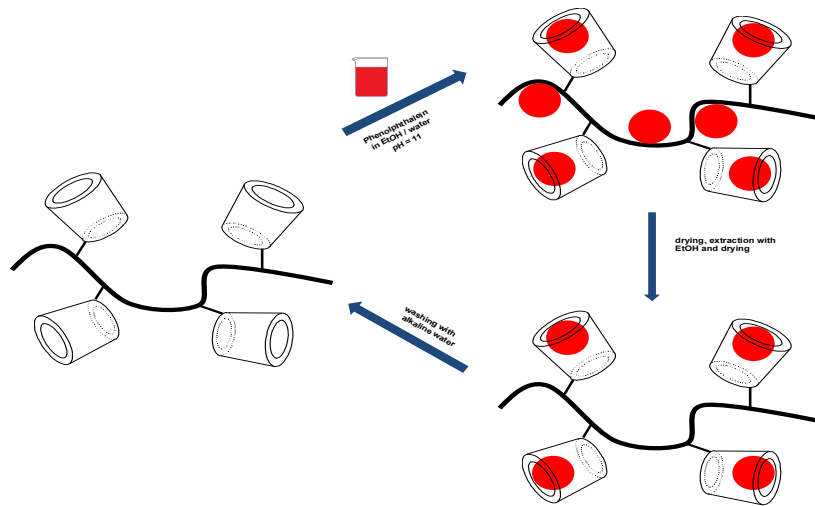




**Spectrophotometric Estimation of the Accessible Inclusion Sites of  $\beta$ -Cyclodextrin Fixed on the Cotton Fabrics Using Phenolic Dyes**

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A schematic representation for quantitative estimation of accessible inclusion sites of  $\beta$ -CDs fixed on cotton textiles, using adsorption and desorption of phenolphthalein

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3 **Title:** Spectrophotometric Estimation of the Accessible Inclusion Sites of  $\beta$ -Cyclodextrin Fixed on the Cotton  
4 Fabrics Using Phenolic Dyestuffs  
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18 **Keywords:**  $\beta$ -cyclodextrins, phenolphthalein, phenol red, UV-Vis-spectroscopy  
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## Abstract

Surface modified textiles with cyclodextrins are used in a wide range of applications. The presence of cyclodextrins fixed on a textile material can be qualitatively proved by application of the alkaline solutions of phenolphthalein and visual evaluation of the color change. However, there is no simple and universal method for quantitative determination of the amount of the accessible cyclodextrins for complexation with the guest molecules. In this article, we report a simple way based on colorimetric investigation of adsorption and desorption of phenolphthalein and phenol red in the cavities of the cyclodextrins. For this aim, woven cotton fabrics finished with different amounts of  $\beta$ -cyclodextrin have been used. With the known stoichiometry of the complex formation of phenolic dyes with  $\beta$ -cyclodextrin, spectrophotometric study of complexation and decomplexation of these dyestuffs in cavities of cyclodextrins enable us to determine the accessible amounts of cyclodextrins sites accessible, quantitatively.

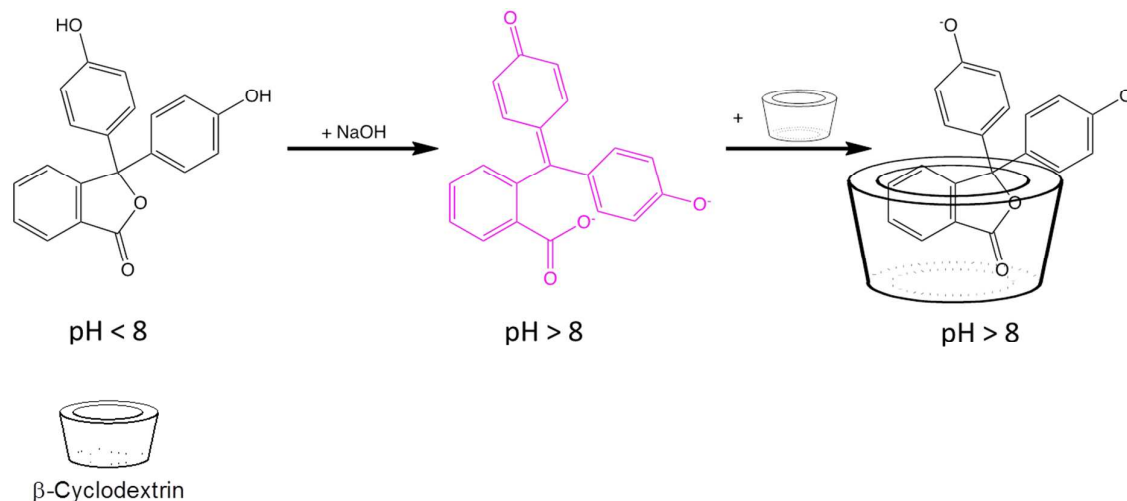
## Introduction

Cyclodextrins (CDs) are cyclic polysaccharides, as byproducts of enzymatic degradation of starch, and composed of six to eight D-glucose units ( $\alpha=6$ ,  $\beta=7$  and  $\gamma=8$ ).<sup>1</sup> According to the X-ray analysis, molecular structure of CDs consists of a hydrophilic outside and a hydrophobic and nonpolar hollow cavity, which makes them able to form stable inclusion complexes with different molecules such as drugs, odor, and dyestuff molecules.<sup>2-4</sup> Regarding industrial applications and due to its readily availability and the appropriate cavity to form inclusion complexes with common aliphatic and aromatic compounds,  $\beta$ -cyclodextrin has received more attention in studies and applications, in comparison to  $\alpha$ -, and  $\gamma$ -cyclodextrins.<sup>5-8</sup> CDs have also been used for surface modification of textiles in order to create new performances such as: absorbance of unpleasant odour, controlled release of fragrances, uv protection, and antibacterial.<sup>9</sup> In addition to the surface modification, CDs provide new opportunities for textile industry, including application in textile processes such as washing, dyeing, and wastewater treatment.<sup>10</sup>

Chemical modification of textiles by cyclodextrin derivatives is achieved through permanent fixation of CDs.<sup>11</sup> For permanent fixation there are two main approaches: covalently fixation onto textiles using reactive derivatives or suitable crosslinking agent: CDs derivatives with reactive group, such as monochlorotriazinyl- $\beta$ -CD (MCT- $\beta$ -CD), dihydroxypropyl-ethylhexylglycidyl- $\beta$ -CD, acrylamidomethylated- $\beta$ -CD;<sup>12-15</sup> and use of crosslinking agents such as epichlorohydrin, N-methylol compounds, and polycarboxylic acids.<sup>16-21</sup>

To find the overall amount of fixed CDs is important and in the case of textiles, the simplest way in practice is gravimetric test, based on the weight difference of the textile material before and after treating with CDs and their derivatives. This method is not enough accurate and provides no information about inclusion properties of the finished textile with CDs. As a matter of fact, the most important determining factor in final performances of a functionalized material with fixed CDs is the ability to make stable inclusion complexes with guest compounds. Therefore, evaluating the accessible CDs sites for inclusion is decisive.<sup>22-27</sup> In this regard, phenolphthalein and phenol red as indicator phenolic dyestuffs have been used for qualitative detection of CDs and evaluation of inclusion sites.<sup>28-34, 40</sup> Phenolphthalein, a well-known chromophoric dye, is widely used for detection of CDs due to its suitable inclusion geometry. Complexation of  $\beta$ -cyclodextrin with phenolphthalein in alkaline conditions decreases the maximum absorption at 552 nm in UV-Vis spectroscopy (Figure 1).<sup>23,24,29,35</sup> In the case of textiles, the color of phenolphthalein changes from pink in absence of the CD molecules to colorless

in the presence of CD.<sup>28</sup> Phenol red behaves as same as phenolphthalein and its color changes from red to yellow in the presence of cyclodextrin molecules.



**Figure 1** Change in chemical structure and color of phenolphthalein under alkaline conditions and in the presence of  $\beta$ -cyclodextrin

Phenolphthalein has been used to determine the concentration of CDs and their derivatives in solution.<sup>23,24, 29, 32, 36,37</sup> In these researches, pure substances in the form of powder or liquid containing of CDs derivatives were dissolved in phenolphthalein solutions and finally the amount of CDs has been quantitatively estimated by measuring the changes in maximum absorbance in UV-spectroscopy. However, this technique cannot be employed for textiles. Apart from the works of Grechin et al.<sup>38</sup> and Bereck et al.<sup>39</sup> there is no detailed method for quantification of the accessible inclusion sites of CDs on textile materials, at the time of this publication. In the work of Grechin and coworkers, the amount of fixed CDs was quantified via coordination and adsorption properties of the cotton fabrics with different volatile aliphatic amines, such as n-propylamine, n-butylamine and cyclohexylamine. This method needs a relative long time (48 h) and surface adsorption of the used volatile aliphatic amine on the textile will be an error source. Furthermore, in the case of fixation of CDs molecules on the surface of textile materials with crosslinking agents containing free amine groups, such as polyaminocarboxylic acid<sup>27</sup>, this method cannot be applied. Bereck et al. have quantified the amount of  $\beta$ -cyclodextrin fixed onto cotton fabric assuming 1:1 complexation of  $\beta$ -cyclodextrin with Ferrocene. Despite the

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3 preciseness of this method, it cannot be widely used in practice, due to its need to electrochemical tools, which is  
4 not available in every industrial unit.  
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8 In this study, we report a simple and accurate method to determine the amount of accessible inclusion sites of  $\beta$ -  
9 cyclodextrin fixed on a cotton fabric, based on adsorption and desorption of phenolic dyes, i.e. phenolphthalein  
10 and phenol red, in the cavities of CDs and measuring the changes of maximum absorbance. This method can be  
11 used for all kinds of textile materials with fixed  $\beta$ -cyclodextrin.  
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## 15 16 17 **Experimental**

### 18 19 **Materials**

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21 A standard plain woven cotton fabric (scoured, bleached and desized; density 111 g/m<sup>2</sup>) was supplied by Testex.  
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23 Ethanol (Merck), sodium hydroxide (99%, Merck), phenolphthalein (Merck), phenol red (Merck) and  
24 monochlorotriazinyl-beta-cyclodextrin (MCT- $\beta$ -CD) (Cavasol W7 MCT, Wacker, Burghausen, Germany) were  
25 used without any further purification.  
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### 30 31 **Methods**

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33 Cotton samples were prepared with different concentrations of MCT-  $\beta$ -cyclodextrin (0,5 – 6,0% w/v) and the  
34 gravimetical determination of the total amount of fixed MCT- $\beta$ -CD was carried out according to the previously  
35 described method in literature.<sup>40</sup>  
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40 In order to obtain calibration curves from UV-Vis-spectroscopy, solutions of phenolphthalein and phenol red  
41 with different concentrations were prepared: the stock solution was made by dissolving of 0.1 g of the dyestuff  
42 in 100 ml water and pH was adjusted at 11.0 $\pm$ 0.1, by adding required amount of sodium hydroxide (0.1 M  
43 NaOH) and stirred 30 min using ultrasonic for a complete dissolution; then solutions with different  
44 concentrations of the dyestuffs were prepared by diluting the stock solutions. The concentrations of dyestuffs in  
45 calibrating solutions were varied from 0.001 to 0.008  $\mu$ M for phenolphthalein and 0.001 to 0.01  $\mu$ M for phenol  
46 red. Afterward, absorbance of each solution was measured using a UV-Vis-spectrometer (Varian Cary 5E) at  
47 room temperature and maximum absorbance was recorded.  
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56 Thus, from each cotton fabric with fixed MCT- $\beta$ -CD and a blank cotton fabric (without MCT- $\beta$ -CD), three  
57 samples with 3 $\times$  3 cm dimensions were cut and they have separately immersed in a solution containing 0.01 g  
58 dyestuff, 40 ml water and 60 ml ethanol (pH of whole solution was adjusted at 11, using sodium hydroxide, and  
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3 30 min stirred in ultrasonic), and stirred for 5 min at room temperature. Then, the samples were dried for 30 min  
4 at 120 °C. After drying, all samples were extracted with pure ethanol during one hour.

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7 The extracted samples were finally dried (100 °C, 10 min) and stirred 5 min in alkaline water (50 ml, pH 11,  
8 adjusted by 0.1M NaOH). When required, the solutions should be diluted before spectroscopy. Then, absorbance  
9 of each remaining solution was measured at  $\lambda_{max}$  of 552 nm and 559 nm for phenolphthalein and phenol red,  
10 respectively. The cotton samples were once again dried (120 °C, 30 min) and weighed precisely.

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13 The weight fraction ( $w^*$ . %) of the fixed  $\beta$ -CDs is calculated according to the following equation, as the mean  
14 value of the three samples:

$$15 \quad w^*. \% = \frac{n_{dye} \times M_{\beta-CD} \times 100}{m_{fabric}} \quad (1)$$

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18 where,  $n_{dye}$  is the mole of the phenolic dyestuff complexed with  $\beta$ -CDs (obtained by spectroscopy of cotton  
19 samples),  $M_{\beta-CD}$  is the molecular weight of  $\beta$ -CD and  $m_{fabric}$  is the weight of cotton sample after final drying. The  
20 accessibility yield of the fixed  $\beta$ -CD (Y. %) (accessible to make inclusion complexes with guest molecules) can  
21 be calculated from:

$$22 \quad Y. \% = \frac{w^*. \%}{w. \%} \times 100 \quad (2)$$

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25 In this equation  $w. \%$  (mean value of three samples) corresponds the overall weight fraction of  $\beta$ -CD fixed on the  
26 cotton samples and determined by gravimetric measuring.



## Results and discussion

The absorbance at 552 nm is responsible for the appearance of a pink color of the phenolphthalein solution and at 559 nm for the solution of phenol red. The calibration line obtained by spectrophotometric study of phenolphthalein solution at different concentrations under alkaline conditions (pH 11) is presented in Figure 2. The pH of solutions was adjusted at 11, in order to achieve better sensitivity for absorbance measurement and reduce the possible deprotonation of hydroxyl groups of  $\beta$ -cyclodextrins.<sup>23, 44</sup> In solutions with pH values of lower than 10, the basic intensity of phenolphthalein and phenol red calorimetric solutions are too low.

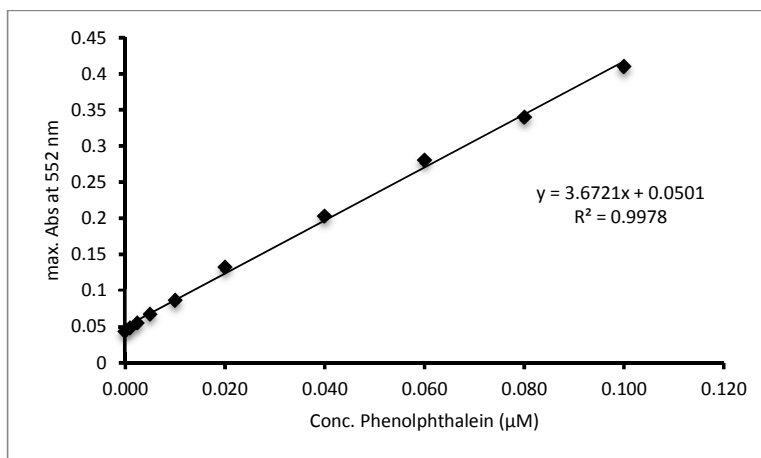


Figure 2 Calibration curve of phenolphthalein solutions (pH 11, 0±0.1)

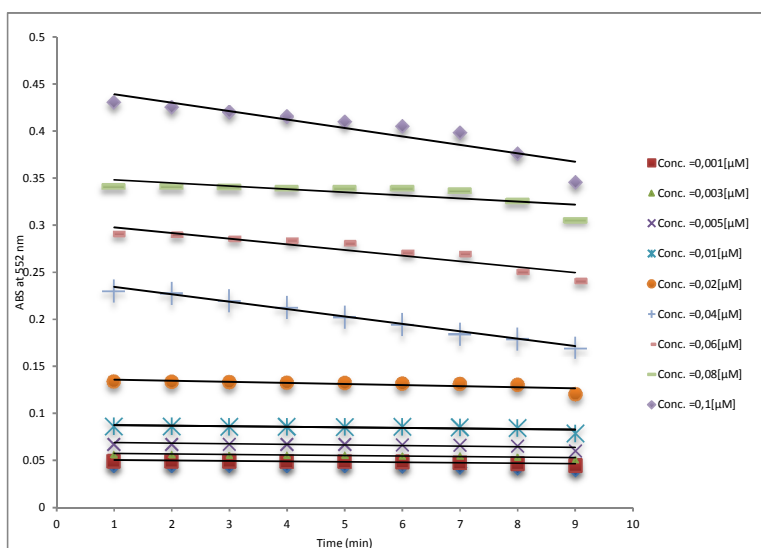


Figure 3 Variation of the absorbance of phenolphthalein solutions at different concentrations as a function of time

As it can be observed from Figure 2, there is a very good linear correlation between absorbance and concentration of phenolphthalein at very low concentrations. By increasing the concentration, fit of a linear calibration was not accurate, which could be attributed to the probable photodegradation of phenolphthalein molecules in exposing to light.<sup>41,42</sup> The other important factor in stability of phenolic dyes is time. Figure 3 shows that, the stability of phenolphthalein in alkaline solution is reduced over time.<sup>41,43</sup> It can be observed that, phenolphthalein solution is more stable at lower concentrations and the absorbance of solutions does not change significantly until 5 min after preparation of solutions. In Figure 4 absorbance stability of phenol red calibration solutions at different concentrations over time is given. The results of Figure 4 indicate that the solutions of phenol red in comparison to phenolphthalein are relatively more stable over time. Therefore, in this study, all UV-Vis-spectroscopy measurements have been carried out within 5 min after preparation of the solutions.<sup>41</sup> The calibration curve of phenol red, prepared in alkaline aqueous solution (pH 11), is presented in Figure 5. For phenol red as well as phenolphthalein linear correlation between absorbance and concentration was observed, meanwhile the absorbance values of phenol red were higher than phenolphthalein.

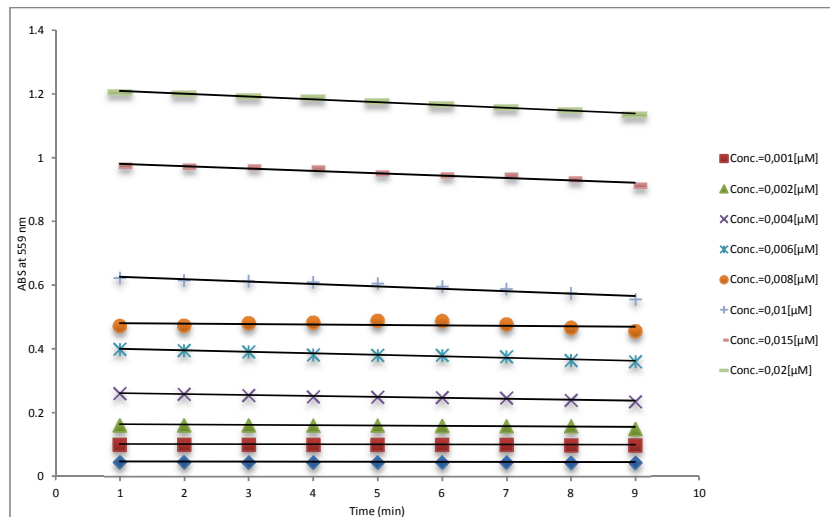
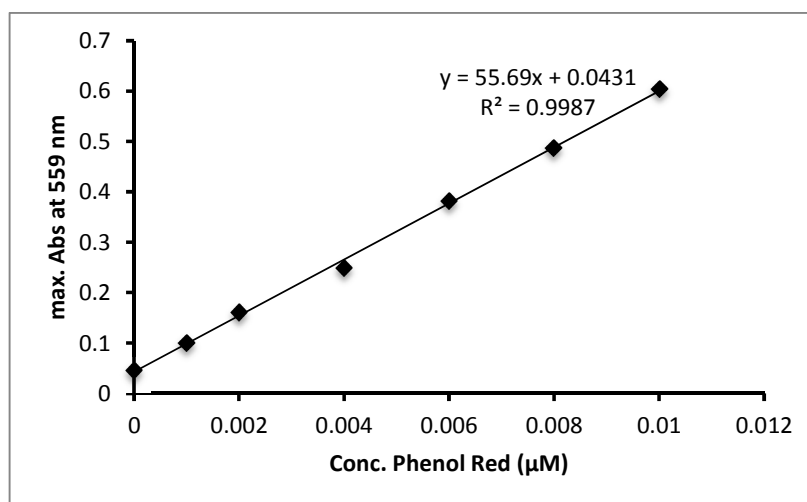
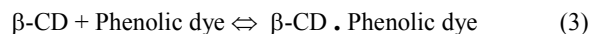


Figure 4 Variation of the absorbance of phenol red solutions at different concentrations as a function of time



**Figure 5 Calibration curve**  
of phenol red solutions (pH 11,0 $\pm$ 0.1)

The principal of estimating the amount of accessible sites of  $\beta$ -CD fixed on cotton fabrics is based on inclusion of CDs and phenolic dyes, and it is assumed this inclusion is a 1:1 complex:



It is known, that phenolphthalein and phenol red possess a low solubility in water and therefore, they are usually prepared with help of ethanol. According to literature,<sup>40</sup> this fact is also concerned in qualitative detection of CDs using phenolphthalein and phenol red. It can be shown that, the dyestuff molecules, which are not adsorbed, will be removed during extraction with ethanol (Figure 6). When the extracted cotton samples with ethanol are immersed into alkaline water (pH 11), the complexed dye molecules in cavities of CDs are released. Therefore, the dye molecules in alkaline water correspond to the accessible inclusion sites of  $\beta$ -CD fixed on the cotton fabric. Color changes of the alkaline water can be easily checked by colorimetric measurement.

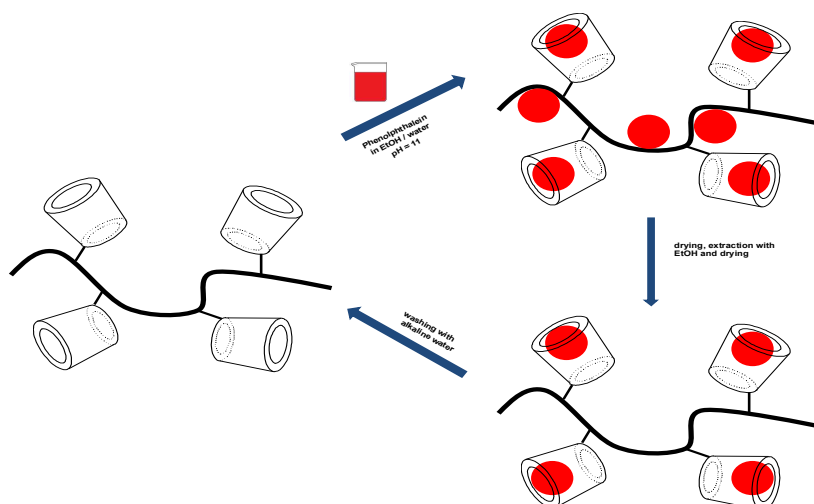


Figure 6 A schematic representation for quantitative estimation of accessible inclusion sites of  $\beta$ -CDs fixed on cotton textiles, using adsorption and desorption of phenolphthalein

Figure 7 and Figure 8 show the changes in absorbance values of the alkaline water solutions after immersing of cotton samples with different amounts of fixed MCT- $\beta$ -CD, which previously extracted with ethanol after exposing to the solutions of phenolphthalein and phenol red, respectively. It can be observed that with increasing amount of fixed MCT- $\beta$ -CD on the textile material, the absorbance values of alkaline water solutions at  $\lambda_{\max}$  increases significantly.

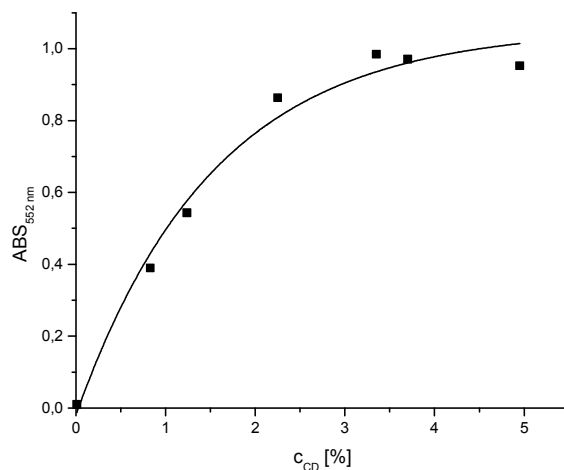


Figure 7 Increase of the absorbance of aqueous solutions after immersing cotton samples with fixed MCT- $\beta$ -CD due to the release of phenolphthalein (pH  $11.0 \pm 0.1$ )

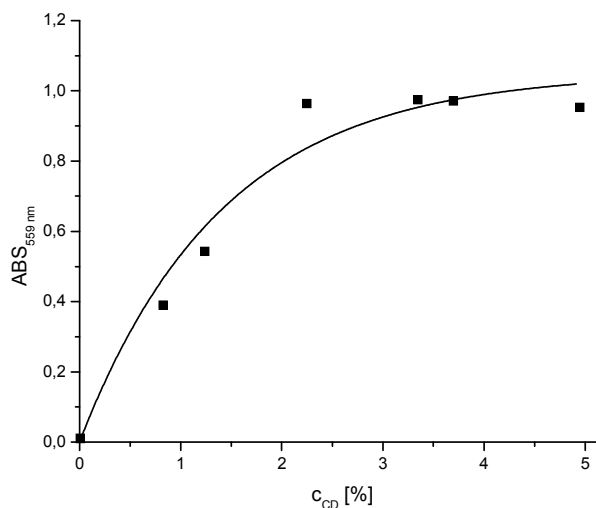


Figure 8 Increase of the absorbance of aqueous solutions after immersing cotton samples with fixes MCT- $\beta$ -CD due to the release of phenol red (pH 11,0 $\pm$ 0,1)

From the known 1:1 complex stoichiometry between the phenolic dyes and  $\beta$ -cyclodextrin,<sup>29-31</sup> the weight fractions of accessible CDs on the surface of cotton textiles ( $w^*$ . %) and accessibility yield (Y. %) are presented in Figure 9 and Figure 10, respectively. The overall weight fraction of  $\beta$ -cyclodextrin fixed on cotton textile samples are gravimetrically determined by precise weighting of the cotton samples before and after fixation of MCT- $\beta$ -CD. Based on different arrangements of  $\beta$ -cyclodextrin molecules on the surface of samples, inclusion of phenolic dyes as guest molecules is only possible in cyclodextrin cavities accessible for the dye molecules. Thus, the amount of cyclodextrin molecules involved in the formation of inclusion complexes depends on the size of the molecules used. Size and shape of the phenolic dyes under given conditions are critical factors in final results.<sup>2, 38</sup>

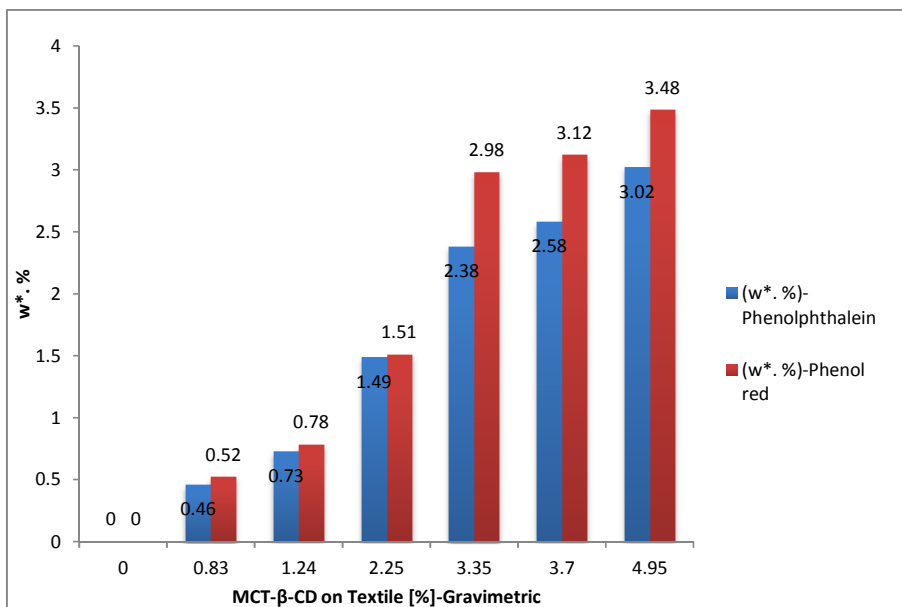


Figure 9 The weigh fractions of accessible CDs on the surface of cotton textiles (w\*. %)

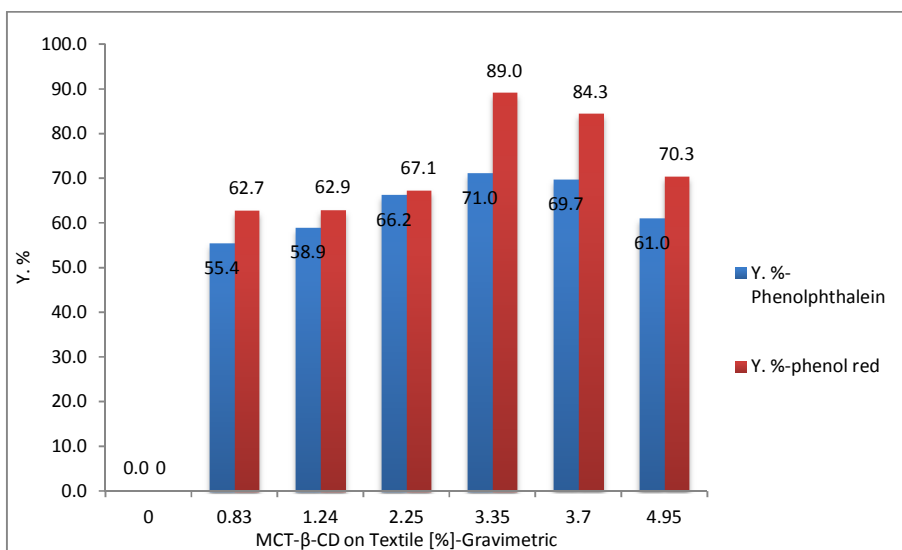


Figure 10 The accessibility yield CDs on the surface of cotton textiles (Y. %)

From Figures 9 and 10 it can be seen that the maximum detectable amount of β-cyclodextrin fixed on a cotton textile was around 3.5% of weight of the sample. The exponential increase of the weight fractions of accessible CDs can be attributed to the limited space for the cyclodextrin molecules on the fiber surface.

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3 Concerning the weigh fractions of accessible CDs on the surface of cotton textiles ( $w^*$ . %) and accessibility yield  
4 (Y. %) (equation 1 and 2), the results demonstrated that at least half of the  $\beta$ -cyclodextrins fixed on the cotton  
5 samples have open cavities and are capable to make inclusion with molecules of phenolic dyestuffs. These  
6 results can be comprised to the results of Grechin et al.,<sup>38</sup> in which the same trend and similar accessibility  
7 yields were obtained based on inclusion of  $\beta$ -cyclodextrins and volatile amines.  
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## 17 Conclusion

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19 The accessible sites of cyclodextrin derivatives fixed onto textile materials can be fast and easily determined  
20 using phenolphthalein and phenol red. Phenolphthalein and phenol red are well-known indicator dyestuffs with  
21 color changes in response to variation of pH value. On the other hand, both dye molecules form inclusion  
22 complexes with cyclodextrins and therefore can be used to determine the presence of cyclodextrins fixed on  
23 textile materials. Concerning 1:1 complexation, adsorption of phenolphthalein in cavities of cyclodextrins, its  
24 desorption by alkaline water and measuring the changes of absorbance in UV-VIS-spectroscopy enable us to  
25 determine the amounts of cyclodextrins accessible for the inclusion with guest molecules, quantitatively. In  
26 comparison to the other analytical methods such as chromatography, HPLC and elemental analysis, this method  
27 is easy, fast and more reliable. Concerning this fact, that the conventional qualitative detection of cyclodextrins  
28 fixed on textile, based on visual assessment of color changes of phenolphthalein, cannot be applied for the  
29 colored textiles. Thus, the described method in this paper does not suffer from this limit and can be applied for  
30 all kinds of colored textiles, it is independent of fixation method of CD on the textile materials and is applicable  
31 for different kinds of CDs.  
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## List of Captures

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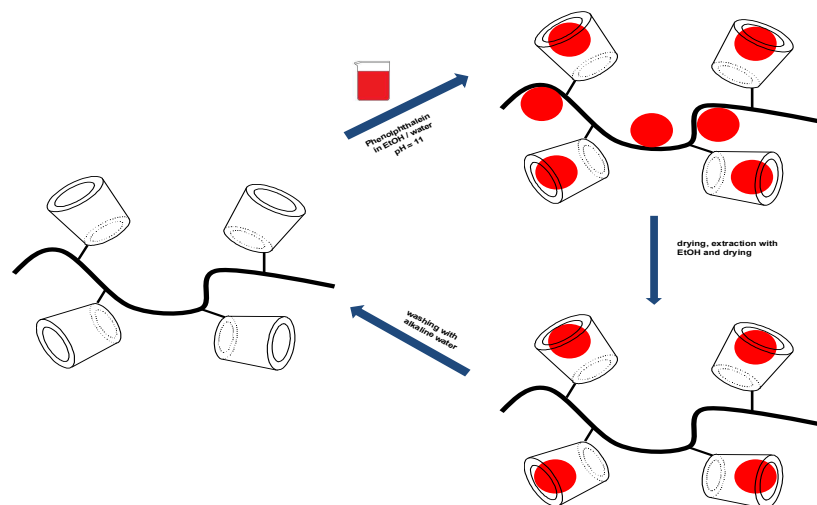
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With the known stoichiometry of the complex formation of phenolic dyes with  $\beta$ -cyclodextrin, spectrophotometric study of complexation and decomplexation of these dyestuffs in cavities of cyclodextrins enable us to determine the accessible amounts of cyclodextrins sites accessible, quantitatively.

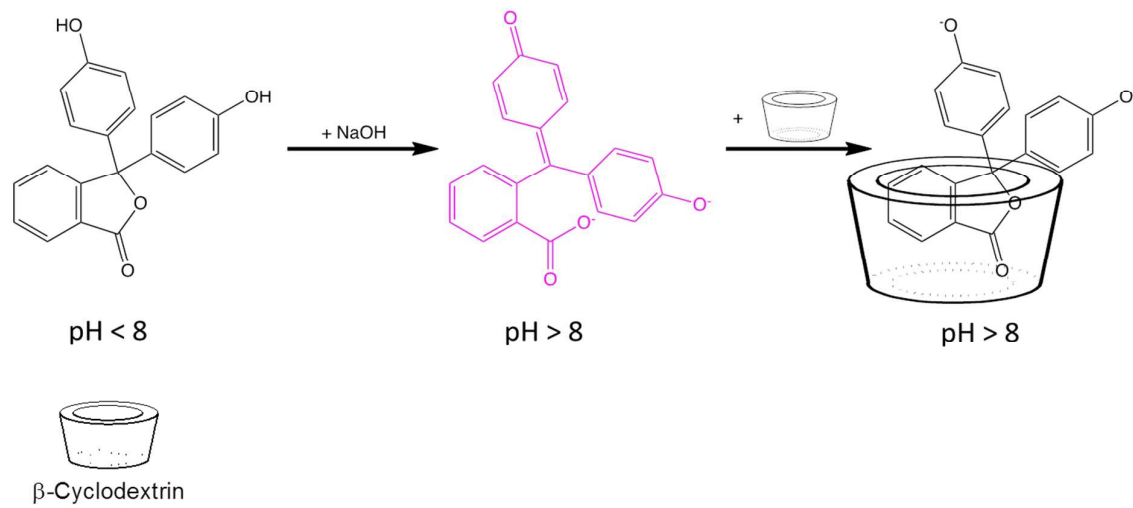


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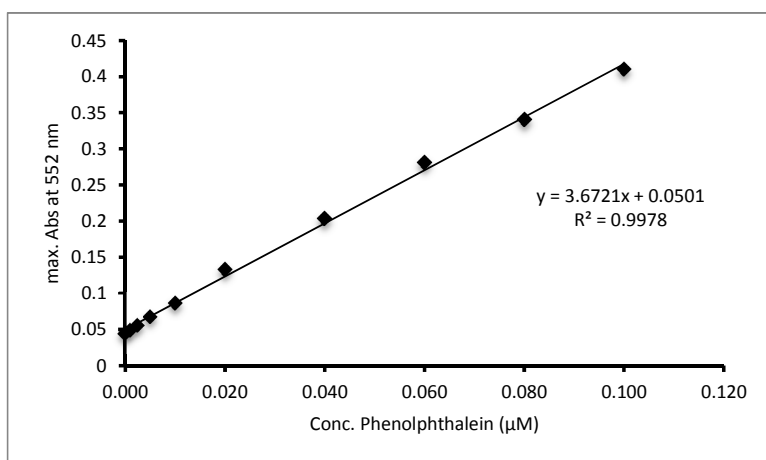


Figure 2 Calibration curve of phenolphthalein solutions (pH 11,0±0.1)

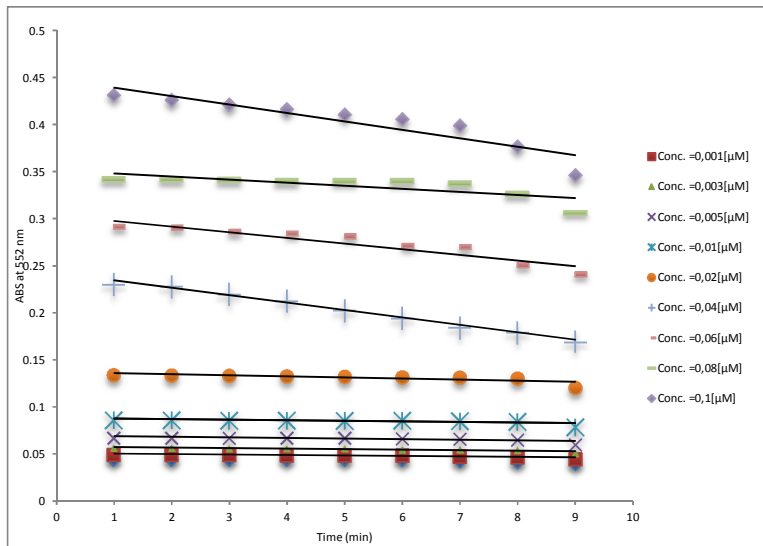


Figure 3 Variation of the absorbance of phenolphthalein solutions at different concentrations as a function of time

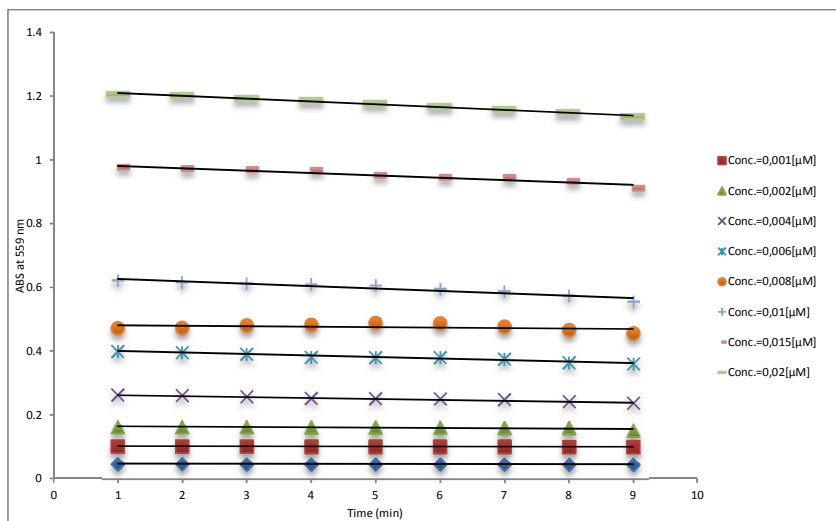


Figure 4 Variation of the absorbance of phenol red solutions at different concentrations as a function of time

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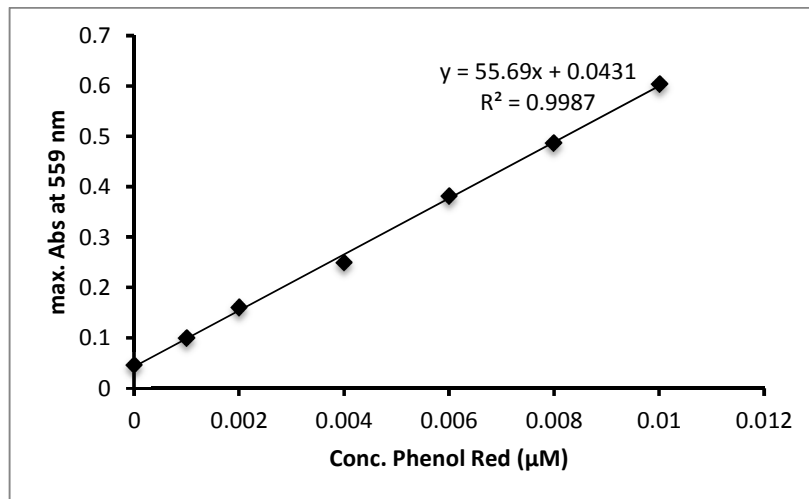


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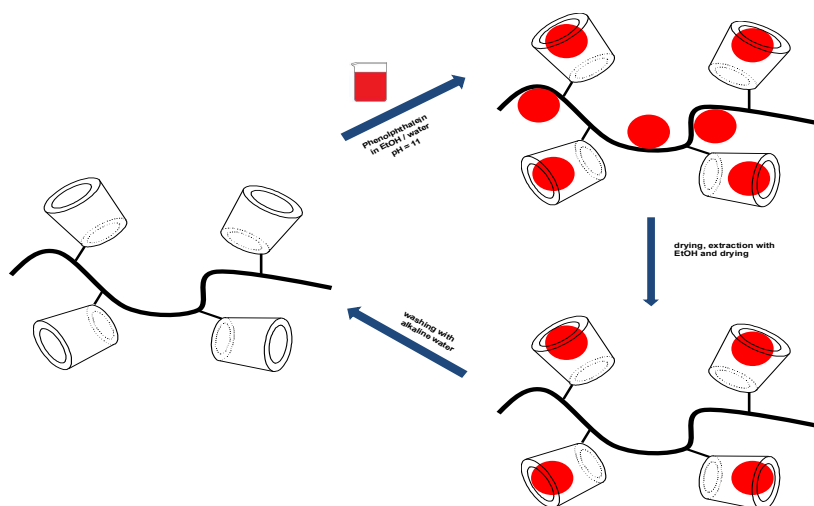


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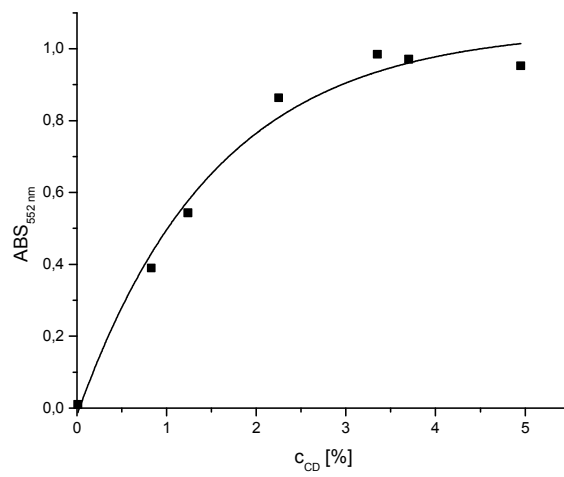


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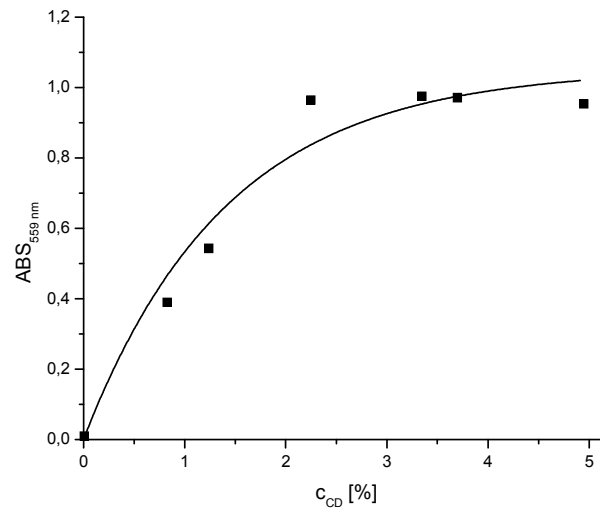


Figure 8 Increase of the absorbance of aqueous solutions after immersing cotton samples with fixes MCT-β-CD due to the release of phenol red (pH 11,0±0,1)

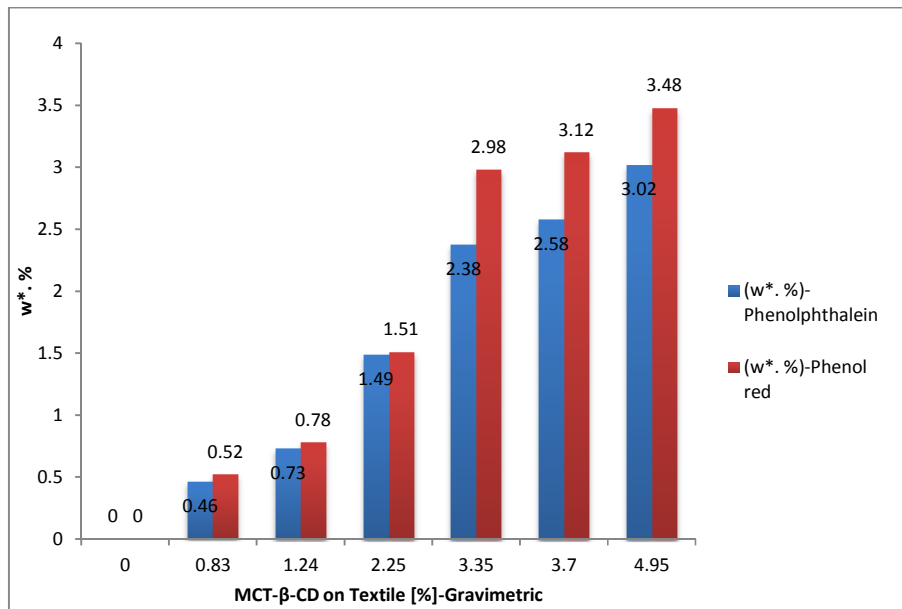


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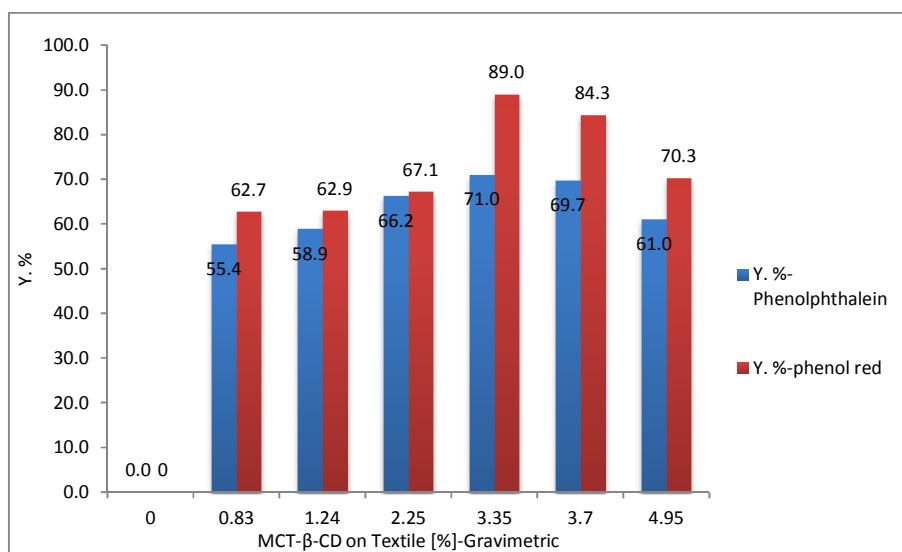


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