCESSES

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ABSTRACT

A new important application field of β-cyclodextrins is the textile dyeing technical process. Their ability to form inclusion complexes with textile dyes is guaranteed by the modification of physical and chemical properties. The possibility of host-guest associations between cyclodextrins and dyes allows modifications of features like: solubility, stability or even affinity of organic dyes for the textile materials.

The production of fluorescent cellulosic materials is conditioned by the unavailability of dyes in market for these propose with a single exception of the Remazol Luminous Yellow FL.

The aim of the work was to find out suitable method of dyeing fluorescent cellulosic fibres using available fluorescent dyes for the dyeing of synthetic fibres.

Two different commercial β-cyclodrextrins, methylated and hydroxypropylated cyclodextrins, were tested in a dyeing process using Rhodamine B as model dye. The influence of process parameters such as pH, cationic agent, CD type and concentration were analysed. It was found that the two-step method, consisting of one impregnation process with CD-dye complexes, at alkaline pH and room temperature followed of a fixation step (reticulation at 180ºC, 1min) is the most convenient process to obtain fluorescent dyed fabrics with suitable performance.

The obtained results demonstrated that the cotton could be dyed using β-cyclodextrins based process with good balance between washing fastness properties and mechanical properties of dyed fabrics.

1. Introduction

The design of fluorescent textile fabrics is interesting for very specific applications like protective materials and fashion children wear effects. In fact, fluorescent dyes cause a significant increase in colour brightness and makes the dyed materials more easily perceptible [1].

To produce fluorescent fabrics requires the availability of dyes and adequate processes for the type of fibres to finish. The commercial fluorescent dyes available in market are scarce and for polyamide fibres. For this reason, the fluorescent effect on cellulosic materials is only possible by printing technology, with the undesired known effect on surface properties namely on the “hand touch” of the fabrics.

To overcome this situation, an innovative approach is proposed using the available commercial dyes combined with cyclodextrins to dyeing cotton material.
Cyclodextrins are cyclic oligosaccharides consisting of six, seven or eight D-glucopyranose units, which are named α-, β- and γ-cyclodextrin respectively. They form inclusion complexes with a variety of molecules, which fit into their hydrophobic cylindrical cavities. Their exterior, bristling with hydroxyl groups, is fairly polar, whereas the interior of the cavity is non-polar [2].
Cyclodextrins are produced from starch by enzymatic conversion in a process environmental compatible. Their syntheses are some interesting advantages, namely in terms of the availability of the raw material (starch), which is unlimited but also cheap. Besides, they are non-toxic and biologically degradable substances [5].
In an aqueous solution the slightly hydrophobic cyclodextrin cavity can be occupied by appropriate “guest molecules” which are less polar than water. The dissolved cyclodextrin is the “host molecule” and the “driving force” for complex formation is the substitution of the high-enthalpy water molecules by an appropriate guest molecule. The complex formation happens when the guest molecule fills totally or in part to the internal cavity of cyclodextrin. Interactions are known to be involved in this process and the Van der Waal and hydrophobic interactions are the most important, both of which depend on how the size and/or shape of a guest molecule fit into the host cavity [3, 4].
The recent attention of research community to cyclodextrins as complex agents for dyes has been resulted in some interesting publications describing the interaction between them as well as their consequences in dyes behaviour in application processes. Fundamental work about complexation of Rhodamine B with β-CD as been conduced by different researchers that find the dye fluorescent behaviour strongly depends on the reaction conditions, namely concentration of dye and CD. In some situations the molecule lakes their fluorescence after encapsulation due to be encapsulated in lactone form [5-8]. Besides this, as far as we known, no studies were conduced in terms of cellulosic materials application.
This work aims to develop a method to produce fluorescent cellulosic materials using Rhodamine B as model dye and two β-cyclodextrin derivatives. The main reason for choosing these β-cyclodextrin derivatives as hosts is that hydroxypropyl-modified β-cyclodextrins and methyl-modified β-cyclodextrins can significantly enhance the solubility of hydrophobic guest molecules compared with native β-cyclodextrin and are available commercially in industrial grade.

2. Experimental section

2.1. Materials

A bleached, cotton fabric (Jersey, 100% cotton) from TIB - Tinturaria de Barcelos (Portugal) was used throughout.
Cavasol W7 M (CD M) (Figure 1 a) and Cavasol W7 HP (CD HP) (Figure 1 b) were purchased from Wacker Chemie (Germany).

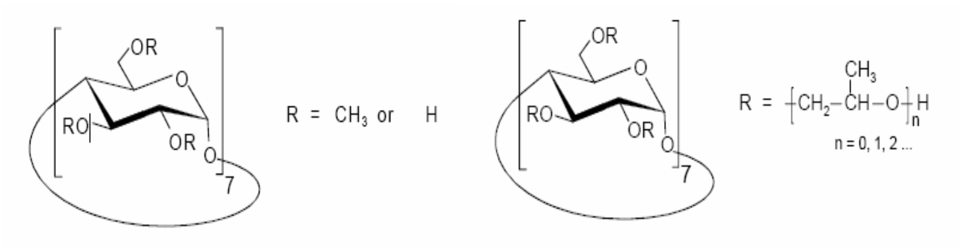


Figure 1- Molecular structure of Cavasol W7 M; CD M (a) and Cavasol W7 HP; CD HP (b)

Rhodamine B (RhB) (Figure 2) was supplied by Clariant (Portugal) and it was used as received.

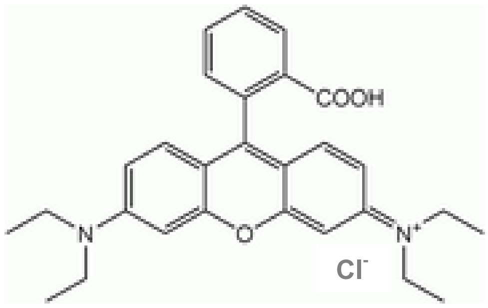


Figure 2- Molecular structure of Rhodamine B

Optifix RSL Liquid, Solusoft Wa liquid and Ledesoft NI were obtained from Clariant (Portugal).
Magnesium Chloride and Kaurit TX 2415 were supplied by BASF.

2.2. Application Method

Fabric samples were padded with solutions containing Rhodamine B (0 to 1%) with Cavasol W7 HP or Cavasol W7 M (10 to 20%) and Optifix RSL (30gL^{-1}) at 80% wet pick-up using laboratory padder (Roaches). The solutions pH was adjusted to 5, 7 or 8-9 with convenient HCL or sodium carbonate amount.
Then, the cotton samples were squeezed and padded again with a solution containing Kaurit TX 2415 (60g L^{-1}), $MgCL_2$ (10g L^{-1}) Ledesoft NI (20g L^{-1}) and Solusoft Wa (20g L^{-1}) and polymerized at 180ºC during 1 minute.
Finally, the treated samples were washed with tap water and air-dried at room temperature.

2.3. Colour fastness tests

The water colour fastness was evaluated according EN ISO 105-E01: 1997 (37ºC±2ºC during 4 hours) and the washing colourfastness was evaluated according EN ISO 105 C06 A2S: 1999 (4gL^{-1} ECE detergent, 1gL^{-1} Sodium Perborate, 150mL of water, 10 steel balls in each container; 40ºC during 30 minutes).

The results were evaluated in terms of colour staining and colour changes through Grey scale to evaluate colour change (EN ISO 105 A02) and staining (EN ISO 105 A03).

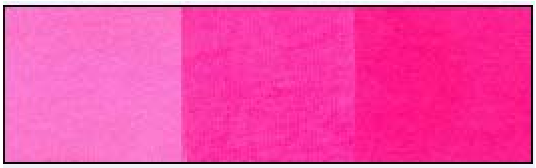
The rubbing colourfastness was tested in dry and wet conditions according EN ISO 105 X12: 2003, and the results were evaluated in terms of colour staining through Grey scale (EN ISO 105 E03).

2.4. Fabric strength tests

To establish the influence of the process on the strength properties of cotton samples, tensile strength tests were performed by Hounsfield Tester, with cross head speed of 100mm/min and sample of 200*50mm according to ISO 13934-1.
An average of 10, 5 for warp and 5 for weft tests runs had been reported for each tested sample.

3. Results and discussion

Rhodamine B (RhB) is one of few textile fluorescent dyes commercially available and the unique dye to produce pink fabrics. It allows a very attractive pink colour in polyamide but as no affinity to cellulosic materials. β-Cyclodextrins (CD) were used as inclusion compounds to complex the dye and change their behaviour in cotton dyeing process.
The encapsulation of dyes has been studied in last years with different proposes, namely to achieve new methods to protecting organic dyes, to prevent aggregation phenomena or to improve some specific properties [3, 8]. But fluorescent molecules are particularly delicate due to their changes in fluorescence intensity by slight geometrical changes. Fluorescent dyes behave differently when trapped inside the cavity of cyclodextrins [9].
The other question to deal is the reversibility of the encapsulation process. In fact, to obtain the desired wet fastness properties of dyed fabrics, we need to find a method for strongly “link” the dye in material. Thus, several experiments were carried out with a variation on type of cyclodextrin, dye and CD concentration, reaction time, temperature of dyeing bath, fixation conditions and the pH value.
The presence of CD, hydroxypropylated (CD HP) or methylated (CD M), was crucial to adsorption of the fluorescent dye to cotton. Only the samples where the RhB-CD was applied present visible fluorescent characteristics (Figure 3).



(1) (2) (3)

Figure 3- Standard sample (1); RhB - CD HP (2); RhB - CD M (3)

The influence of pH on dyeing results was evaluated. The dyeing process was developed under acidic conditions (pH 5), neutral and alkaline conditions (pH 8-9) by adding convenient amount of HCl or Na_2CO_3 respectively. The worse results were obtained at pH7 but similar dye uptake was observed at pH5 or 8. Because alkaline pH is more friendly to cotton fibre, it was chosen for all other comparative tests.
The samples were finished at different dyeing bath temperatures, and as expected, the increase of temperature results in less fluorescent dye fixation. Usually, the dye-CD stability complex decreases with the increase of temperature [10].
Nevertheless, CD HP promotes less fluorescent fabrics compared with CD M, in similar concentration and reaction conditions (Figures 4 and 5). The chemical structural differences between the tested CDs had an evident influence in the complex formation with of the dye.

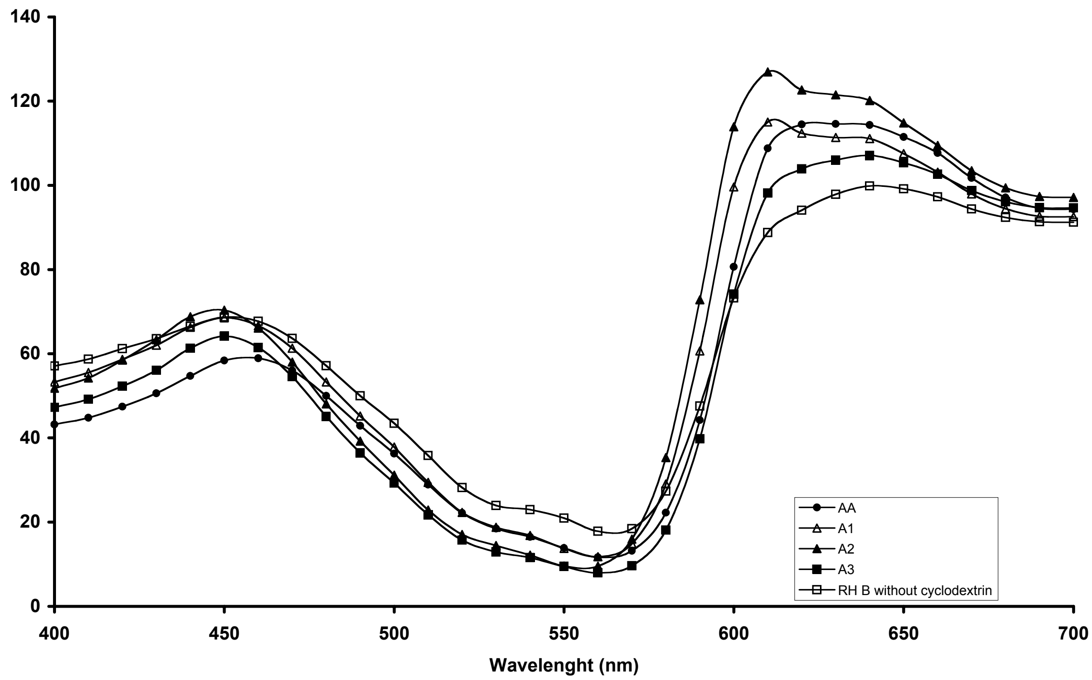


Figure 4- Values of Reflectance (%) presented by the different samples dyed with Rhodamine dye and CD HP: AA- 10% CD HP with 1%RhD and aftertreatment; A1- 10% CD HP with 1%RhB; A2- 20% CD HP with 1%RhB; A3- 10% CD HP with 2%RhB.

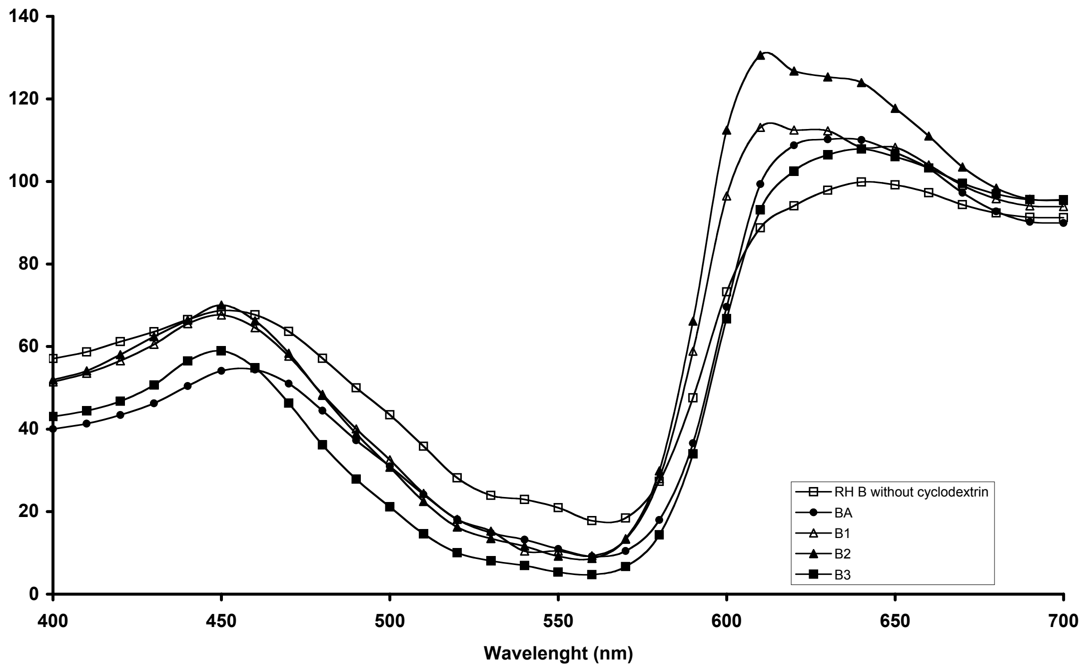


Figure 5- Values of Reflectance (%) presented by the different samples dyed with Rhodamine dye and CD M: BB- 10% CD M with 1%Rh B and aftertreatment, B1- 10% CD M with 1%RhB; B2- 20% CD M with 1%RhB; B3- 10% CD M with 2%RhB.

The best results were obtained with 20% of CD in terms of colour uniformity and fluorescent properties as shown in figures 4 and 5. That could be explained by the increase of the amount of dye encapsulated in CD in solution and retained by the fiber.

The fixation conduced at 180ºC are more effective than 170ºC (results not shown) and 1 minute was enough to obtain good results. Nevertheless, the samples showed bad water fastness. To improve their wet fastness properties, a cationic agent was added to the padding bath, however the washing fastness remains lower (3 in grey scale). To above this it was defined an additional aftertreatment as described in experimental part.

The fastness properties of the samples were assessed according to the ISO standards as described before. Results obtained with sample padded with 10% of CD M, 1% dye and aftertreated are shown in Figures 6 and 7.

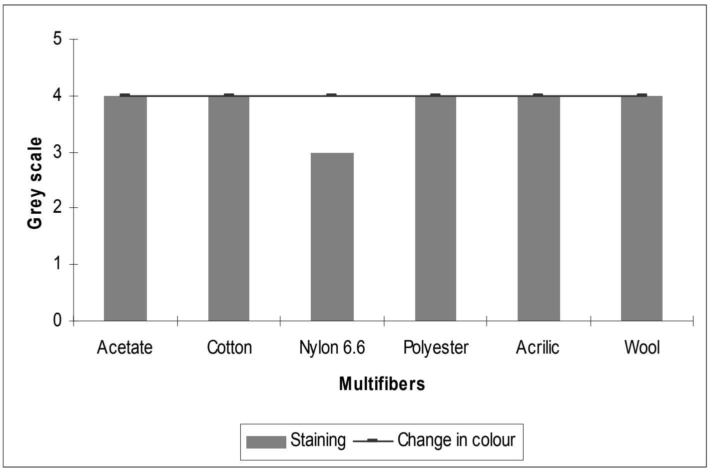


Figure 6- Water colourfastness including colour staining and colour change values

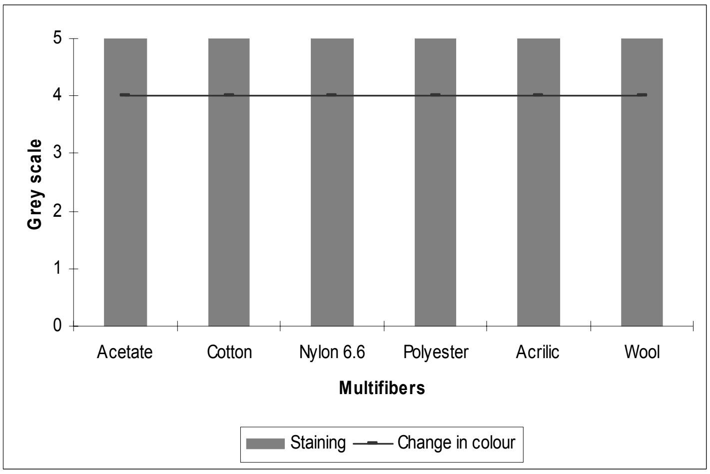


Figure 7- Washing colourfastness including colour staining and colour change values

In fact, the aftertreatment doesn't change the hue of the fabrics.
The rubbing colourfastness of dyed fabrics in wet and dry conditions was evaluated. The samples presented level 4 and 3 depending the conditions performed. The colour rubbing fastness is higher in dry sample.
The mechanical properties usually changed during finishing processes and Table 1 presents the medium values obtained for tensile strength properties evaluated according standard method ISO 13934-1. Tensile strength results of untreated and specimens are shown in table 1 (warp and weft directions).

Table 1 - Mechanical properties of fabrics

Sample	Tensile strength (N)	
	Warp	Weft
Standard	351.2	291.2
Dye and CD HP	345.2	311.5
Dye and CD M	345.3	298.5

It was found that the process did not significantly affect the strength of the fibres.

4. Conclusions

The obtained results demonstrated that cotton material could be dyed with the available fluorescent dyes for polyamide using β-cyclodextrins. Two steps compose the process, the first to dyeing the material and second to link the dye properly to the fibre. In fact, it was found that the simple impregnation with dye plus CD, at alkaline pH and room temperature fowled by a fixation step at 180ºC during 1min, is the most convenient process to obtain fluorescent dyed fabrics with Rhodamine B dye.

The dyed samples presented a good balance between washing fastness properties and mechanical properties.

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