The efficiency of β-cyclodextrin in the post-dyeing removal of hydrolyzed reactive dyes

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Reactive dyes are the most commonly used dye class in cellulosic fibers dyeing. But during dyeing with these dyes, the hydrolyzation of dye may decrease dyeing efficiency and may cause the washing treatments after dyeing to be much harder. It is very important to remove hydrolyzed reactive dye from the textile material by washing treatments to obtain the desired fastness properties. In this research, usage possibilities of β-cyclodextrins, that are nano-substances structurally consist of 7 D-glucopyranosyl units connected by alpha-(1,4) glycosidic linkages, to enhance hydrolyzed reactive dye in washing treatments after reactive dyeing were investigated. According to the experimental results, it can be said that usage of β-CD is possible in washing treatments after reactive dyeing for dyes which form inclusion complex with it.
Key words: *β-cyclodextrin, reactive dye, hydrolyzed dye, washing-off, cellulosic fiber*

1. Introduction

Several classes of dyes are used for dyeing cotton, but in recent years, as the most important, stand out classes of reactive, direct and vat dyes, with a share of over 80 % in the consumption of cotton dyes. Water soluble direct and reactive dyes have the advantage over non soluble vat dyes as they are more environmentally friendly and managing of technological dyeing procedure is simpler [1]. Reactive dyes are colorants applied mainly to cotton to achieve high wash fastness properties. The basis for their high wash fastness is the formation of a covalent bond to cellulose chains during the fixation step [2]. When dyeing with reactive dyes only part of the dye applied is chemically bonded to the cellulosic fiber. The rest reacts with the water molecules hydrolyzing the reactive groups [3, 4]. This unfixed hydrolyzed dye must be effectively removed from the fiber via the washing process in order to meet the required wet and wash fastness specification. The removal of unfixed reactive dye takes place in three phases:

- dilution of dye and chemicals in solution and on the surface of cellulose,
- diffusion out of the deeply penetrated unfixed hydrolysed dye to the fiber surface,
- dilution and removal of the diffused-out dye [5, 6].

Naturally, there is some degree of overlap between these phases. Seperation into three phases permits a more simplified description of the rinsing process [7]. The efficiency of these processes is associated with various parameters such as substantivity and diffusion rate of dye, hardness of water, pH of washing liquor, type and concentration of washing agent and etc. [8]. During the washing processes auxiliaries are often used in large doses, even though the dyehouse personel may realize that not all rinsings require these concentrations, if at all [4]. There are two types of washing agents used in washing treatments. These are non-ionic and anionic. Although non-ionic washing agents are recommended for the elimination of hydrolyzed reactive dyes, since they enable the hydrolyzed dyes to be expelled from the fiber rapidly, anionic washing agents cannot be recommended, because they make the elimination of hydrolyzed dyes difficult. This disadvantage was also observed in the research of K.-H. Weible for the dyes having high substantivity. According to the researcher, the electrolyte effect of anionic washing agents is sufficient for the wet fastness to decline significantly [3]. In the study of P. Anis and H. Eren, anionic/non-ionic washing agent was used and it was found that soaping does not have any important effect on the final color of the fabric or its colorfastness, but it increases organic pollution [4].

Although there are many studies [2-4, 7, 9-14] on washing treatments after reactive dyeing, there are limited articles related to the usage of β-cyclodextrins. Cyclodextrins are a family of oligosaccharides which are obtained from the degradation of starch by the cyclodextrin transglycosylase enzyme. Cyclodextrins are cyclic oligosaccharides composed of 6, 7, 8 or more glucopyranose units that are bonded to each other with α-1,4 linkages and these are respectively named as alpha (α), beta (β) and gamma (γ) cyclodextrins [15, 16]. Polar and hydrophilic outer surface and hydrophobic cavitation of cyclodextrins enable them to retain hydrophobic compounds in a hydrophilic medium [17]. The relatively hydrophobic inside imparts β-cyclodextrin the ability of forming complexes with many hydrophobic molecules [1, 18].

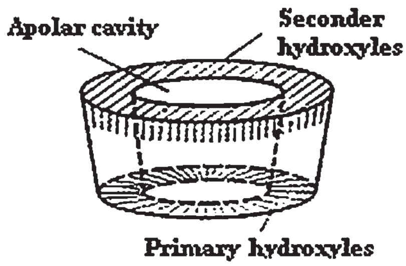


Fig.1 Molecular structure of cyclodextrins [19]

For many years, cyclodextrins were taken into account just because of curiosity, without having any significance for their practical and technical usage [20]. Today, cyclodextrins are used in many areas such as the food industry, pharmacy, cosmetics, environmental protection, and textile industry [16, 21]. Cyclodextrins can be used in dyeing (as a equalizing agent, retarder exc.), washing and finishing treatments in textile industry [20].

In the previous study, we have examined the effects of different washing agents (anionic, non-ionic), washing agent concentration, and liquor ratio and treatment time parameters on hydrolyzed dye removal efficiency [8]. In this research, the usage possibilities of β-cyclodextrins in washing treatments after reactive dyeing were investigated. Fabric samples impregnated with hydrolyzed dye were washed with β-cyclodextrin and with the aim of comparing anionic and non-ionic washing agents at various washing times and β-cyclodextrin concentrations. Hydrolyzed dye removal efficiencies were compared by evaluating the washed fabrics' color yield with the aid of spectral method.

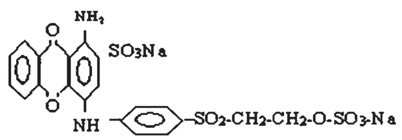
2. Material and method

2.1. Materials

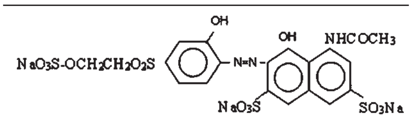
In this study, 100 % mercerised cotton plain woven fabric was used. 4 reactive dyes; Remazol Brilliant Blue R Special (C.I. Reactive Blue 19), Remazol Turquise G 133 (C.I. Reactive Blue 21), Remazol Brilliant Violet 5R (C.I. Reactive Violet 5) and Remazol Red 3B (C.I. Reactive Red 23) were kindly supplied by Dystar and their chemical formulas are given in Tab.1.

Tab.1 Chemical structures of the dyes used in experiments

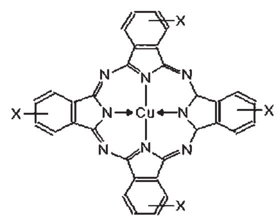
C.I. Reactive Blue 19



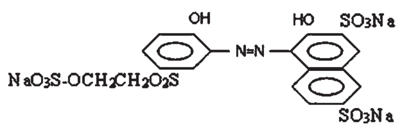
C.I. Reactive Violet 5



C.I. Reactive Blue 21*



C.I. Reactive Red 23



* The chemical formula of this dye couldn't be achieved, because its constition number was not given. Therefore, only general structure of its chromophore group (phthalocyanine) is given [22].

All of the reactive dyes used in the study are vinylsulphone based and monofunctional. Reactivity and subtantivity of the dyes used in experiments can be seen in Tab.2.

For solutions which were prepared for spectral measurements, distilled

Tab.2 Structural properties of the dyes used in experiments

Dye	Reactivity	Substantivity
C.I. Reactive Blue 19	Low-Medium	High
C.I. Reactive Blue 21	Medium	Low
C.I. Reactive Violet 5	High	Low
C.I. Reactive Red 23	Medium	Low

water was used. Rinsings were carried out by using soft water (0.5-1°F). CavamaxâW7 (Wacker Chemie) was selected as b-cyclodextrin and anionic (mixture of organic and anorganic compounds) and non-ionic (combination of polyfunctional nitrogenes) washing agents were used for comparison. Both of the washing agents were in liquid form and were supplied by CHT.

In this study, for the application of hydrolyzed reactive dye solutions Rapid Loboratex Co. KTD-1 trademark padding mangle and for washing treatments HT type Thermal Dyeing Machine were used. Remission measurements were realized using X-rite SP78 model spectral photometer (with D65 daylight and 10° measurement angle), and absorbance measurements of hydrolyzed dye solutions were performed on Shimadzu UV-1201 trade mark absorbency measurement device.

2.2. Method

It is known that cyclodextrin molecules do not interact with all dyes, instead they form inclusion complexes with only dyes having appropriate molecular size and structure. For this reason, in order to determine the reactive dyes that form inclusion complexes with b-CD, dyeing processes (isoterm dyeing at 95 °C for 20 minutes) were realized with 4 hydrolyzed reactive dyes in the presence and absence of β-cyclodextrin (4 g/l).

For determining if there is a complex formation between β-CD and dye molecules or not, dyeings in the presence (4 g/l) and absence of β-CD were carried out. Then relative colour yields of dyed samples in the presence of β-CD were calculated by taking the colour yield of dyed samples in the absence of β-CD as 100 %. If β-CD interacts with dye molecules, it is expected that the colour yield of dyed samples in the presence of β-CD will be lower.

In the following stage of our study, the interaction of these dyes with b-cyclodextrin was also investigated by the spectrophotometric method. When b-CD forms an inclusion complex with a dye molecule, high electron density in the cyclodextrin cavity mobilizes the electron system of the guest compound. As a result of that, characteristic changes are observed in the visible spectrum of the dye. For this reason in order to determine the interaction, aqueous solutions of dye hydrolyzates (0,1 g/l) were prepared in the presence (4 g/l) or absence of b-CD and then spectral measurements were carried out.

To observe the efficiency of β-cyclodextrin in the removal of hydrolyzed dye during the washing treatment**,** two hydrolyzed reactive dyes (C.I. Reactive Blue 19 and C. I. Reactive Blue 21) which interact with β-cyclodextrin and one hydrolyzed reactive dye (C.I. Reactive Violet 5) which does not interact with β-cyclodextrin were impregnated onto the fabrics at room temperature and by maintaining the pick-up at 80%. After applications, the fabrics were dried at room temperature.

2.2.1. Preparation of hydrolyzed dye

The dye solution prepared with 2.5 g/l reactive dye and 10 g/l Soda (Merck) was boiled at 95°C for 4 h to form hydrolyzed dye, and then cooled to room temperature. After that, hydrolyzed dye was neutralized to pH 7 with acetic acid, because in normal reactive dyeing process alcali residues are removed from fabric by the effect of cold/warm rinsings and especially neutralization treatment for vinylsulphone based reactive dyes up to hot rinsing step.

2.2.2. Washing tests

Three washing stages of 15 min at 95 °C were applied to the basic fabric samples. Washing processes realized in liqour ratios 10:1, in the absence of any auxiliary and in the presence of 1, 2 and 4 g/l β-CD, 2 g/l anionic washing agent and 2 g/l non-ionic washing agent.

At the end of the first washing stage of 15 min, samples were removed from the containers and squeezed. Then one of the samples was allocated and dried, the others were taken to the second washing stage. The same treatments were repeated for the second washing stage and the washing test ended after the third 15 min washing stage. Effects of usage of β-CD in washing treatments were determined by evaluating the remission measurements of the samples.

Colour yield of samples, which were expressed as K/S, calculated with the aid of Kubelka Munk equation.

$K/S = (1-R)^2 / 2R$

R - reflectance value in the maximum absorption wave length

K - absorption coefficient

S - scattering coefficient

3. Results and discussions

3.1. Examining the interactions between reactive dyes and β-cyclodextrin

Results of spectrophotometric measuruments can be seen from Fig.2. As it can be seen clearly from Figure 2, when β-CD was used the co-

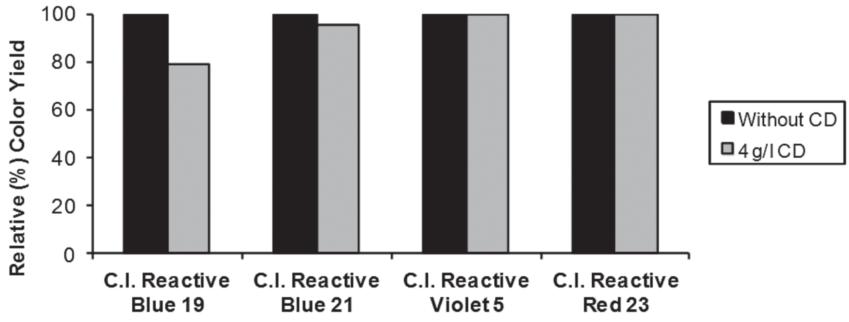


Fig.2 Relative (%) colour yield (K/S) values of dyeings carried out with various hydrolyzed dyes

lour yield of C.I. Reactive Blue 19 and C.I. Reactive Blue 21 dyes decreased. This means both of the two dyes interact with β-CD. Furthermore, it can be understood from relative color yields that the interaction between C.I. Reactive Blue 19 and β-CD is stronger. On the other hand, there is no significant change in colour yields of samples dyed with C.I. Reactive Violet 5 and C.I. Reactive Red 23 in the presence of β-CD, thus it can be said that there is no interaction between those dyes and β-CD.

The spectrophotometric measurement results of C.I. Reactive Blue 19, C.I. Reactive Blue 21, C.I. Reactive Violet 5 and C.I. Reactive Red 23 dyes are shown in Fig.3.

The λ_{max} and A_0 values of all invesitigated dyes and hydrolyzed dye solutions in the presence and absence of β-CD are given in Tab.3.

As it can be seen from Table 3, there is no difference between the max. absorbance wavelength of C.I. Reactive Blue 19, Violet 5 and Red 23 dyes and their hydrolyzed forms, but the max. absorbance wavelength of C.I. Reactive Blue 21 dye is decreased from 660 nm to 620 nm, when it is hydrolyzed. This can be explained with the degredation of chromophore group by the effect of heat during boiling in an alkali medium.

When the spectral curves of C.I. Reactive Blue 19 and C.I. Reactive Blue 21 hydrolyzed dyes in the presence and absence of cyclodextrin were examined, it can be said that, no significant change in max. absorbance wavelength of C.I. Reactive Blue 19 dye was observed, where maximum absorbance wave length

Tab.3 The λ_{max} and A_0 values of all invesitigated dyes and hydolyzed dye solutions (0,1 g/l) in the presence and absence of β-CD

	C.I. Reactive Blue 19	C.I. Reactive Blue 21	C.I. Reactive Violet 5	C.I. Reactive Red 23
λ_{max} (nm) of dye	600	660	560	520
λ_{max} (nm) of hydrolyzed dye	600	620	560	520
λ_{max} (nm) of hydrolyzed dye + β-CD	600	660	560	520
$\Delta\lambda_{max}$ (nm)	0	40	0	0
A_0 of hydrolyzed dye	0,495	1,424	1,22	1,44
A_0 of hydrolyzed dye + β-CD	0,720	1,589	1,22	1,44
% ΔA_0	+ 45,45	+ 11,59	0	0

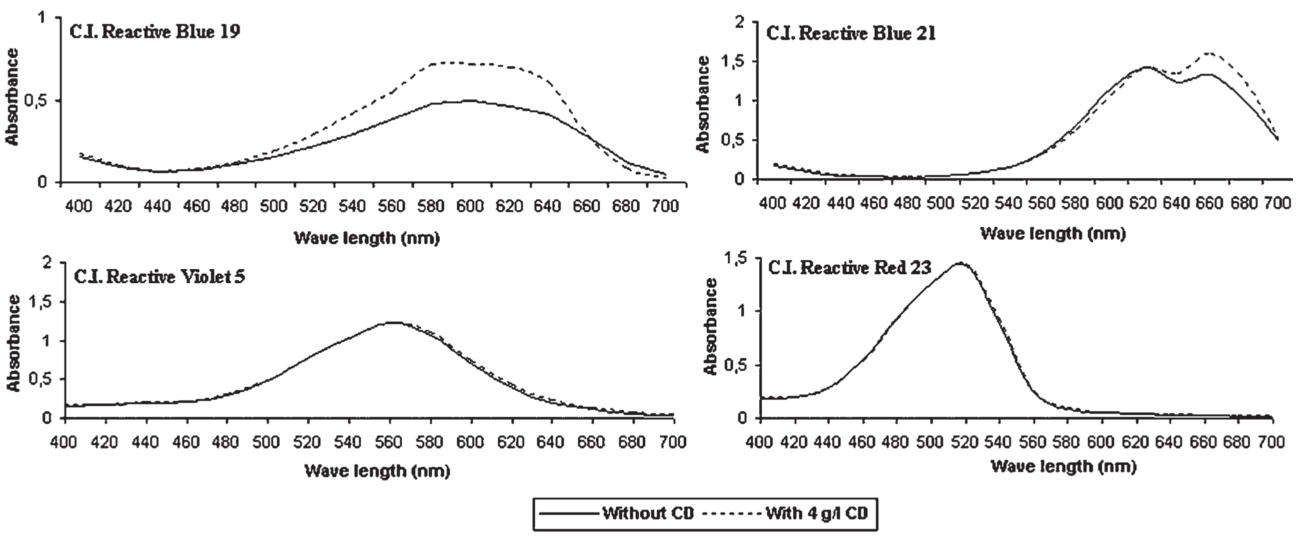


Fig.3 The absorbance measurements of hydrolyzed dye solutions in the presence and absence of β-CD

of C.I. Reactive Blue 21 has increased from 540 to 560 nm (Batochromic effect). Hyperchromic effect (increase in absorbance value) was observed in the max. absorbance values of these two dyes. This increase is comparatively more obvious for C.I. Reactive Blue 19 dye. It is thought that the reason of this is its molecular structure to be smaller than the other's. In spite of this, no significant change was determined in spectrums of hydrolyzed forms of C.I. Reactive Viloet 5 and C.I. Reactive Red 23 dyes in the presence of β-CD. This is absolutely attributed to the chemical structure and molecular size of the dyes.

The reason C.I. Reactive Blue 21 dye able to form inclusion complex with β-CD can be attributed to the fact that it has a free phenyl ring that can form an inclusion complex with β-CD. For C.I. Reactive Blue 19 dye, it is thought that β-CD may form inclusion complex on the anthraquinone rings and also on the phenyl rings containing substituent groups.

3.2. Determination of the hydrolyzed dye removal efficiency of β-cyclodextrin

Influence of β-cyclodextrin concentration on hydrolyzed dye removal efficiency can be seen from the Fig.4-6.

As it can be seen clearly from the figures, depending on the dye structure β-CD shows different effects during washing treatments. Better hydrolyzed dye removal is achieved in washing treatments of C.I. Reactive Blue 19 hyrolyzate in the presence of cyclodextrin than washing with only soft water. For example, when liquor ratio was 10:1 with only water, K/S value of the washed sample decreases to 0.77 as it is 0.57 when liquor includes 4 g/l β-CD. It is thought that the reason for the increase in the efficiency of hydrolyzed dye removal in the presence of β-CD is, the effect of an

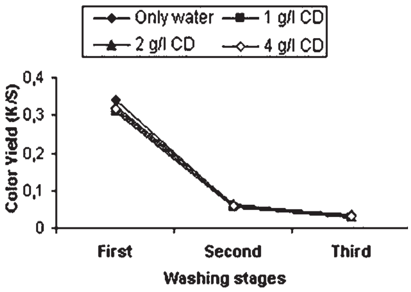


Fig.4 Effect of β-CD concentration on hydrolyzed dye removal efficiency for C.I. Reactive Blue 19

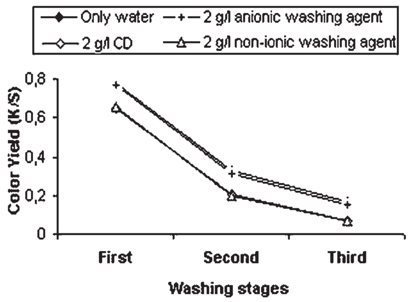


Fig.5 Effect of β-CD concentration on hydrolyzed dye removal efficiency for C.I. Reactive Blue 21

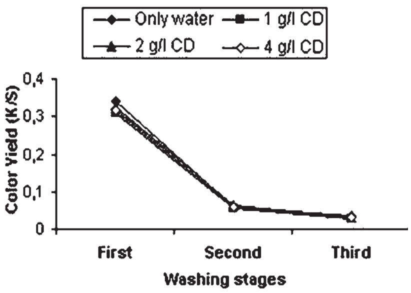


Fig.6 Effect of β-CD concentration on hydrolyzed dye removal efficiency for C.I. Reactive Violet 5

equilibrium reaction (desorption) which is installed with interaction forces between dye and β-CD, more than chemical removal of the dye. Remembering the determination of inclusion complex formation with spectral analysis between β-CD and these dyes, it can be said that, by forming inclusion complex with the hydrolyzed dye, β-CD pulls hydrolyzed dye away from fabric surface and carries it to the washing liquor. Furthermore, when the effect of β-CD concentration is examined, it can be said that for C.I. Reactive Blue 19 dye, hydrolyzed dye removal rises as the concentration of β-CD increases. But low concentrations of β-CD could also be enough to achieve a good hydrolyzed dye removal.

On the other hand, usage of β-CD in washing treatments of C.I. Reactive Violet 5 dye, which has no interaction with β-CD, has no beneficial effect on washing efficiency. The interesting point here is, for C. I. Reactive Blue 21 dye no beneficial effect was observed after washing in the presence of 1 or 2 g/l β-CD, although it has an interaction with β-CD. The reason of this is thought to be the 1-2 g/l β-CD concentration is not sufficient for this highly substantive dye. As a matter of fact, as it can be clearly seen from Figure 5, washing efficiency increased when 4 g/l β-CD was used.

3.3. Comparison of the hydrolyzed dye removal efficiency of β-cyclodextrin and washing agents

Results of the experiments carrried out for comparing the hydrolyzed dye removal efficiency of β-CD and washing agents are given in Fig.7-9.

If the effects of washing agents and β-CD are compared, it can be said that for C.I. Reactive Blue 19 and C.I. Reactive Blue 21 dyes better results were obtained after washings in the presence of β-CD than anionic washing agent. If its effectiveness is compared with non-ionic washing agent, it can be understood that same hydrolyzed dye removal was achieved with β-CD for C.I. Reactive Blue 19, but for C.I. Reactive Blue 21, hydrolyzed dye removal was less with β-CD compared to non-ionic washing agent.

C.I. Reactive Blue 21 is a phthalocyanine based dye having big molecule and hence its substantivity is high. Thus, removal of this hydrolyzed dye from fabric is much harder. As generally known, washing agen-

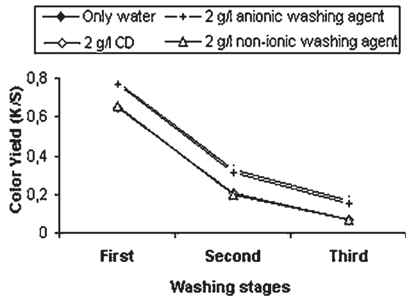


Fig.7 Washing results of C.I. Reactive Blue 19 dye

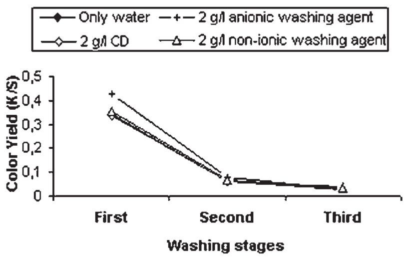


Fig.8 Washing results of C.I. Reactive Blue 21 dye

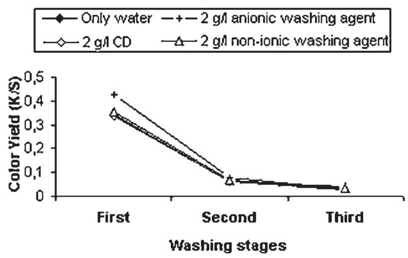


Fig.9 Washing results of C.I. Reactive Violet 5 dye

ts have good wetting properties and a high dispersing capacity, because they are surfactants. An efficient removal of highly substantive hydrolyzed dye from the fabric surface could not be achieved with the use of β-CD, because it does not have such properties. Also it was shown that, interaction between β-CD and C.I. Reactive Blue 21 is weaker. Thus, effectiveness of the non-ionic washing agent found to be better compared to β-CD.

On the other hand, for C.I. Reactive Violet 5, which does not interact with β-CD, usage of β-CD or washing agents in washing treatments did not have a significant effect on washing efficiency; however, usage of non-ionic washing agent may be a little bit beneficial. These results are related to dye's low substantivity. In washing treatments one of the most important parameters is dye substantivity and as generally known washing treatments of low substantive dyes are easier. For that reason it can be said that for these dyes only water is enough.

4. Conclusion

From experimental results, it can be concluded that usage of β-cyclodextrin is possible in washing treatments after reactive dyeing, however it is limited. Because inclusion complex formation between cyclodextrin and the dye molecule is necessary. So, usage of β-CD can be possible in washing treatments of dyes which forms inclusion complex with it. But, an important factor concerning possible applications in the washing treatments is that the use of cyclodextrins does not cause any problems in waste water and they are biodegradable. For that reason it can be said that β-CD could be a good alternative to washing agents which are not eco-friendly materials as they cause toxicity in effluent.

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