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Novel approach for improving disperse dyeing and UV-protective function of cotton-containing fabrics using MCT-β-CD

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ABSTRACT

The main goal of this work was to increase disperse dye substantivity for cotton cellulose containing fabrics via modification with monochlorotriazine-β-CD (MCT-β-CD), which posses hydrophobic cavities along with remarkable capability to form inclusion complexes with organic substances through host–guest interactions. The proper conditions for simultaneous alkaline-disperse dyeing as well as grafting of MCT-β-CD onto and/or within cotton and cotton/PET (50/50) blend fabrics were presented. As a result of this novel approach, the obtained dyeings showed a remarkable improvement in their depth of shades along with a significant enhancement in their UV-protection properties. The extent of improvement in disperse dyeing and in subsequent UV-protecting is determined by the nature of substrate, extent of modification, type and concentration of PEG and disperse dye as well as the union-bath conditions, i.e. temperature, time and pH. Mode of interactions, SEM of untreated and grafted C/PET fabric, as well as fastness properties of the obtained dyeings were also investigated.

1. Introduction

Blending of cotton and polyester, the major textile fibers, results in a significant improvement in the physico-mechanical properties of the obtained textile materials taking in consideration both the economical and aesthetics aspects (Ibrahim, Awad, Fahmy, & El-Badawy, 2005a) Polyester/cotton blends are dyed batchwise with disperse/reactive dyes using several sequences. Nonionic disperse dyes have little substantivity for cellulosic fibers. Increasing the hydrophobicity character of cotton cellulose or grafting of cyclodextrin (CD) derivatives onto cotton fibers with their hosting hydrophobic cavities that can form inclusion complexes with other molecules such as disperse dyes, gives a natural fiber that is more readily dyeable with disperse dyes (Lewis, 1998). On the other, many studies have been tackled alkaline-disperse dyeing of polyester and polyester/cellulosic blends using Dianix® disperse dyestuffs (DyStar) (Ern & Anis, 2005; Ibrahim, Youssef, Helal, & Shaaban, 2003; Imafuku, 1993).

Additionally, there is a growing demands in the market place for apparel textiles that offers comfort and UV-protection from the harmful effects of the UV-B radiation, (320–280 nm), i.e. skin cancer (Curiskis & Pailthorpe, 1996). The protective abilities of textiles depend on fiber composition, fabric construction as well as wet processing history of the fabric such as dyeing, printing and/or chemical finishing using different colorants and textile auxiliaries which possess their own significant absorption in the UV-region thereby upgrading the UV-protection factor (UPF) of textiles. The higher the UPF, the better the protection is from UV-B radiation (El-Tahlawy, El-Nagar, & El-Hendawy, 2007; Gorensek & Sluga, 2004; Ibrahim & El-Zairy, 2009; Ibrahim, Refai, Youssef, & Ahmed, 2005b; Sarkar, 2004; Savarino, Viscardi, Quagliotto, Montoneri, & Barni, 1999).

This innovative study examines the technical feasibility of combined grafting of monochlorotriazine-β-cyclodextrin (MCT-β-CD) and alkaline dyeing of cotton and cotton/polyester blend fabrics in one step as well as to search for the proper treatment conditions for attaining union-disperse dyeings with remarkable UV-protection properties. In addition, the proposed reaction mechanism among the substrate, MCT-β-CD and alkaline-disperse dye was given.

2. Experimental

2.1. Materials

Mill-scoured and bleached cotton (130 g/m^3) and cotton/polyester blend (50/50, 235 g/m^3) woven fabrics were used throughout this work.

An alkali-stable disperse dyes used in this study were Dianix® Scarlet AD-RG, Dianix® Blue S-BG and Dianix® Rubbin S-3B (DyStar, Egypt).

Cavasol® W7MC monochlorotriazine-β-cyclodextrin MCT-β-CD, [Fig. 1, average molecular weight ≈1560, degree of substitution

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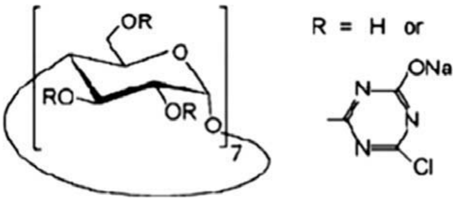


Fig. 1. Chemical structure of MCT-β-CD.

0.3–0.6 per anhydroglucose unit, Wacker, Germany], Hostapal® CV-ET [a nonionic wetting agent based on alkyl aryl poly (glycol ether)-Clariant], as well as Diaserver® AD-95 (Stabilizing, sequestering, buffering and dissolving olgimers agent, DyStar) and Eganal® PSN (linear polycondensate, leveling and dispersing agent, Clariant) were of technical grade. Polyethylene glycol's (PEG-200, PEG-600 and PEG-1000) as well as other chemicals were of laboratory grade.

2.2. Methods

2.2.1. Simultaneous dyeing and chemical modifying of the used substrates

Woven fabric samples were alkaline-disperse dyeing in the absence and presence of MCT-β-CD (0–30 g/L) along with other additives at 100 °C for 60 min according to dyeing profile (Fig. 2) and reported methods (Ern & Anis, 2005; Imafuku, 1993). Typical formulations as well as treatment conditions are given in the text.

2.2.2. Testing

Nitrogen content was determined according to the Kjeldahl method. The color strength (K/S) of the obtained dyeings was measured at the wavelength of the maximum absorbance using an automatic spectrophotometer, and calculated by the Kubelka Munk equation (Duff & Sinclair, 1989). UV-protection factor (UPF) was determined according to the Australian/Newzeland Standard (AS/NZS 4399-1996) (Ibrahim & El-Zairy, 2009). A scanning electron microscope (SEM) examination was carried out by mounting the untreated and modified fabric samples on sub with double stick adhesive tape and coated with gold in a S150A sputter coater unit (Edwards, UK), the gold film thickness was 150°A, then viewed in a JEAOL JXA-840 A electron probe microanalysis. Fastness properties to washing, rubbing and light of the modified-disperse dyeings were evaluated according AATCC test methods: (61-1972), (8-1972), and (16 A-1972), respectively. All the determinations in this study were performed in triplicate and the results represent mean values with less than 0.2% of error.

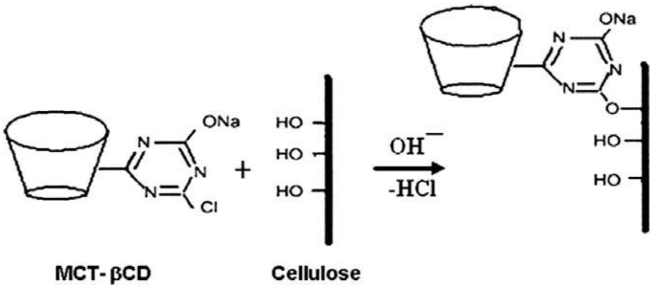
3. Results and discussion

Since the main tasks of the present work were (i) to enhance the affinity of cotton cellulose to disperse dyes via grafting of MCT-β-CD, with its hydrophobic cavities, onto/within its structure, (ii) to study the technical feasibility of union-disperse dyeing of polyester/cotton blend under alkaline conditions, as well as (iii) to evaluate the positive impact of the used reactive β-CD on upgrading both the dyeing and UV-protection properties of the obtained disperse dyeings, a wide range of treatment conditions were examined. Results obtained along with appropriate discussion follow.

3.1. Tentative mechanism

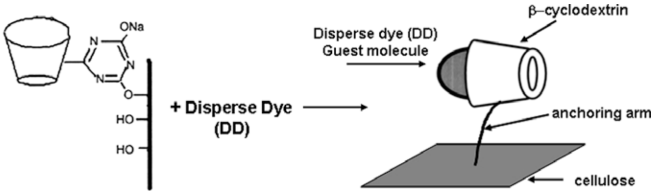
Presence of MCT-β-CD, as a reactive polysaccharide, alkali-stable disperse dye (DD) along with cotton cellulose or cotton/polyester blend as a textile substrate, under alkaline-disperse dyeing conditions would be expected to promote several reactions, the most dominant of which are:

(i) Grafting of β-CD onto/within the cotton cellulose (Ibrahim & El-Zairy, 2009; Ibrahim et al., 2003; Wang & Cai, 2008)



(1)

(ii) Formation of inclusion complexes (Savarino et al., 1999)



(2)

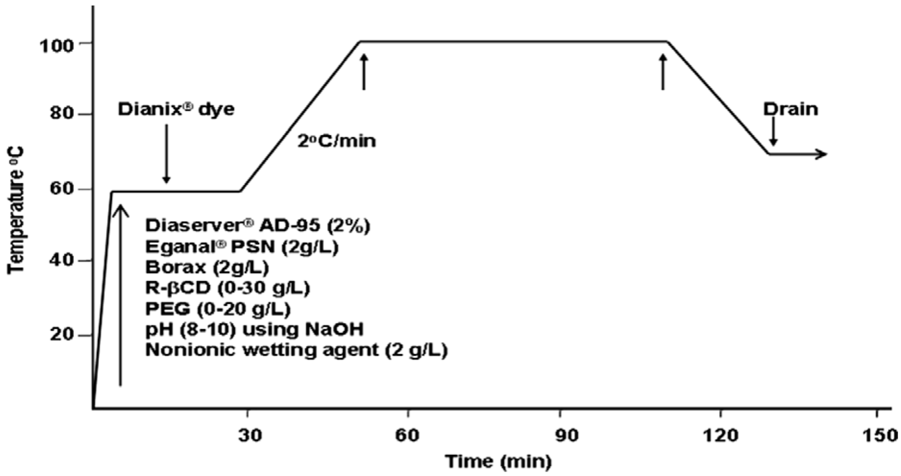
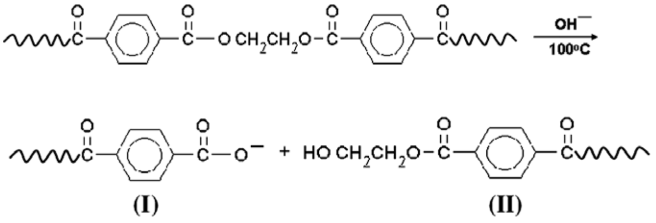


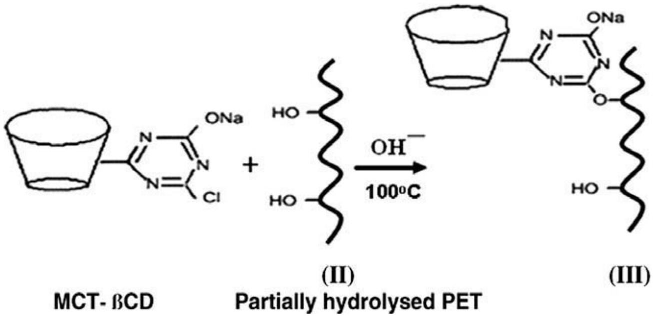
Fig. 2. Disperse dying and chemical modifying cycle used in the present study.

(iii) Partial alkali-hydrolysis of PET (Ibrahim, 1990; Montazer & Sudighi, 2005)



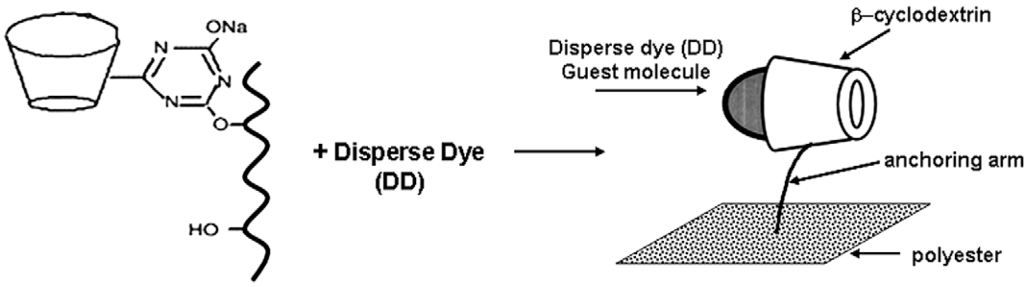
(3)

(iv) Anchoring of β-CD film onto the fabric surface



(4)

(v) Fixation of disperse dye (DD) onto the modified PET-structure



(5)

(vi) Disperse-dye/MCT-β-CD side interaction

$$\text{MCT- }\beta\text{CD} + \text{DD} \rightleftharpoons \text{MCT- }\beta\text{CD - DD} \tag{6}$$

(vii) Deposition of β-CD film onto the fabric surface

$$\text{n MCT-ßCD} \xrightarrow[100^{\circ}\text{C}]{\text{OH}^{-}} \text{Self condensate by products} \tag{7}$$

(viii) Partial deactivation of MCT-β-CD

$$\text{MCT- }\beta\text{CD} + \text{H}_2\text{O} \xrightarrow[100^{\circ}\text{C}]{\text{OH}^{-}} \text{HO-T- }\beta\text{CD} + \text{HCl} \tag{8}$$

3.2. MCT-β-CD concentration

The effect of MCT-β-CD concentration on nitrogen content (%N-Fig. 3a), dye uptake (K/S – Fig. 3b) as well as UV-protection properties (UPF – Fig. 3c) was investigated. For a given set of the "all-in" exhaustion method conditions, it is evident that: (i) increasing MCT-β-CD concentration up to 20 g/L is accompanied by a remarkable increase in the %N, K/S as well as the UPF values of the treated substrates indicating a high levels of grafting and fixation of the reactive β-CD, with its hydrophobic cavities, onto and/or into the treated substrates thereby increasing the %N as well as providing more accommodation sites into which disperse dye molecules can be trapped. i.e. higher K/S, (Eqs. (1)–(5)) with subsequent upgrading of the UV-absorption and/or blocking capacities of the treated substrates, i.e. darker the shade depth, greater is the UV-protection degree afforded by the dye substrate (Gorensek & Sluga, 2004; Ibrahim, Allam, El-Hossamy, & El-Zairy, 2007; Ibrahim & El-Zairy, 2009), (ii) further increase in the MCT-β-CD concentration, i.e. beyond 20 g/L, has practically a slight or no positive effect on the above mentioned properties most probably due to: a shortage in accessible —OH groups of cotton cellulose for covalent bonding, side interactions of disperse dye (DD) molecules with the abundant MCT-β-CD molecules thereby leading to formation of washable inclusion complexes (Eq. (6)) and/or formation of easily removable β-CD deposits adsorbed to the fabric surface (Eq. (7)), thereby hindering the extent of penetration and diffusion of the reactants within the fabric structure, rather than covalently anchored (Xia & Lin, 2004), and (iii) the extent of improvement in the aforementioned properties is determined by the nature of substrate i.e. C/PET>C, and can be attributed to their differences in: chemical structure, extent of modification, affinity to the used disperse dyes as well as the UV-absorption capacity of the untreated substrates (Algaba, Riva, & Crews, 2004; Ibrahim et al., 2005b).

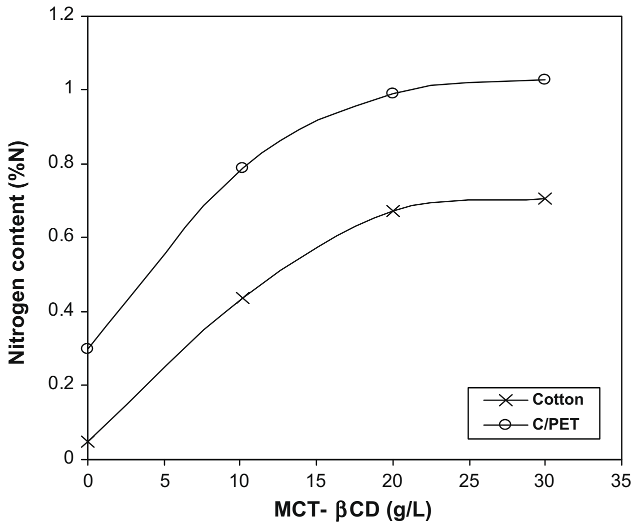


Fig. 3a. Dependence of %N on the concentration of MCT-β-CD. Treatment condition: Dianix® Scarlet (5% owf); MCT-β-CD (0–30 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

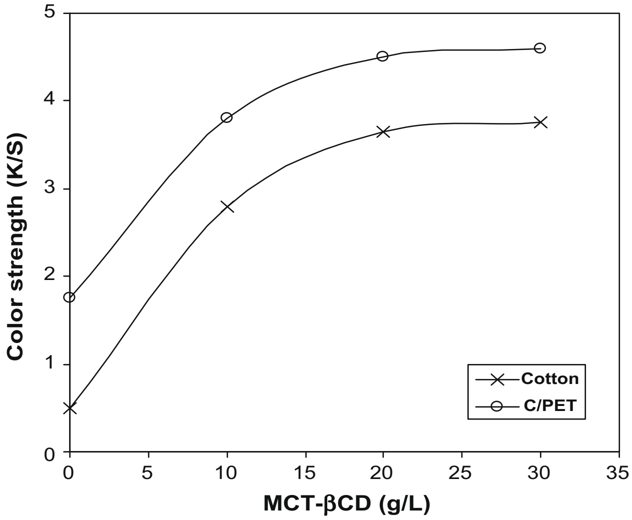


Fig. 3b. Dependence of K/S on the MCT-β-CD concentration. Treatment condition: Dianix® Scarlet (5% owf); MCT-β-CD (0–30 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

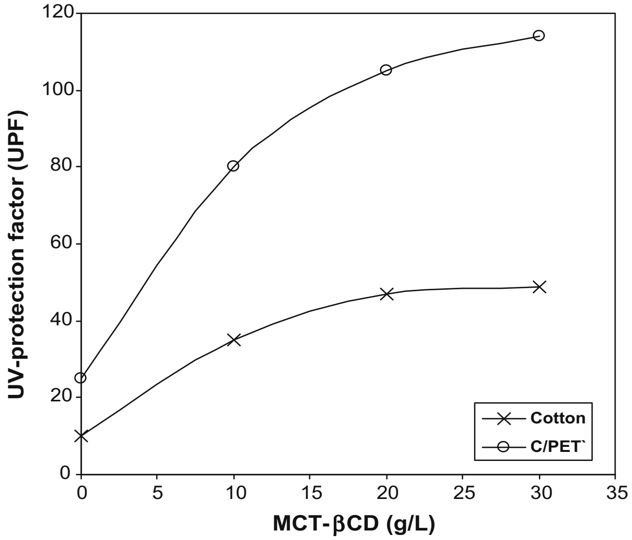
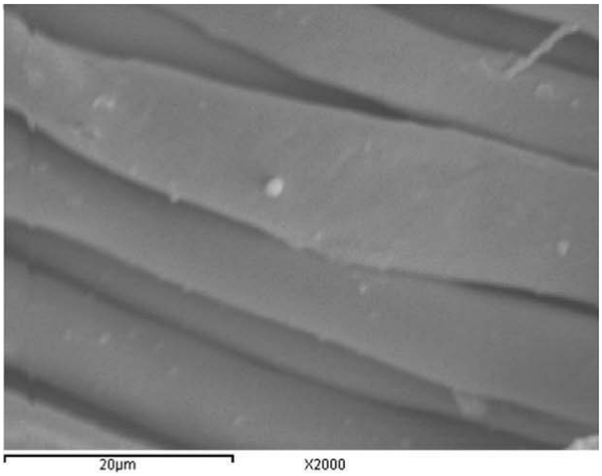


Fig. 3c. Dependence of UPF on the MCT-β-CD concentration. Treatment condition: Dianix® Scarlet (5% owf); MCT-β-CD (0–30 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

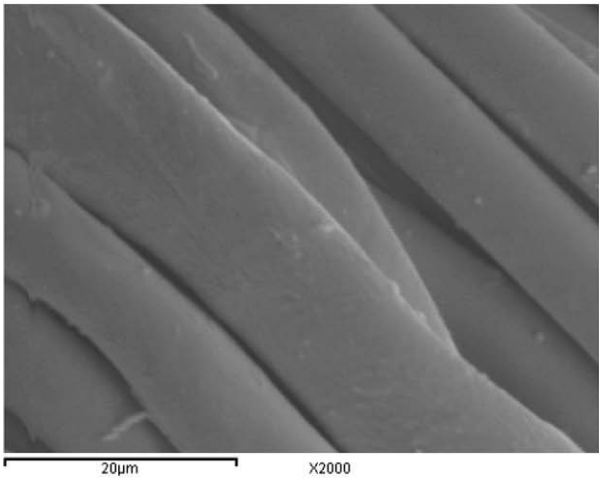
The SEM images of untreated and treated fabric samples were presented in (Fig. 4) The SEM image of the treated sample show a formation of a thin layer of β-cyclodextrin on the fiber surface.

3.3. The union-bath pH

The variation in the %N, K/S and UPF values of the obtained disperse dyeings as a function of pH, is shown in Fig. 5a, 5b and 5c, respectively. As can be seen from the values in these figures, the %N, K/S as well as UPF values, improved by raising the pH of the union-bath from 8 to 9. These results can be discussed in terms of: enhancing the extent of interaction and fixation of the MCT-β-CD onto and/or within the treated substrates, and improving the extent of picking up and forming inclusion complexes with the used disperse dye molecules under proper alkaline dyeing conditions i.e. pH 9, thereby getting darker shade along with affording better degree of UV-protection and consequently providing higher UPF values regardless of the used substrate.



Untreated C/PET



Treated C/PET

Fig. 4. SEM of untreated and treated cotton/polyester fabric samples.

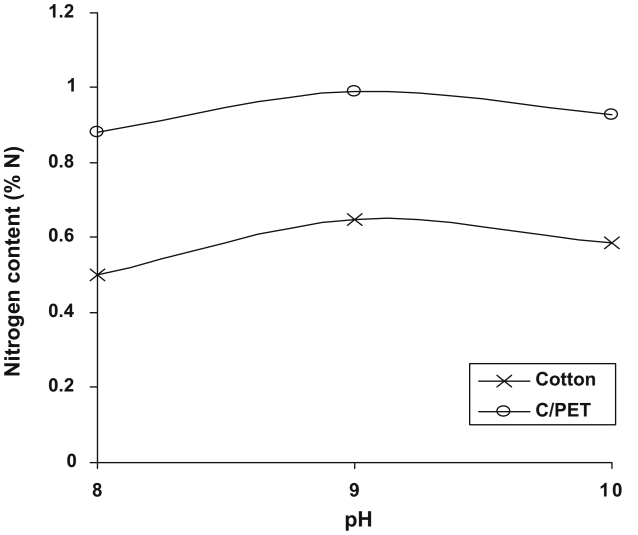


Fig. 5a. Dependence of the nitrogen content on the pH of the "all-in" exhaustion bath. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); pH (8–10); LR (1/25); at 100 °C for 60 min.

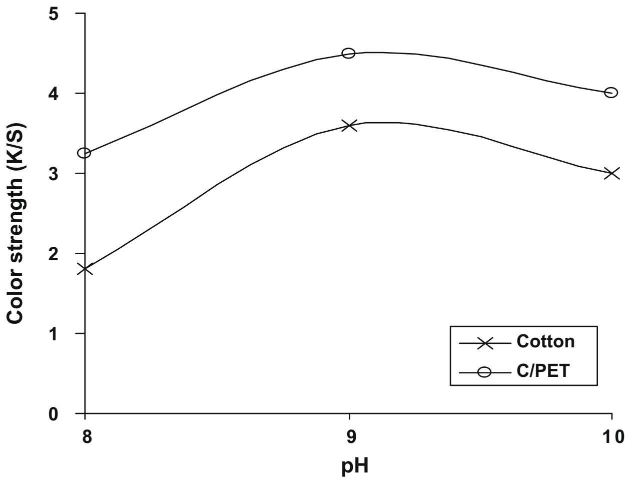


Fig. 5b. Dependence of K/S on the pH of the all-in exhaustion bath. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); pH (8–10); LR (1/25); at 100 °C for 60 min.

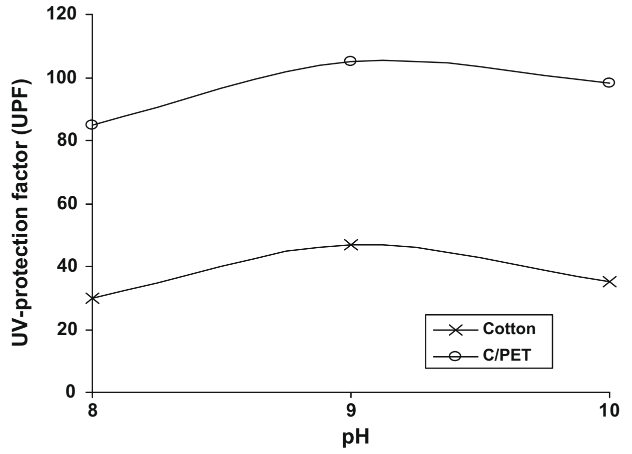


Fig. 5c. Dependence of the UPF on the pH of the all-in exhaustion bath. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); pH (8–10); LR (1/25); at 100 °C for 60 min.

On the other hand, further increase in the union-bath pH up to 10 results in a slight decrease in the aforementioned properties, irrespective of the used substrate, which can be explained in terms of lower stability of the used disperse dye dispersion at a higher pH, i.e. pH 10, and/or partial deactivation of the MCT-β-CD via partial hydrolysis of the active chlorine atoms in the triazine ring (Eq. (8)) thereby resulting in a lower extent of modification, i.e. lower %N as well as lesser hydrophobic cavities, along with subsequent lower dye retention and fixation, i.e. lighter depth of shade with lower degree of UV-protection. Once again the extent of changes in these properties is determined by the type of substrate as discussed before.

3.4. PEG-200 concentration

As far as the changes in %N (Fig. 6a), K/S (Fig. 6b) and UPF (Fig. 6c) values as a function of PEG-200 concentration, the obtained results disclose that: (i) incorporation of PEG-200 into the “all-in” bath up to 10 g/L, is accompanied by a slight increase in the %N along with a remarkable improvement in the K/S of the obtained dyeings, (ii) the enhancement in both %N and K/S reflects

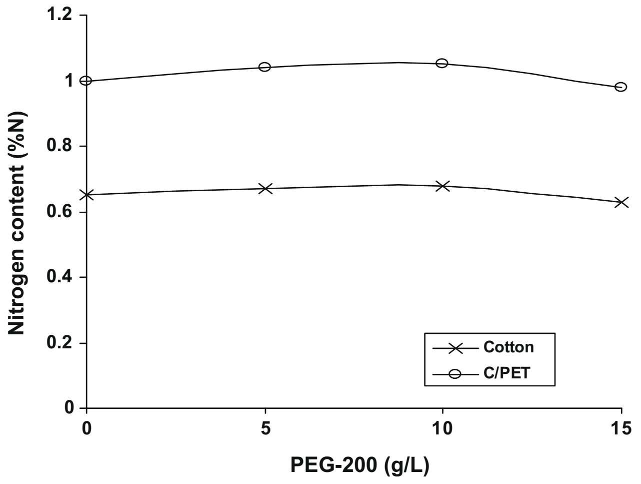


Fig. 6a. Dependence of the nitrogen content on the concentration of the added PEG-200. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG-200 (0–15); pH (9); LR (1/25); at 100 °C for 60 min.

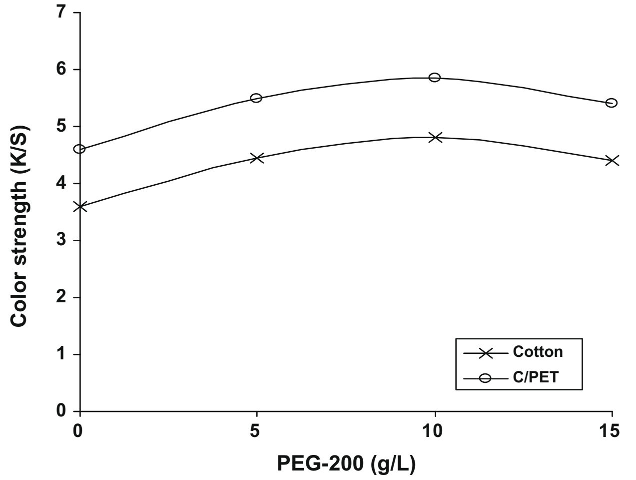


Fig. 6b. Dependence of K/S on the concentration of the added PEG-200. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG-200 (0–15); pH (9); LR (1/25); at 100 °C for 60 min.

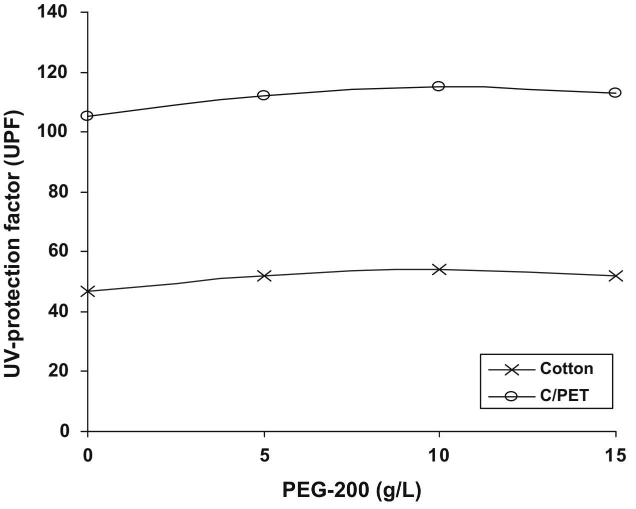


Fig. 6c. Dependence of the UPF on the concentration of the added PEG-200. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG-200 (0–15); pH (9); LR (1/25); at 100 °C for 60 min.

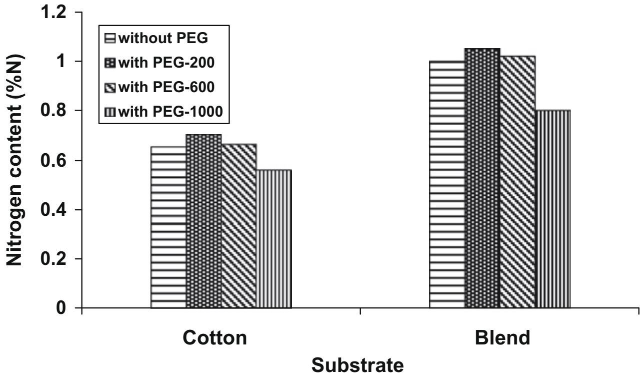


Fig. 7a. The N% of treated cotton and blend fabrics as a function of PEG-molecular weight. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG (10 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

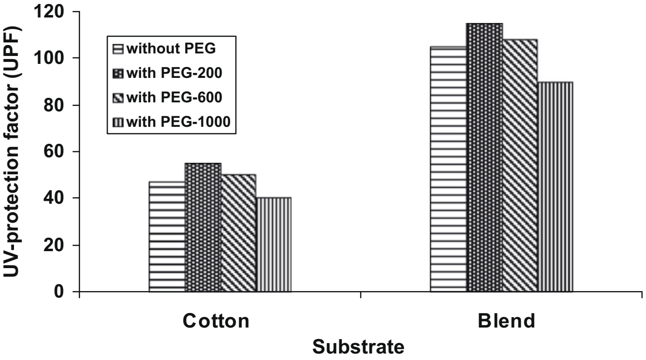


Fig. 7c. The UPF value of treated cotton and blend fabrics as a function of PEG-molecular weight. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG (10 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

the positive impact of PEG-200 on enhancing the swellability of the treated substrates as well as solubility of the reactants thereby opening the cellulose structure, enhancing the extent of penetration and diffusion of both the MCT-β-CD and disperse dye molecules, and this in turn improves extent of modification, i.e. more accessible hydrophobic cavities, as well as the extent of fixation and inclusion of the disperse dye molecules, i.e. higher K/S values, regardless of the used substrates, (iii) the deep dyed fabric samples show higher UPF values (UPF 115 and UPF 54 for C/PET and cotton dyeings, respectively), and (iv) further increase in PEG-200 concentration has practically a slight negative effect on the aforementioned properties most probably due to a side interaction between the terminal —OH groups of the PEG and the MCT-β-CD in alkaline medium (Eq. (9)) thereby minimizing the extent of fixation of MCT-β-CD onto/within the treated substrates, i.e. lower %N, K/S and UPF values (Ibrahim & El-Zairy, 2009).

$$\text{PEG}\sim\sim\text{OH} + \text{MCT-}\beta\text{CD} \xrightarrow{\text{OH}^-} \text{soluble/removal adducts} \tag{9}$$

3.5. PEG-molecular weight

The influence of PEG-molecular weight on the %N, K/S as well as UPF values of the treated fabric samples are shown in Fig. 7a, 7b and 7c, respectively. For a given set of treatment conditions, it is clear that: (i) the higher the PEG-molecular weight, the lower the %N, K/S and UPF values of the treated fabric samples, regardless of the used substrate, (ii) the decrease in the aforementioned properties reflects the negative impacts of higher molecular weight on increasing the viscosity of the union-bath, enhancing the side interactions among reactants, retarding the extent of penetration and diffusion of the reactants within the cotton cellulose structure along with minimizing the building up of MCT-β-CD onto the PET component thereby decreasing the extent of grafting of MCT-β-CD, reducing the number of inner hydrophobic cavities, as well as hindering the extent of sublimation, diffusion and retention of the disperse dye, i.e. lower %N, K/S and UPF values.

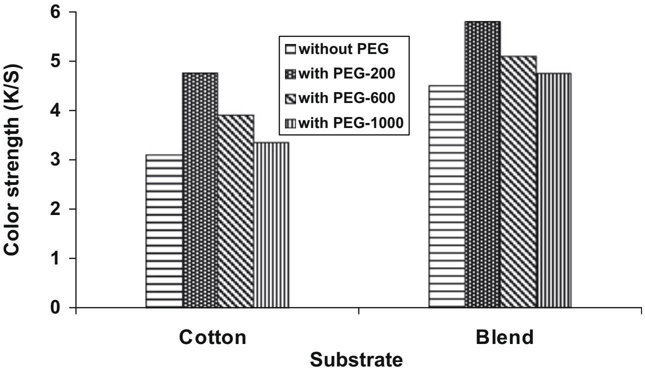


Fig. 7b. The K/S value of treated cotton and blend fabrics as a function of PEG-molecular weight. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG (10 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

3.6. Dye concentration

In Fig. 8a, 8b and 8c, it is observed that increasing the dye concentration up to 5% owf brings about a remarkable improvement in the %N, K/S as well as the UV-protective properties of the obtained dyeings. On one hand, this feature could be discussed in terms of the higher availability and accessibility of the sublimable and diffusible disperse dye into/onto the accessible/immobilized hydrophobic cavities of grafted-reactive β-CD, thereby increasing the extent of the dye fixation, i.e. higher %N and greater K/S values, along with upgrading the ability of dark shaded fabric samples to provide a remarkable protection capacity against the harmful UV-B radiation, i.e. outstanding UPF values, irrespective of the used substrate. On the other hand presence of PET component in the

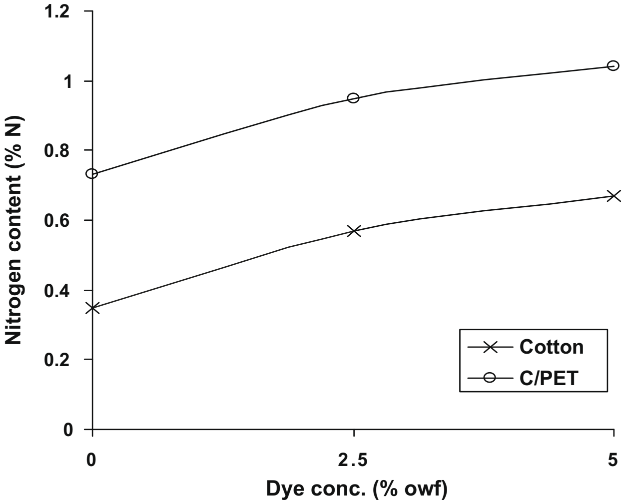


Fig. 8a. The %N treated samples as a function of dye concentration. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (0–5% owf); PEG-200 (10 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

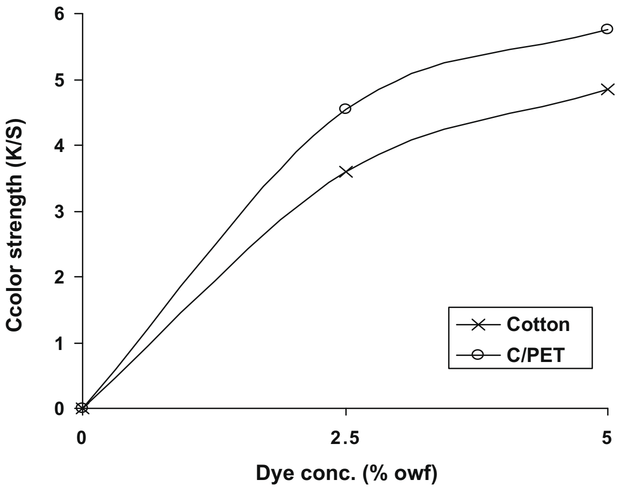


Fig. 8b. The K/S value of treated samples as a function of dye concentration. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (0–5% owf); PEG-200 (10 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

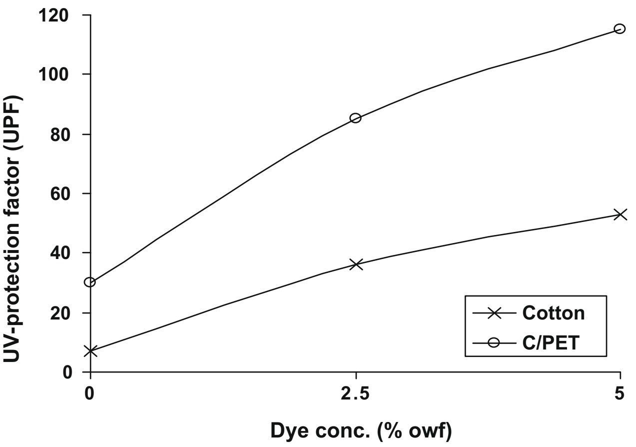


Fig. 8c. The UPF value of treated samples as a function of dye concentration. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (0–5% owf); PEG-200 (10 g/L); pH (9); LR (1/25); at 100 °C for 60 min.

C/PET blend gives rise to dyeings with higher extent of dyeing as well as better UV-protecting properties compared to the cotton dyeings (Algaba et al., 2004; Ibrahim & El-Zairy, 2009).

3.7. Union-bath temperature

Fig. 9a, 9b and 9c show the effect of the exhaustion bath temperature on the extent of grafting of the MCT-β-CD, expressed as %N, extent of disperse dyeing, expressed as K/S, as well as extent of UV-protecting, expressed as UPF, respectively. As is evident, raising the temperature up to 100 °C for 1 h brings about a remarkable increase in the aforementioned properties. Nevertheless, the extent of improvement is governed by the nature of the substrate, i.e. cotton/polyester > cotton.

The remarkable improvement in the aforementioned properties is a direct consequence of (Ibrahim et al., 2003): (i) enhancing the solubility and mobility of the reactants, (ii) improving the swellability and opening up the fabric structure and (iii) overcoming the activation energy barrier of grafting/disperse-dyeing process. The net effect is facilitating diffusion and penetration of the reactants, along with speeding up and improving the extent of grafting/disperse-dye uptaking, which in turn upgrades the UV-protection capacity of the obtained disperse dyeings.

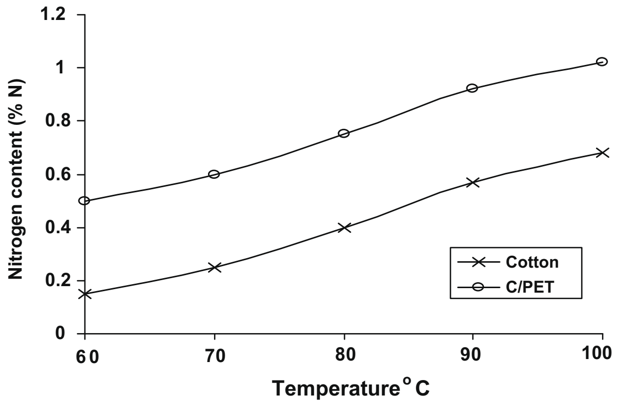


Fig. 9a. The %N of treated fabric samples versus union-bath temperature. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG-200 (10 g/L); pH (9); LR (1/25); time 60 min.

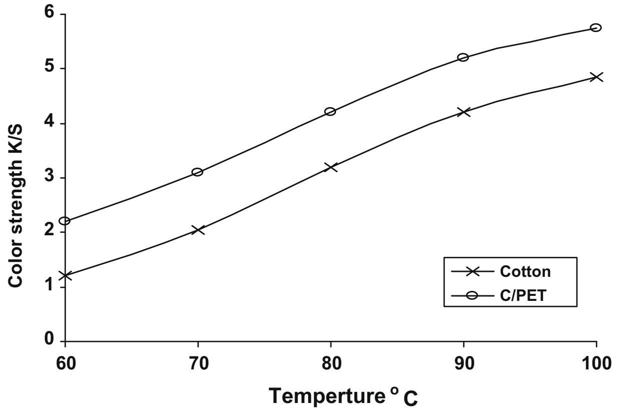


Fig. 9b. The K/S value of treated fabric samples versus union-bath temperature. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG-200 (10 g/L); pH (9); LR (1/25); time 60 min.

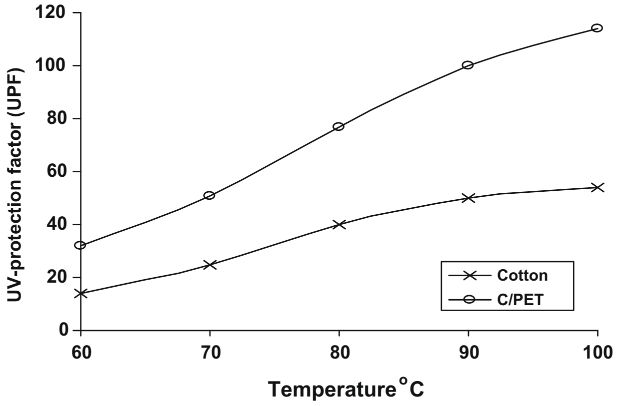


Fig. 9c. The UPF value of treated fabric samples versus union-bath temperature. Treatment condition: MCT-β-CD (20 g/L); Dianix® Scarlet (5% owf); PEG-200 (10 g/L); pH (9); LR (1/25); time 60 min.

3.8. Type of disperse dye

As far as the change in the %N, K/S, UPF as well as fastness properties of the grafted/dyed samples as a function of the type of the disperse dye, the data in Table 1 reveal that: (i) incorporation of the

Table 1
Performance properties of the obtained dyeings using different alkali-stable disperse dyes.

Disperse dye	Substrate	%N	K/S	UPF	WF		RF		LF
					Alt	C	Dry	Wet	
Dianix® Blue S-BG	Cotton	0.535	3.08	44	4–5	4–5	4	4	6
	C/PET	1.038	3.94	80	5	5	5	4–5	6
Dianix® Rubbine S-3B	Cotton	0.511	1.93	52	4–5	4–5	4	3–4	6
	C/PET	1.022	2.77	130	5	5	4–5	4	6
Dianix® Scarlet AD-RG	Cotton	0.682	4.82	54	4–5	4–5	4	4	6
	C/PET	1.030	5.75	115	5	5	5	4–5	6
None	Cotton	0.352	–	7	–	–	–	–	–
	C/PET	0.740	–	30	–	–	–	–	–

Treatments conditions: MCT-β-CD (20 g/L); disperse dye (5% owf); PEG-200 (10 g/L); pH (9); LR(1:20); at 100 °C for 60 min WF: washing fastness, RF: rubbing fastness, LF: light fastness.

alkaline-stable disperse dye in the exhaustion bath with other additives, i.e. MCT-β-CD (20 g/L) and PEG-200 (10 g/L) at pH (9) and temperature 100 °C for 60 min, results in a significant improvement in the nitrogen content as well as a dramatic increase in the UPF values of the obtained dyeings, (ii) the K/S values as well as the fastness properties of the dyed fabric samples are governed by the type of the disperse dye (Gorensek & Sluga, 2004; Ibrahim & El-Zairy, 2009; Ibrahim et al., 2003; Veatch & Gatewood, 2002), i.e. molecular structure, chemical composition, chromophores, location and aggregation of the dye, extent and mode of fixation and retention within and/or onto the grafted fabric samples, via physical and/or formation of inclusion complexes within the grafted β-CD cavities, and (iii) type of disperse dye as well as nature of substrate has practically a significant impact on the performance properties of the obtained dyeings except the light fastness.

4. Conclusions

The results reported in this study demonstrate the technical feasibility of combined alkaline-disperse dyeing and anchoring of MCT-β-CD to cotton-containing fabrics in one step. Fixation of MCT-β-CD, with its hydrophobic cavities, onto and/or within the used substrates under alkaline dyeing conditions results in a significant increase in the dye uptake, expressed as color strength, via formation of an inclusion complexes with disperse dye molecules, through host–guest interactions, thereby enhancing the extent of interaction and fixation, i.e. deeper depth of shades. Deep dyed cotton and cotton/polyester blend fabrics show excellent UV-protection from harmful UV-B radiation. The nature of substrate, the extent of grafting of MCT-β-CD, the type of disperse dye as well as the conditions of the "all-in" bath play an important role in determining the extent of disperse dyeing as well as subsequent improvement in UV-blocking.

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