Abstract
The effect of biopolishing treatment on color yield of cotton is of great importance to the dyers. Such treatment using cellulase has an influential role on dye ability of the fabric. Research into this area of dyeing has yielded apparently contradictory results. Cellulase treatment prior to dyeing can facilitate the dyeing process resulting in the higher color yield. However, zero impact or negative influence on the color yield of dyed fabric has also been reported. On the other hand, cellulase treatment after dyeing can be retarded by the presence of dye molecules or due to the interaction between dye molecules and cellulose. Though lots of research works have been done on bio polishing and as the application of the process in the textile industry has increased to a greater extent, the information on the effects of this process on color yield, both in cases of cellulase pre-treatment and post-treatment are absolutely necessary. Considering this the paper mainly focuses the previous works regarding the effects of cellulase action (Both before and after dyeing) on the color yield of dyed cotton.

Keywords: Biopolishing before dyeing; Biopolishing after dyeing; Cellulose; Cellulase; Color yield; Dyeability

Introduction
Biopolishing is a biological process in which the cellulase enzyme acts on the surface of the cellulosic materials. The process employs basically the same cellulase action i.e., cleavage 1-4β glucosidic linkage of cellobiose chain to remove fine surface fibrils and micro fibrils from cellulose. The presence of fibrils leads to problems with the final articles related to the formation of pilling and a faded or dull appearance due to an apparent loss of color and increased diffuse reflection of white light on fabric surface with reduced pilling propensity. The enzymatic removal of fibrils results in softer and cleaner articles, which retain the original color [1-6]. Again, biopolishing is a sustainable way as enzymes are a sustainable alternative to the use of harsh chemicals in industry and reduce energy and water consumption, as well as chemical waste production during manufacturing processes [1].

The chemical composition of cellulose consist of anhydro glucose units joined by β-1,4-glucosidic bonds to form linear polymeric chains [1,7]. It is a good hydrophilic fiber because of the presence of hydroxyl groups on the glucose rings. The presence of these groups as well as its amorphous content enables cotton not only to bind well with water, but also allow for dye molecules to form bonds.

Generally biopolishing of cotton fabric is carried out either before or after the dyeing process. The effect of cellulase treatment on color yield of cotton is of great importance to the dyers in both cases. Research into this area has yielded apparently contradictory results. The biopolishing action has an influential role on dye ability of the cotton fabrics. Though lots of research works have been done on biopolishing and as the application of the process in the textile industry has increased to a greater extent, the information on their effects on color yield, both in cases of cellulase pre-treatment and post-treatment are absolutely necessary. Considering this the paper mainly focuses the previous works regarding the effects of cellulase action (Both before and after dyeing) on the color yield of dyed cotton.

Cellulases
Cellulase treatment is an environmentally friendly and economical process of improving the property of cellulose fibers. Cellulases have been commercially available for more than 30 years, and these enzymes have recognized as a target for both academic as well as industrial research. They are commonly used enzymes for processes such as biopolishing, biopreparation and softening of cellulosic fibers. They have also been used in the processes for providing a localized variation in the color density of fibers [8-13]. Cellulase comprises a multicomponent enzyme system, including endoglucanases (EGs) that hydrolyze cellulose polymers

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randomly along the chains attacking on amorphous region, cellobiohydrolases (CBHs) that hydrolyze cellobiose from the polymer ends and cellobiases that hydrolyse cellobiose to glucose [14,15]. All these enzyme components act in a synergistic fashion during the degradation of cellulose. They are inducible enzymes which are synthesized by microorganisms during their growth on cellulotic materials [16,17]. Commercial cellulases for bio-finishing originate from *Trichoderma reesei* and *Humicola insolens* [18-20]. They are usually classified by the pH range in which they are more effective and, accordingly, acid cellulase, neutral cellulase and alkaline cellulase. Acid cellulases are *Trichoderma*-based products work best at pH 4.5-5.5 at a temperature of 45-55°C [14,21]. Such cellulases extract substantial amount of dyestuff from the fabric, particularly indigo dyes (Denim washing) which may in turn deposit on the white portion of the fabric (Back staining). Neutral cellulases from *Humicola* are more effective at pH 6.0-7.0 and in the temperature range of 40-55°C [1]. They are less reactive and therefore require longer treatment time compared to the acid cellulases. Generally a treatment of 45-120 min is appropriate [22]. Alkali stable cellulases are incorporated in household detergent formulations for effective stain removal.

### Biopolishing of cotton fabrics before dyeing

Color yield is the ratio of light absorption (K) and scatter (S) expressed via the Kubelka-Munk function [23] which is well established. Color yield was found improved for most dyes if the fabrics were enzymatically pretreated. In a study, K/S values of fabric dyed after cellulase treatment improved by 16–19% in case of reactive dyes [24]. Vat dyes also showed an improvement in K/S but it decreased with increase in weight loss. Buschle-Diller and Traore [25] also reported that K/S values of cotton samples dyed after treatment with cellulase were higher than that of samples dyed without a cellulase pre-treatment. In this case, the authors argued that the removal of protruding fibers would decrease the scattering coefficient, which depends on degree of polymerization, ratio of amorphous to crystalline regions, swellability, accessibility, chemical reactivity, surface morphology and affinity of dyes [24-26].

Similarly, in another study, Ibrahim et al. [27] reported an increase in color yield for direct and reactive dyes of cellulase treated cotton with the increase in weight loss due to the decrease in scattering coefficient [28]. In apparent contradiction, Koo et al. [29] reported that color yield decreased with increasing weight loss. In this case, a decrease in amorphous regions of cotton fibers was cited as the reason for decreased color yield. In addition, in a study Kanchagar [30] also showed a difference in results that indicated lower color yield values for cellulase treated samples as compared to those of scoured samples. In this study, weight loss in samples after cellulase treatment was taken into account during calculating amount of dyes required for dyeing. The author explained that if the weight loss observed due to cellulase treatment was not taken into account, there was a likelihood of observing an increase in K/S value for cellulase treated samples, as the amount of dye added per unit weight of fabric was increased. As a result, significant savings in dye consumption might not be found due to cellulose treatment, since the amount of dyes per unit weight of fabric required for a particular depth of shade did not change. It has also been reported in the same study that for small weight losses upon cellulose treatment there was no significant difference in color yields between cellulase treated and scoured samples.

However, Cavaco-Paulo [31] reported that there should be no change in the dyeability and moisture recovery of cellulose, as no change in crystallinity due to cellulase treatment was observed. In addition, Mori et al. [32] found that dyeing affinity of treated and untreated fabrics was equal and remained constant regardless of the extent of enzymatic hydrolysis. In the same study, the authors hypothesized that there are two kinds of regions accessible to dye molecules: areas that are readily digested by the enzyme and other regions that are additionally developed by the attack of cellulase. They reported that dyeing affinity was found to increase and then decrease with the increase in weight loss indicating that additionally developed accessible regions eventually decrease with extended hydrolysis. Based on the dyeing isotherms, they suggested that the dyeing mechanism for untreated and cellulase treated cotton fabrics are the same [33].

Hebeish et al. [34] reported that 30 min time of bio treatment favored the maximum color strength mono functional and bifunctional reactive dyes. Longer times adversely affected the color strength. Again, the maximum color yield was reported upon raising the bio treatment temperature from 20°C to 40°C. Raising the temperature further to 60°C was accompanied by decrement in the enzyme activity. It was also reported that activity of the cellulase as well as color strength was improved gradually by increasing the material to liquor ratio from 1:10 to 1:50. Further increase to 1:60 decreased the color strength. Moreover, it was shown in the same study that cellulose activity and color yield increased gradually by increasing the enzyme concentration from 1% to 5% and further increase to 6% decreased color yield.

In another study, Hebeish et al. [34] reported that increase in color yield is a direct consequence of the action of cellulase on the structure of cotton. The authors explained that cellulase enzyme converts the cotton structure to a more accessible textile substrate which is much more amenable to the dye, beside its biopolishing effect which plays a key role in reflectance based measurements of the color on the fabric. Bifunctional dyes produce higher K/S values than that of the monofunctional dyes due to the double reactivity of the former in the same study.

Pretreatment of cotton fabrics with cellulases reduce the problems related to immature fiber neps, which do not pick up same amount of dye as that of matured cotton fibers [35]. Studies have also been conducted on the effects of mercerization and dyeing on cellulase activity [36].

### Biopolishing of dyed fabrics

Researchers have studied cellulase action on dyed cotton using direct, reactive and vat dyes [37-40]. In case of fabric dyed with direct dyes, the efficiency of biopolishing is highly influenced by size, substantivity, molecular weight and amount of dyes in the fabrics [31,32,41-43]. Cotton fibers dyed with direct dyes have been reported to show lower levels of cellulase hydrolysis and substantivity of dyes as well as hydrogen bonds formed between dyes and fibers appears to block the hydrolysis [24].

A strong inhibition of reactive dyed substrate is expected as reactive dyes are covalently linked to cellulose chains [30]. Dichlorotriazine (DCT) dyes extensively retard cellulase hydrolysis compared to vinyl sulphone dyes, perhaps due to cross link...
effects of dichlorotriazine dyes between two cellulose molecules, which cause steric hindrance for such hydrolysis [21]. Hetero-
bifunctional dyes have higher substantivity than DCT dyes, and offer resistance to cellulase hydrolysis [24].

Presence of vat dyes does not influence the weight loss during cellulase treatment in many cases as the dyes are firmly trapped inside the fibers; however, planar anthraquinone dyes obstruct cellulase access efficiently than indigo dyes [41,44,45].

In case of sulphur dyes, color strengths are not altered with lower dye pick-up, but presence of acidic groups in sulphur black often inhibits cellulase actions and results in lower weight losses than vat dyed samples [46].

Again, in case of cellulase treatment on dyed fabric, results indicated that cellulase action can be retarded either by the presence of dye molecules or due to interactions between dye molecules and cellulose. It is suggested that physical interactions of cellulose chains with dye molecules, such as hydrogen bonding might inhibit hydrolysis of cellulose by cellulase [38]. Factors which influence the extent of retardation of cellulase action on dyed cotton are dye class, size of dye molecule, dye/fiber interactions, substantivity, aggregation of dye molecules and functionality of the dyes and all these factors have also been investigated [31,37,38]. Moreover, dyes with larger molecular size, higher substantivity and higher functionality are found to retard cellulase action to a larger extent as compared to other dyes. However, irrespective of size of the dye molecules similar weight loss values can be reached as that of undyed samples, on extended hydrolysis [24].

Moreover, the effect of cellulase treatment on color for denim is of different. Due to effect of enzyme and physical aberration of cellulose, the exposed areas became white and indigo dyed.

This type of effect on denim is called ‘salt and pepper effect’ [47]. When the pH of treatment increases from 5 to 7, whiteness retention value also increases for acid cellulase, mainly because of lower activities of acid cellulases at pH 7. In case of neutral cellulases, maximum color removal takes place at pH 6 and retains about 90% of color removing activity at pH 7.0–7.5, while the acid cellulases have maximum color removing activity at pH 5.0 and less than 40% of that at pH 6.0 [24].

Conclusion
Biopolishing of cotton fabric can play an important role in changing the dyeability of fabric. It depends whether the cellulose treatment is carried out before or after dyeing. As no change in the crystallinity is observed due to cellulase pre-treatment, no change in dyeability of cellulose is reported. Dyeability is expected to increase and then decrease in this case with increasing the weight loss, as the additionally developed accessible regions decreases with the extended hydrolysis. Color yield increases due to removal of protruding fibers as this would decrease the scattering coefficient. In contrast, a decrease in the amorphous region of cotton can be the probable reason of decreasing the color yield. However, cellulase action can be retarded by the presence of dye molecules in case of cellulase treatment after dyeing. Higher size of dye molecules, higher substantivity and higher functionality of dyes can affect the retarding process to a larger extent. Color yield can also be changed due to optimum enzyme activity and corresponding weight loss.

Competing Interest
The author declares that he has no competing interests.
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