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Modification of cellulosic fibers to enhance their dyeability using UV-irradiation

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ABSTRACT

Present research was proposed to evaluate the effect of UV radiation on the dyeing of cellulosic fabrics with direct dyes. The cellulosic fabric was irradiated by using UV radiation assembly (180 W) for different time intervals i.e., 30, 45, 60, 75 and 90 min respectively. The alike set of fabrics was prepared varying the concentration of NaOH during mercerization of the fabrics. All the treated fabrics were dyed with direct dyes. The dyeing parameters such as temperature, time, pH and salt concentration were optimized. The standard methods were employed to evaluate the color strength at various levels of pH, temperature, dyeing contact time and salt concentration. Scanning electron microscope test was performed in order to evaluate the change in fibril structure and surface. The obtained results of the dyed fabrics previously treated with UV radiation and after mercerization were compared. The results revealed that the color strength of UV-irradiated fabric was high as compared to mercerized cellulosic fabrics.

1. Introduction

The grey cloth contains impurities so one or more pretreatment processes are applied to attain its full textile prospective. The pretreatment processes of cotton yarns include scouring to get rid of non cellulosic impurities, pigments and waxes. The mercerization is used to give increased luster, smoothness, increased dye and finishing chemical uptake, dimensional constancy and better mechanical properties, oxidative bleaching to wipe out natural coloring matter for white or dyeing, and singing to eliminate the protruding loose fibers (Perkin, 1996). Non-cellulosic impurities are conventionally removed by treating fabric with alkali solution for 1 to 2 h at boiling temperature in the presence of chelating agent. Fats and waxes are saponified or emulsified by using this process. The process also dissolves hemi-cellulose, solubilizes proteins into sodium salts of different amino acids and changes pectin into soluble sodium pectate (Buschle-Diller, El Mogahzy, Inglesby, & Zeronian, 1998). Scoured cotton has almost completely removed cuticle and non-cellulosic components and enhanced the wet-ability of the fabrics (Jordanov & Mangovska, 2009).

Mercerization is treatment of fabric with 15–20% solution of NaOH. After alkali treatment, fabrics are rinsed many times with hot and cold water. In order to gain good results, the cotton fabrics are properly neutralized and washed after mercerization (Gemci, 2010). After mercerization, native cellulose I, which is the major polymorphic form of cellulose in composites, is modified to cellulose II crystal packing. Mercerized (cellulose II) composites exhibited better mechanical properties than the un-mercerized composites that have cellulose I. The significant increase in mechanical properties of mercerized composites is more amazing in light of transition from cellulose I to cellulose II as cellulose II usually displays a lower chain modulus. This is due to two different conformations of the hydroxymethyl group that causes variations in intra-molecular hydrogen bonding (Northolt et al., 2001).

Direct or substantive dyeing is normally carried out in a neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride or sodium sulfate. Direct dyes are used on cotton, leather, paper, silk, wool and nylon. They are also used as pH indicators and biological stains. These dyes are soluble anionic dyes that consist of an aromatic structure containing a chromogen and solubilizing groups. These are called direct dyes as they have direct affinity for cotton. They do not require pretreatment with a mordant to be used for cotton (Micheal & El-Zaher, 2005; Mokhtari, Duncan, Phillips, & Taylor, 2005). Irradiated fabrics dyed in heat solubilized aqueous extract gave more color strength as compared to non irradiated fabrics due to oxidative degradation of cellulose fibers. The treatment of fabric by high-energy radiation causes degradation and fragmentation (Földváry, Takács, & Wojnárovits, 2003; Takács et al., 2000).

The modification of cellulosic fabrics has been reported in the literature by using polyurethane acrylates copolymers (Sultan, Bhatti, Zuber, Bhatti, & Sheikh, 2011; Sultan et al., 2012) and by using polyvinyl alcohol (Zia, Zuber, Rizwan, Jamil, & Shahid, 2012; Zuber,

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Zia, Bhatti, Rizwan, & Jamil, 2012). Regarding textile applications of the material few reports on amino silicone based softener are also available (Zia et al., 2011; Zuber et al., 2011). Evidence for phytotoxic effects of cellulose acetate in UV exclusion studies have been clearly established (Krizek & Mirecki, 2004). The physical properties of the crosslinked cellulose catalyzed with nanotitanium dioxide under UV irradiation and electronic field have been presented elsewhere (Wang & Chen, 2005). The effect of additives on the enhancement of methyl methacrylate grafting to cellulose in the presence of UV and ionizing radiation has also been reported (Viengkhou, Ng, & Garnett, 1997). Some reports are also available on the pre-treatment of cotton to enhance the dyeability of sulfur dyes (Burkinshaw & Gotsopoulos, 1996). Efforts have been dedicated to the combination of polyurethanes with acrylic polymers to increase the performance-to-cost of coatings of the textile materials (Wang, Hu, & Tu, 2008). No such report is available presenting the cellulose fiber modification by UV radiation treatment and hence to improve the dyeability of the cellulosic fibers using direct dyes. Considering higher effect of UV radiation to modify and swell the cellulosic fibers the present project is designed to compare the color strength of dyed fabrics with direct dyes after UV irradiation and industrially mercerized fabrics without irradiation.

2. Experimental

2.1. Materials

2.1.1. Chemicals

All of the reagents used in this study were of analytical grade which include: sodium carbonate, sodium hydroxide, sodium chloride, hydrochloric acid, hydrogen peroxide, ammonium hydroxide, potassium iodide, iodine, distilled water, Direct Congo Red (Direct Red 28), and plain weave grey cellulosic fabrics (cotton).

2.1.2. Plain weave cotton fabric—a substrate

Mill un-desized, unscoured, non bleached, unprocessed, cellulosic fabrics (100% cotton); plain weave was supplied by Sadaqat Textiles Mills Ltd, Khurrianwala, Faisalabad, Pakistan. The characteristics i.e., quality of the fabric, construction, count, blend ratio, etc., are presented in Table 1. Before the application of the direct dyes the fabrics were either treated by UV radiation or mercerized following the traditional industrial mercerization process.

2.1.3. Desizing and bleaching of cellulosic fabrics

The grey cellulosic fabric samples were chemically desized using 1% HCl solution for 15 min at boiling temperature. Desizing was done in order to remove starch, polyvinyl alcohol, etc. from the surface of cotton. Desized cellulosic fabric samples were then subjected to bleaching. The process was done by treating cotton fabrics with hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH).

2.1.4. UV exposure of cellulosic fabric

Irradiation of desized bleached cellulosic fabrics was carried out in an UV exposure unit in which irradiation chamber uses 180 W (ten lamps 18 W each) medium pressure mercury vapor lamps constructed with borosilicate glass envelopes which filter all wavelengths below 300 nm. As such, the spectral distribution of the light is good match for terrestrial solar radiation. Irradiation was performed with sample to lamp distance of 20 cm at ambient relative humidity. Cellulosic fabric samples were irradiated for the time of 30, 45, 60, 75 and 90 min at ambient temperature.

2.1.5. Mercerization of cellulosic fabric

Mercerization is a process in which the desized bleached cellulosic fabrics are treated with aqueous solution of NaOH (i.e., 16%). The desized bleached cellulosic fabric samples were dipped into the above solution for 10 min. This process swells the cellulosic fabrics which results in increasing the dye uptake. The same procedure was employed for various concentrations of NaOH i.e., 18, 20, 22, and 24%.

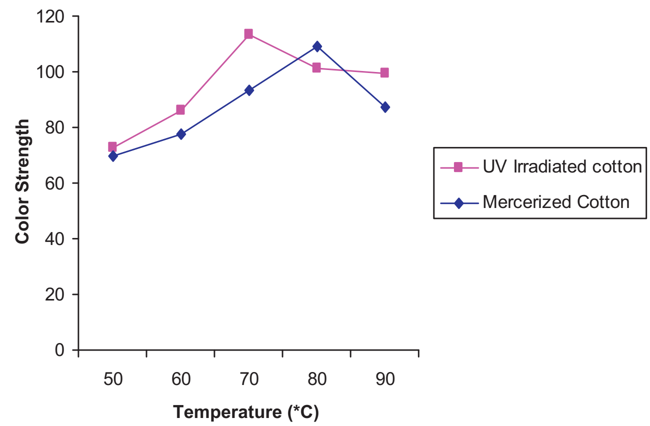

Fig. 1. Color strength versus temperature (°C) curves of UV irradiated and mercerized cotton fabrics.

2.1.6. Application of Direct Congo Red (direct dye)

Before dyeing, the fabric was further cleaned in the laboratory by washing at 100 °C for 60 min using a solution containing 2 g/L Na_2CO_3, 1 g/L polyoxyethylene glycol octylphenol ether: C_8H_{17}-(C_6H_4)-(O-C_2H_4)$_{1–25}$-OH (Triton X-100), a non-ionic surfactant (BASF). The fabric was then washed several times with hot water then rinsed with cold water and finally dried at ambient conditions. Different dyeing methods for applying direct dyes to cellulose have been established. During this research, the direct dye was applied by exhaustion method due to its wide usage in the textile industry. In practice the dyeing procedure employed depends on the type of equipment, the fiber form and the exhaustion rate of the dyes chosen for dyeing. Optimization of different dyeing conditions such as temperature, salt, pH and dyeing time was done by varying conditions i.e., temperature, 50–90 °C; salt concentration, 2–10 g/100 mL; pH, 7–11; dyeing time, 30–70 min.

2.1.7. Surface morphology

Cellulose surface morphology was examined by Scanning electron microscopy (SEM) at 10 kV and 300× magnification, using a SEM-S2380 model (Hitachi, Japan).

3. Results and discussion

Cellulose fibers exhibit a highly polar surface due to the presence of hydroxyl groups. These hydroxyl groups enable the formation of hydrogen bonds in the interface of reinforced composite materials. But in order to get access to these hydroxyl groups, a cover of pectin and other waxy substances must be removed. Direct dye (Congo Red) was applied to the mercerized and UV treated cellulosic fabrics. In order to compare the suitability of the methods applied in the pretreatment process and to evaluate their application properties, the parameters and conditions for dyeing were optimized varying the salt concentration, pH, dyeing time and temperature accordingly (Mokhtari et al., 2005).

3.1. Effect of temperature on color strength

The data presented in Fig. 1 showed the comparison of color strength of mercerized and UV treated fabrics dyed at different temperatures. The results revealed that dye uptake is enhanced by increasing temperature up to a certain limit and then further

Table 1
Fabric specification with quality and processed applications.

S. no.	Quality	Construction/count	Blend ratio Cotton/polyester	Application
01	Plain weave cellulosic fabrics	(100 × 80/40 × 40)	100% cotton	Bleached, desized, mercerized or UV treated fabrics

increase in temperature reverts the effect of dye uptake. However, the UV irradiated fabric swatches showed better results than mercerized one. This phenomenon may be due to the effect that temperature plays an important role in dyeing as low temperature causes partial dyeing while very high temperature may cause degradation of dyes (Perkin, 1996). Hence, dyeing must be done at moderate temperature. The dyestuff is present in water as ionized single molecule and as clusters of molecules. These aggregates are strikingly large to enter the inner surface of fibers at room temperature. Breakdown of these aggregates is improved by raising the temperature, hence, the number of single molecules in solution increases. When fabric absorbed a single molecule, additional monomers are formed from the aggregates, which are taken up by the fabric resulting in complete dyeing (Mokhtari et al., 2005).

3.2. Effect of salt concentration on color strength

The results of effect of salt concentration on the color strength are presented in Fig. 2. It can be seen that color strength of the UV treated fabrics is maximum for the samples dyed in 4 g NaCl/100 mL of dye solution. The color strength of mercerized fabrics was higher at 6 g NaCl/100 mL of dye solution and is less as compared to the UV treated fabric even at 4 g NaCl/100 mL of dye solution. However, in both the cases, the higher addition of the salt results to decrease in the color strength considering both the pretreatment processes which are beyond the scientific approach and require a brief study. It is worth mentioning that the addition of inorganic salts to dyeing bath results to enhance in dyestuff affinity and accelerating the dyestuff association and lowering solubility. The sodium ion present in salt interacts with negative charge side of cotton fabric and neutralizes it. The fabric loses its proton of hydroxyl group and becomes negatively charged. As a result water becomes slightly more acidic. This produces a negative charged layer on fabric and then supports the uptake of colorant on cotton fiber from the dye bath. When sodium ion neutralizes the negative charge of fiber, it facilitates the approach of dye molecules to interact with the fiber within range of hydrogen bond already formed between the fiber and dye molecule. As a result maximum dye is attached to fiber (Perkin, 1996). The reduction in color strength when the concentration of salt is in excess amount could be due to pronounced aggregation of dye molecules in the bath, leading to reduced solubility (even partial precipitation) and prevention of the dye being adsorbed onto the cotton (Mokhtari et al., 2005).

3.3. Effect of pH on color strength

To optimize the dyeing conditions, the mercerized and UV treated cellulosic fabrics were also dyed at different pH values (Fig. 3). The results shows that there is remarkable increase in color strength at pH 8, however there is continuous decline in the results after this pH. The phenomenon can be best explained by reviewing the literature. Previous studies revealed that at higher pH values, the color strength values decrease because of alkaline degradation of colorant into fissionable products that get significant chance of sorption onto fabric instead of colorant. It has been previously reported in the literature that at higher pH, some of the hydroxyl groups on the hydroxymethyl side chains may also be ionized increasing the negative charge considerably (Carr, 1995). The negative charges on the surface of cellulose repel anionic dyes and hence the efficiency of dye fixation on cellulosic fibers is decreased. It is reported in the established literature that the surface of various fibers for textile and technical application may be characterized by their zeta potential. The maximal zeta potential of the fiber surface, which generally occurs in the alkaline range (at higher pH), indicates their hydrophilic or hydrophobic behavior (Bellmann, Caspari, Loan Doan, & Mäder, 2004).

3.4. Effect of time on color strength

The data presented in Fig. 4 revealed that the color strength increases with increase in the dyeing time up to a certain level. It can be seen that there is pronounced increase in the color strength if fabrics remain in the dyeing process up to 50 min. However there is a decrease in the color strength accordingly with increase in dyeing time. In comparison of the UV irradiated and mercerized cellulosic fabrics, the UV irradiated fabric swatches showed better results than mercerized one. It has been reported elsewhere

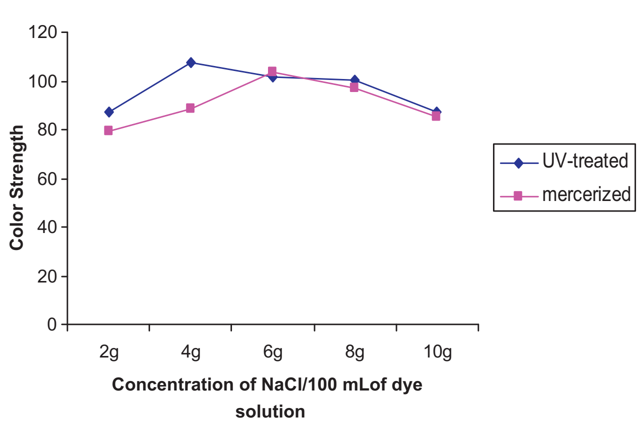

Fig. 2. Color strength versus salt concentration (%) graph of UV irradiated and mercerized cotton fabrics.

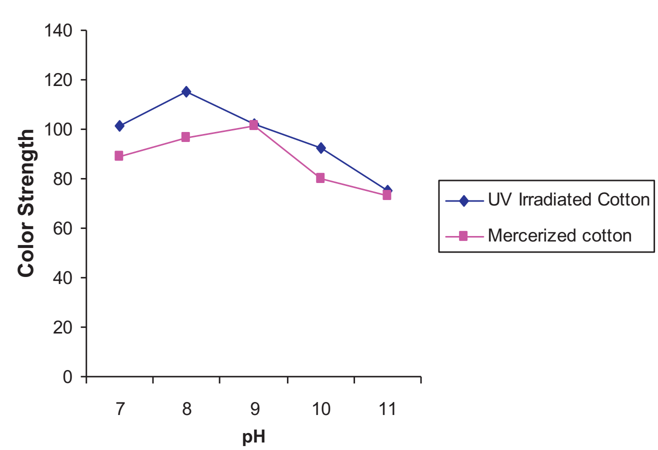

Fig. 3. Color strength of mercerized and UV irradiated cotton fabrics on various levels of pH of dyeing solution.

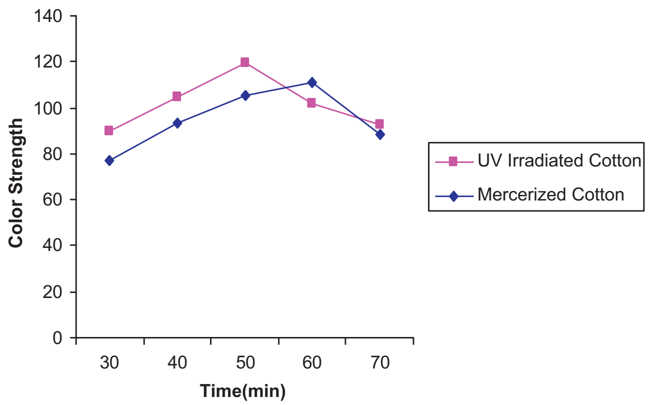

Fig. 4. Color strength of mercerized and UV irradiated cotton fabrics at various contact time of cellulose and dye solution.

(Sharif, Ahmad, & Siddiqui, 2008) that an increase in dyeing time also results in an increase in the color strength up to a certain limit of dying time and then further increase in dyeing time resulted in a decrease in the color strength of dyeing. This may be due to deterioration of dye-fixing agent complex on prolonged heating. In another study Micheal and El-Zaher (2005) reported that the irradiation of cellulose fiber creates spaces between fibers, which absorb more dye and as a result the interaction between dye and cellulose fabric becomes significant. The dye molecules rush rapidly into the fabric and as a result darker shade was obtained on irradiated fabric.

3.5. Surface morphology of treated and untreated fabrics

Scanning electron microscopy (SEM) has been an important technique for assessment of fiber structures since its introduction (Atack & Smith, 1956). SEM has been applied for exploring surface structures in secondary electron mode. The data obtained from SEM analysis is presented in Fig. 5(a)–(c). Fig. 5(a) shows the fibril structure of simple bleached fabric, while Fig. 5(b) and (c) represents the SEM images for mercerized (20% NaOH) and UV irradiated (treated for 75 min) cellulosic fabrics. The comparative study regarding the SEM analysis of both mercerized and UV irradiated cellulosic fabrics showed that both treatments have somewhat similar effect on the morphology of the cellulosic fabrics, so these two pretreatment processes can be used as an alternate for each other. Cellulosic surface modification by mercerization may result in conversion of cellulose I to cellulose II. In traditional industrial mercerization the dye uptake is increased due to the swelling of the cellulosic fabrics. The mercerized fabrics become rounded; having more OH group on surface with uniformity and lustrous appearance so result in higher reflection and ultimately enhance the color strength. In contrast to this UV irradiation of the cellulosic fabric causes oxidation of cellulose, resulting in formation of carboxylic acid groups as well as creates spaces between fiber linings, due to which the interaction between dye and cellulose fiber becomes more significant as compared to the simply swelled fabrics processed through mercerization. It can be stated that both the treatments result in enhancing the dye uptake but have shown different chemistry in their structure modification. Regarding the polymorphy of cellulose I to cellulose II, it is worth mentioning that six polymorphs of cellulose (I, II, IIIi, IIIii, IVi and IVii) can be interconverted, as shown in Fig. 6 (Marchessault & Sarko, 1967; Marchessault & Sundararajan, 1983; Walton & Blackwell, 1973). Evidence for two polymorphs of cellulose I has been offered (Sugiyama, Persson, & Chanzy, 1991; VanderHart & Atalla, 1984); that is previously thought polymorph (I) has now been found to be a mixture of two polymorphs (Iá and Iâ). Proof of the polymorphism of cellulose comes from

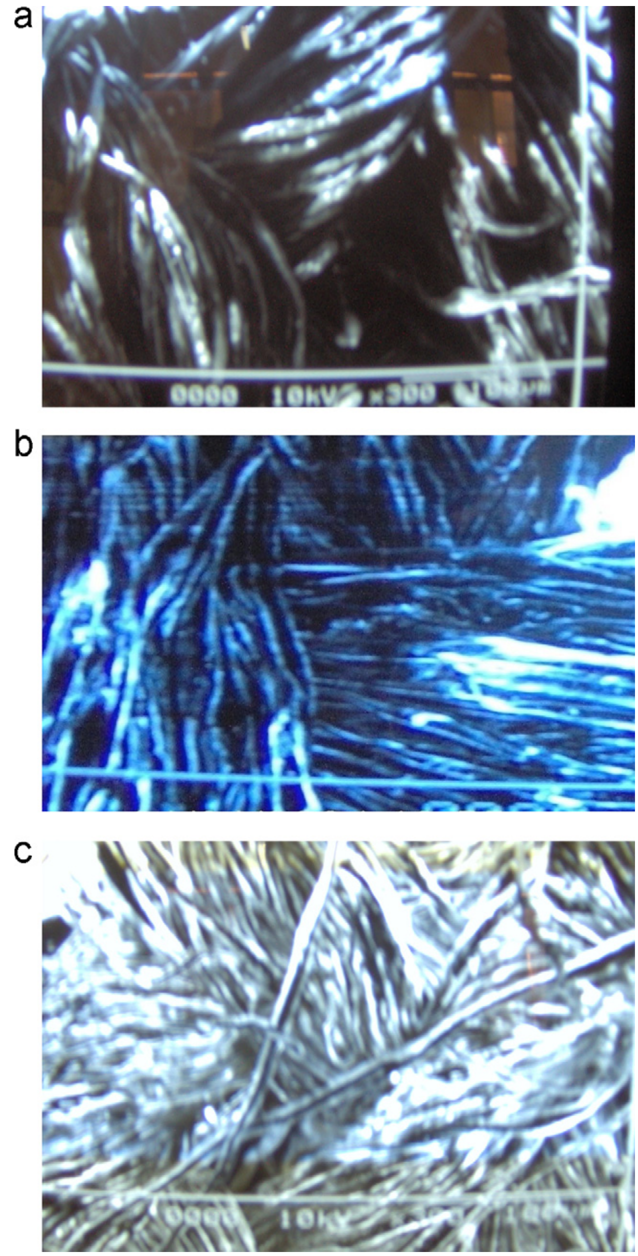

Fig. 5. SEM image of (a) bleached (untreated), (b) mercerized and (c) UV irradiated cellulosic fabrics (magnification 300×).

nuclear magnetic resonance (NMR), infrared and diffraction studies (Blackwell, 1982; Blackwell & Marchessault, 1971). Cellulose I, or native cellulose, is the form found in nature. Cellulose II, the second most extensively studied form, may be obtained from cellulose I by either of two processes: (a) regeneration, which is the solubilization of cellulose I in a solvent followed by re-precipitation by dilution in water to give cellulose II or (b) mercerization, which is the process of swelling native fibers in concentrated sodium hydroxide, to yield cellulose II on removal of the swelling agent. Celluloses IIIi and IIIii (Hayashi, Sufoka, Ohkita, & Watanabe, 1975; Marrinan & Mann, 1956) are formed, in a reversible process, from celluloses I and II, respectively, by treatment with liquid ammonia or some amines, and the subsequent evaporation of excess ammonia (Davis, Barry, Peterson, & King, 1943; Sarko, 1987). Polymorphs IVi and IVii (Gardiner & Sarko, 1985) may be prepared by heating celluloses IIIi and IIIii respectively, to 206 °C, in glycerol.

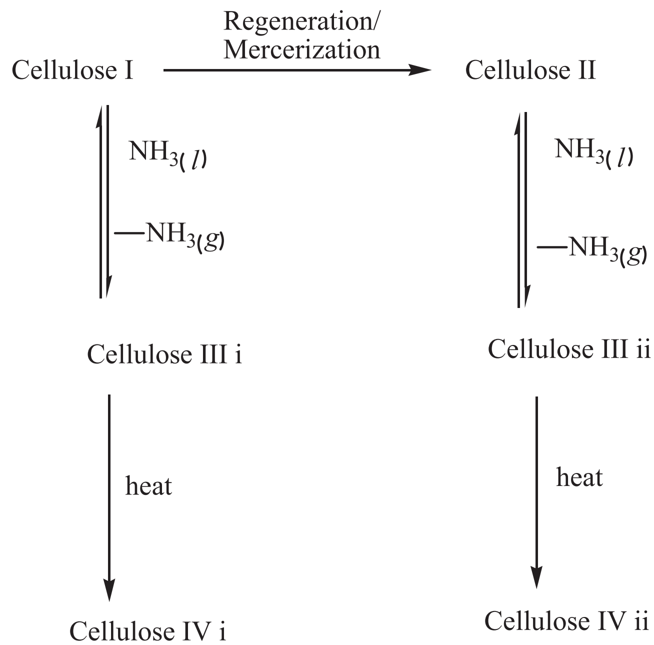

Fig. 6. Inter-conversion of the polymorphs of cellulose.

4. Conclusion

The present research is designed to compare the industrial mercerization and UV treatment of cotton in order to replace conventional mercerization with UV treatment at industrial scale. Cellulosic fabrics were bleached and then modified by applying conventional mercerization technique and UV irradiation in order to enhance the dyeability. The modified cellulosic fabrics with either treatment (UV irradiated and mercerized) were dyed using direct dyes. The effect of mercerization and UV radiation treatment on the color strength of direct dyed fabric was studied and discussed. SEM analysis confirmed the cellulosic fiber modification in either of the treatment. In comparison of both the treatments, the UV irradiated cellulosic fabrics have shown better dye uptake as compared to the mercerized one.

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