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The adsorptive and hydrolytic performance of cellulase on cationised cotton

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ABSTRACT

In this research, the cotton fabrics were cationised by a cationic agent to change their surface electric properties. The cationised cotton fabrics were then bio-polished by cellulase to explore the influence of cationisation on the adsorptive and hydrolytic performance of cellulase. The experimental results from cellulase adsorption reveal the cationisation of cotton can obviously improve the binding efficiency of cellulase protein mainly by the improved electrostatic attraction between oppositely charged cellulase and cationised cotton. The adsorption parameters calculated can further prove this improvement trend. Through measuring the concentration of reducing sugars released and weight loss of cotton during the bio-polishing, it is found the hydrolytic activity toward cotton is partially damaged by the cationisation. The reason can be attributed to the movement restriction and dysfunction of cellulase protein by the cationisation.

1. Introduction

In recent years, cellulase enzymes have been widely used to produce specific finishing effects on cotton substrates such as bio-treating denims to produce stone-washed appearance or bio-polishing knit fabrics to remove fuzz-fibres (Kan, Yuen, & Wong, 2011; Pazarlioglu, Sariisik, & Telefoncu, 2005; Saravanan, Vasanthi, & Ramachandran, 2009; Sariisik, 2004; Vishnu Vardhini & Selvakumar, 2006). Cellulase enzyme consists of three major types of enzymes: Endoglucanase (EC 3.2.1.4) that attacks β-1,4 bonds randomly within the cellulose chains, exoglucanase (EC 3.2.1.91) that consecutively removes cellobiose units from free chain ends and β-glucosidases (EC 3.2.1.21) that breaks these cellobiose up into glucose units (Al-Zuhair, 2008; Cavaco-Paulo, Almeida, & Bishop, 1996a). The efficiency of enzymatic hydrolysis of natural cotton using cellulase enzymes is governed by the synergetic actions of these three types of enzymes (Cavaco-Paulo, 1998; Sarkar & Etters, 2001). Cotton hydrolysis by cellulase involves the adsorption of cellulase protein onto the cotton surface and following breakdown of molecular chains in cotton. This process is influenced by cellulase properties and working variables such as the enzyme concentration, liquor ratio, treating time and temperature, processing pH and agitation level (Choe, Park, Cha, & Jeon, 1997; Schimper, Ibanescu, & Bechtold, 2006; Traore & Buschle-Diller, 1999). Clearly, the adsorption properties of cellulase protein play an important role in controlling its accessibility to cotton substrate and influence its catalytic activity towards insoluble cotton by altering the effective enzyme concentration on the cotton substrate (Cortez, Ellis, & Bishop, 2001; Traore & Buschle-Diller, 1999). The physical and chemical form of cotton substrate such as the degree of swelling, the cross-linking of molecules, the existing of various dyes and surfactants, the tightness of the yarn twist, the hairiness of the fabric surface, the fabric structure and the hydrophilic/hydrophobic property of fabric surface, will affect the adsorption and activity of cellulase on cotton (Buschle-Diller & Zeroniam, 1994; Cavaco-Paulo, Almeida, & Bishop, 1996b, 1998; Eriksson, Borjesson, & Tjerneld, 2002; Hebeish et al., 2009; Koo, Ueda, Wakida, Yoshiura, & Igarashi, 1994; Paul & Teli, 2010, 2011; Rastegari, Bordbar, & Taheri-Kafrani, 2009; Schimper, Ibanescu, & Bechtold, 2011). Besides, the electric state of cotton will theoretically also affect the performance of cellulase on cotton. A fact that cannot be ignored is that the bath pH during the application of cellulase, especially the neutral cellulase, is usually set in the range over the isoelectric point of crude cellulase (Linder & Teeri, 1997; Saravanan et al., 2009). Therefore, the net charges on the cellulase protein surface would be negative at this condition. As we know, natural cotton fibres carry a few negative charges owing to the presence of some carboxylic acid groups from oxidation at the primary hydroxylic site (Rattanaphani, Chairat, Bremner, & Rattanaphani, 2007). The negative charges on the surface of cotton repel anionic cellulase protein and therefore the adsorption efficiency of cellulase protein is low.

Cationisation of cotton fabrics with cationic agents, which can alter the surface electric properties of cotton and make it positively charged in nature, has caused extensive attentions in textile colouration industry (Fang, Wang, Zhang, & Xu, 2005; Haroun & Mansour, 2007; Morris & Hauser, 2003). Cationised cotton can be dyed with anionic acid or reactive dyes without electrolyte by

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ion–ion interactions between the sulfonic acid groups present in the dye molecules and the persistent cationic sites present in the cationised cotton (Jiang, Ju, Zhang, & Yang, 2010; Ma, Zhang, Tang, & Yang, 2005). Similarly, cationisation of cotton can improve the binding efficiency of negatively charged cellulase protein by reverse charge attraction and thus change its following hydrolytic performance. So far, however, no researches about this issue have been reported. The relationship between cationisation degree of cotton and its enzymatic hydrolysis remains unclear.

In this research, a reactive cationic agent with quaternary ammonium was used to modify the cotton fabrics by exhaustion method, and then the resulted fabrics were bio-polished with a commercial neutral cellulase at predetermined conditions. The purpose of this study is to find out the effect of cationisation of cotton on adsorptive and hydrolytic behaviour of cellulase and provide useful information for possible application of cellulase biopolishing on cationised cotton.

2. Materials and methods

2.1. Materials

A total crude cellulase (100 mg/ml protein content and 12,000 ECU/ml activity) from *Trechoderma reesei* was supplied by Haiyi Chemicals, China. Hundred percent mill scoured and bleached cotton knit fabrics (180 g/m^2, 20 tex single yarn) were offered by Furi Textile Factory, China. The fabric was treated with a solution containing 2 g/L nonionic detergent (DNS, Haiyi chemical company) at 90 °C for 30 min prior to utilisation. Cationic agent, based on poly-aminochlorohydrin quaternary ammonium compound with epoxide reactivity functionality, was obtained from Hongcheng Chemical Co. Ltd., China. Other chemical agents were all A.R. grade.

2.2. Methods

2.2.1. Cationisation treatment

The treatment was carried out according to the exhaustion method. 10 g cotton fabrics was immersed in aqueous solutions of cationic agent (2–12%, owf) at a liquor ratio of 30:1 using a SW-2 dyeing instrument. pH of the resulting solution was adjusted to 10 with 0.5 M sodium hydroxide. The temperature was raised to 85 °C and held at this temperature for 30 min. The resulted cationised fabrics were rinsed thoroughly using tap water, followed by soaping with 2 g/L nonionic detergent at 90 °C for 10 min and then dried at room temperature.

2.2.2. Enzymatic hydrolysis

The enzymatic hydrolysis was carried out in a thermostatic reactor with mechanical stirring of 120 rpm. All treatments were involved 5 g of untreated and cationised fabrics (by 2–12% cationic agent, owf) at a temperature of 45 °C in 0.1 M acetate buffer (pH 6.5) with a liquor ratio of 30:1 for 60 min, and initial enzyme concentrations of 20 mg/g of fabric were used. After the hydrolysis, all samples were thoroughly rinsed with tap water and then dried in air.

In order to determine the adsorption parameter of cellulase, 5 g of untreated and cationised fabrics (by 10% cationic agent, owf) was treated with the above-mentioned conditions, and initial enzyme concentrations of 5, 10, 15, 20 mg/g of fabric were used. During the process, the amounts of enzyme protein adsorbed were measured using the Bradford method (Bradford, 1976) after predetermined time intervals, and the adsorption amount of cellulase onto the fabrics was obtained by means of the loss of protein in solution. The experiments were carried out in triplicate, and the final results were the average of the three values obtained.

For measuring the hydrolytic parameters, 5 g of untreated and cationised fabrics (by 10% cationic agent, owf) was hydrolysed with the above-mentioned conditions, and initial enzyme concentrations of 5, 10, 15, 20 mg/g of fabric were used. The soluble reducing sugars as glucose released were determined using the DNS method using glucose for calibration. The experiments were carried out in triplicate, and the final results were the average of the three values obtained.

2.3. Measurements

2.3.1. Determination of nitrogen content

Nitrogen content of cationic cotton was determined in triplicate by the modification of the Kjeldahl method. The samples were dried under vacuum at the temperature of 50 °C before measurement.

2.3.2. Measurement of zeta potentials

Zeta potentials of untreated and cationised cotton were determined in triplicate at pH 6.5 with a zeta potentials analyser. The samples were ground in a mill to pass a 20-mesh screen. 0.1 M aqueous potassium hydroxide and 0.1 N hydrochloric acid were used to adjust the pH.

2.3.3. Scanning electron microscope

A scanning electron microscope (SEM) examination was carried out by mounting the fabric samples on sub with double stick adhesive tape and coated with gold in Sputter Coater Unit. The samples were then viewed using a JSM-6390LV Scanning Electron Microscope (JEOL, Japan) with accelerating voltage of 15 kV and magnification between 10 and 20,000.

2.3.4. The weight loss and strength loss of fabrics

Loss in weight (WL%) was calculated as the difference in the weight of samples before and after cellulase treatment according to the following equation:

$$\mathrm{WL}(\%) = \frac{W_{\text{before treatment}} - W_{\text{after treatment}}}{W_{\text{before treatment}}} \times 100 \qquad (1)$$

The tensile strength of the cotton fabrics was tested according to ISO 13934-1-1999 using YG-2 testing machine (Laizhou, China). Samples were tested five times and the average value was used. The loss in tensile strength (SL%) was measured as % loss in breaking load of cellulase treated samples relative to untreated one according to the following equation:

$$\mathrm{SL}(\%) = \frac{S_{\text{before treatment}} - S_{\text{after treatment}}}{S_{\text{before treatment}}} \times 100 \qquad (2)$$

All samples were conditioned at 20 °C in 65% RH for 24 h before testing weight and tensile strength.

3. Results and discussion

3.1. Effect of cationisation on cellulase adsorption

3.1.1. Effect of cationic agent dosage

During cationisation, the molecules of cationic agent gradually transfer from the treatment bath to the solid surface of the fabrics and then react with the cellulosic molecular chains by forming ether bond between the epoxide and hydroxyl groups. There are quaternary ammonium groups in the cationic agent, so the cationisation extent of cotton can be determined by testing its nitrogen content (El-Shishtawy & Nassar, 2002; Kamel, El-Zawahry, Ahmed, & Abdelghaffar, 2009). The result in Fig. 1 shows that as the concentration of cationic agent increases from 0 to 12%, owf, the nitrogen content (N%) is increased from 0% to 0.482%, revealing that more

Table 1
Adsorptive and kinetic parameters for untreated and cationised cotton.

Samples	K_A (ml/mg)	$A_{\max}$ (mg/g)	v_{em} (mg/ml h)	k_e (mg/ml)	v_{em}/k_e (h^{-1})
Untreated	2.18	9.08	1.51	0.21	7.12
Cationised	3.22	24.45	0.83	0.18	4.56

cationic agents have been attached on cotton fibre with the increasing cationic agent dosage. It is also noted that N% increases slowly when the concentration of cationic agent reaches 10%, suggesting the full modification of cotton by cationic agent has been nearly achieved at this point.

As we know, the enzyme protein must be bound onto the cotton surface before enzymatic hydrolysis can start. Due to the change of the surface electric properties, the adsorption properties of cellulase protein on cotton were modified after cationisation. The effect of cationic agent concentration on the amount of protein bound on cotton fabrics was also shown in Fig. 1. It is indicated that the higher cationic agent concentration or cationisation degree results in higher adsorption amount of cellulase protein. The cellulase protein is bound onto the cotton surface either specifically or non-specifically, mainly by hydrophobic and electrostatic interactions (Sild, Stahlberg, Pettersson, & Johansson, 1996). In this experimental condition, the electrostatic interactions may play a determining role. As we know, the ratio of positively and negatively charged amino acids side chains will vary depending on the pH condition. The pH (6.5) of treatment bath in this experiment is higher than the isoelectric point (3.5–5.5) of cellulase used, so the surfaces of cellulase protein are negatively charged on the whole. At the same time, there are some pendant hydroxymethyl groups in cotton fibre which are naturally oxidised to carboxylic acid groups during growth or following wet processing (Rattanaphani et al., 2007). Thus, the cotton fibres carry weak negative charges when solution pH higher than 4, resulting in mutual repulsion between similarly charged cotton and cellulase protein. The reaction of cationic agent with cellulose chains would change the surface electric properties by introducing permanent positive charges. The zeta potential of cotton turns from ca. −20.8 mV in its original state to ca. 12.6 mV when introducing sufficient cationic agent (10%, owf). Therefore, the cationised cotton would attract the cellulase protein by opposite charges instead of repelling it, resulting obvious improvement of bound amount of cellulase protein.

3.1.2. Adsorption parameters

The adsorption of cellulase protein is a solid/liquid process, advancing by the movement of the protein from aqueous phase to the solid surface of the fabric. First, cellulase protein is bound by affinity after effective contact with the cotton fabric resulting in forming an enzyme–substrate (E–S) complex. Then, the water molecules are transferred to the active sites of the E–S complex and surface reaction between water and cellulose is catalysed by the E–S complex (Sarkar & Etters, 2001). The most widely used two-parameter equation describing the adsorption process is the Langmuir equation, which has the linear form (Banka & Mishra, 2002; Cavaco-Paulo et al., 1998; Kim & Hong, 2000):

$$\frac{E}{A}=\frac{1}{K_A A_{\max}}+\frac{E}{A_{\max}} \tag{3}$$

where K_A and $A_{\max}$ are the adsorption equilibrium constant and the maximum amount of enzyme adsorbed per unit weight of fabrics, respectively. E is the concentration of enzyme in liquid phase at the adsorption equilibrium. The K_A and $A_{\max}$ were determined from the slope of plots using a least-square analysis and shown in Table 1. It can be observed the adsorption constant K_A for cationised fabrics is higher than that of untreated cotton, suggesting a higher affinity between cellulase protein and cationised cotton. This result also means the adsorption of cellulase protein on untreated cotton is more reversible than that on cationised cotton. Table 1 also shows the $A_{\max}$ is improved after cationisation, meaning there are more adsorption sites available for cellulase. This increased availability of adsorption sites is likely to be related to the change in fibre surface electric property, which could provide extra adsorption positions for the cellulase protein.

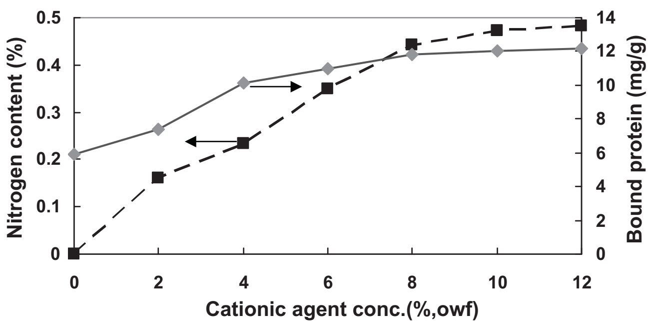

Fig. 1. Effect of cationic agent concentration on nitrogen content and the amount of protein bound on cotton fabrics.

3.1.3. Adsorption rate

Time-cellulase uptake isotherms of untreated and cationised (10%, owf of cationic agent) cotton fabrics are illustrated in Fig. 2. It can be noted the bound cellulase increases rapidly after short-time contact with both the substrates, and then the slope of the adsorption isotherms decreases. In general, the adsorption of protein on both the substrate is a quick process and the equilibrium can be gained within a 30 min contact period. By contrast, the cellulase protein has higher adsorption rate on cationised cotton than that on untreated one because of the existing of strong charge attraction between them.

3.2. Effect of cationisation on enzymatic hydrolysis

3.2.1. Effect of cationic agent concentration

The hydrolysis of cotton substrate will begin as the cellulase protein is adsorbed on the cotton surface. The aggressive attack of cellulase on the surface and accessible amorphous areas of the cotton will yield short-chain oligomers and glucose (Ibrahim, El-Badry, Eid, & Hassan, 2011; Vascocelos & Cavaco-Paulo, 2006). The

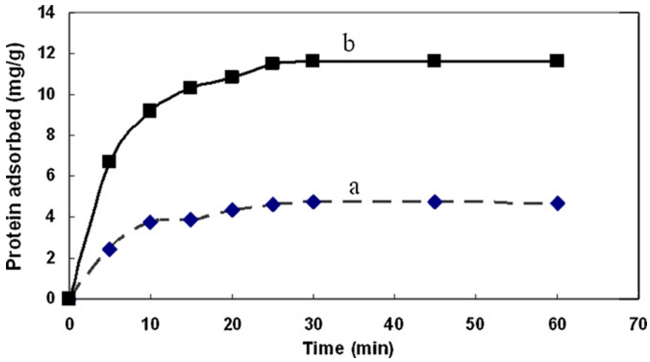

Fig. 2. Adsorption of cellulase protein on (a) untreated and (b) cationised cotton at different time.

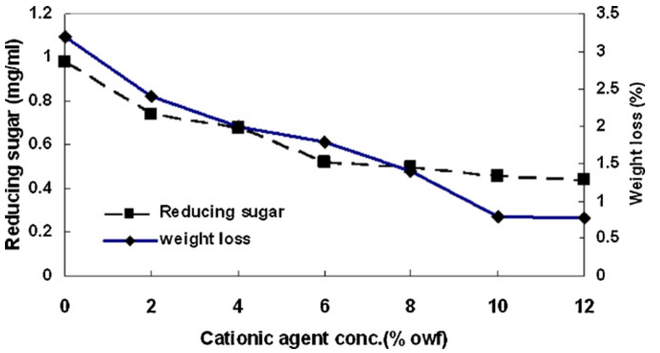

Fig. 3. Effect of cationic agent concentration on the reducing sugars released and weight loss % of cotton.

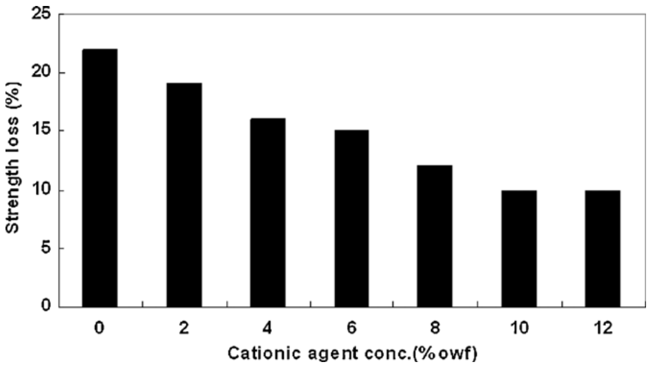

Fig. 4. Effect of cationic agent concentration on strength loss.

effect of cationic agent concentration on hydrolysis is evaluated by measuring the concentration of reducing sugars released and weight loss % of cotton, and the results shown in Fig. 3. It is demonstrated that both of them decrease with the increasing cationic agent concentration, revealing the existence of cationic molecules displays inhibition to the enzymatic activity. The following discussion is devoted to analyse the dysfunction of the bound cellulase by the cationic agent on cotton. First, how tightly or irreversibly the protein binds to cotton should be considered for the enzymatic activity (Cavaco-Paulo, 1998; Linder & Teeri, 1997). In normal conditions, the cellulase protein is adsorbed onto the cotton surface both productively and non-productively and they can hydrolyse the cotton substrate processively (Valjamae, Sild, Pettersson, & Johansson, 1998). For the untreated cotton with low affinity to cellulase protein, the cellulase easily undergoes a dynamic process of binding and desorption allowing the relocation of cellulase to new accessible sites on the cotton surface. For the cationised one, it is probable the hydrolysis is sterically hindered by irreversible non-productive cellulase protein because the non-productively bound enzyme cannot move rapidly on the cationised cotton to find a new productive position under the strong attraction between them. Anther reason that we should bear in mind is that the protein function is exactly linked with protein conformation, so the conformal changes of cellulase after adsorption is vital to the decrease of enzymatic activity (Ran, Jia, Liu, & Wu, 2009). Non-polar amino acids make up one half of surface area of cellulase protein and are organised as hydrophobic surface cluster (Gusakov, Sinitsyn, Berlin, Markov, & Ankudimova, 2000). Once bound onto the cationised cotton, the exposure to polar NH^{4+} groups may cause conformal changes of cellulase protein at secondary and tertiary levels or even total denaturation of cellulase, leading to an obvious decline in enzymatic activity.

The effect of cationisation on enzymatic hydrolysis can also be evidenced by measuring the mechanical properties of the hydrolysed fabrics. The crystalline part of cotton is rigid and mainly responsible for the tensile strength of the fibre along its axis, so the loss in tensile strength can partially reflect the degrading of cellulose and the enzymatic efficacy during the bio-polishing. Fig. 4 shows the loss in tensile strength of fabrics decreases with the increasing concentrations of cationic agent, providing another evidence for the activity inhibition by cationisation.

3.2.2. The rate of enzymatic hydrolysis

The rate of enzymatic hydrolysis can also be manipulated by the cationisation of cotton. Fig. 5 shows the concentrations of reducing sugar released from untreated and cationised cotton (10%, owf of cationic agent) at different processing time. At the early stage, the hydrolytic rate is fast, and then the pace of hydrolysis will gradually decline with the elongation of treatment time. Both the fabrics release more reducing sugars with the increasing treatment time, but at different rate. The cationised cotton exhibits a much slower hydrolytic rate than its untreated counterpart, also showing the inhibition of cationisation to enzymatic activity.

Kinetics parameters were calculated for both the untreated and cationised cotton fabrics in the following method (Cavaco-Paulo et al., 1998; Carrillo et al., 2003):

$$v_0 = \frac{v_{em}[E_0]}{k_e + [E_0]} \tag{4}$$

where v_0 is the initial reaction rate, $[E_0]$ the initial enzyme concentration, v_{em} the maximum rate of reaction at saturation with enzyme and k_e the half saturation constant relative to the substrate sites. The kinetics parameters were determined from the linearisation of Eq. (4) and listed in Table 1. The maximum reaction rate v_{em} is found to be lower for cationised cotton than that for untreated one, which is consistent with the results discussed above. The half saturation constant k_e is lower for the cationised cotton because it has a higher affinity for the cellulase protein. This suggests the concentration of the enzyme–substrate complex at the equilibrium is relatively high and more protein is in the associated form (Carrillo et al., 2003). At last, the v_{em}/k_e relationship, which is directly correlated to the maximum rate of hydrolysis respect of the protein affinity for substrate, is also lower for cationised cotton.

3.3. Characterisation of bio-polished cotton fabrics

The enzymatic hydrolysis towards cotton fabrics by cellulase can improve fabric appearance by removing fuzz fibres and pills on the fabric surface (Cavaco-Paulo, 1998). During the bio-polishing, cellulase can result in systematic removal of primary and secondary walls of the cotton, progressively (Saravanan et al., 2009). After hydrolysis, microfibrillar becomes so weakened that the enzyme causes scission and rupture of fibres (Paralikar & Bhatawdekar,

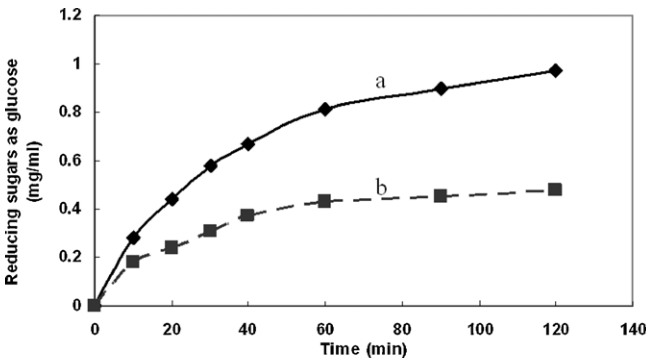

Fig. 5. The concentration of reducing sugars from (a) untreated and (b) cationised cotton at different time.

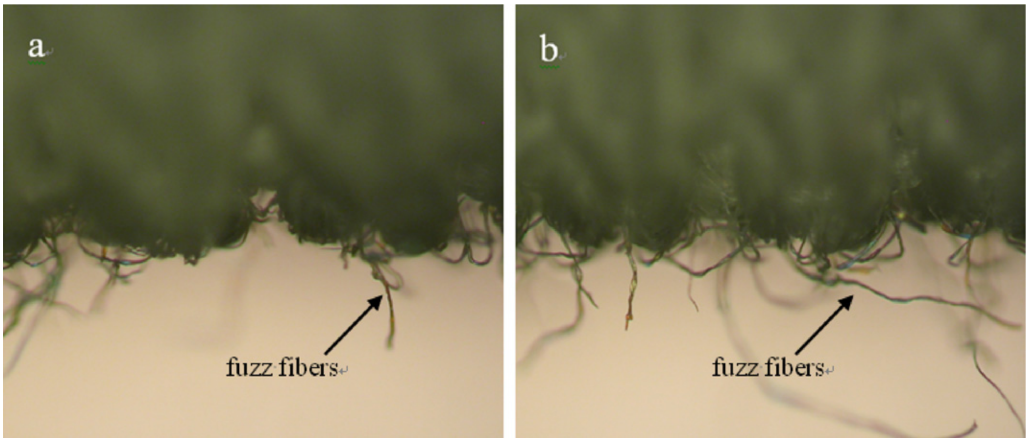

Fig. 6. Photos of (a) untreated and (b) cationised cotton fabrics after bio-polishing.

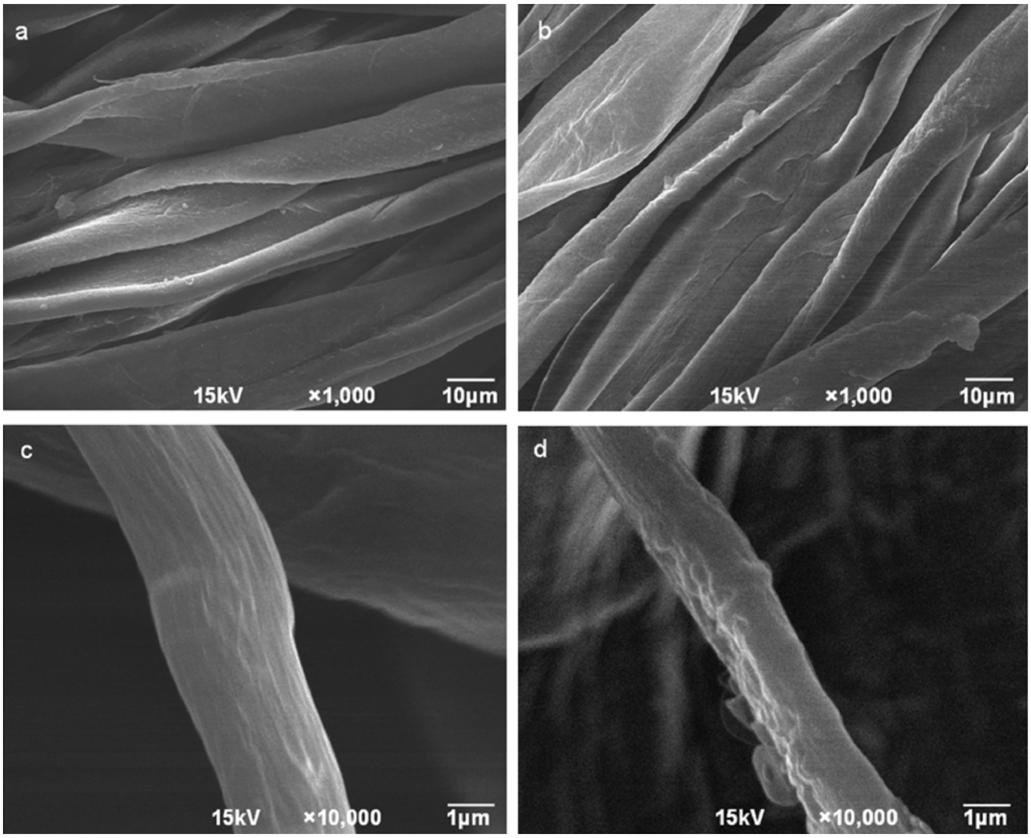

Fig. 7. SEM of cotton fabrics after cellulase bio-polishing. (a) Untreated (1000×) and (b) cationised (1000×). (c) Untreated (10,000×) and (d) cationised (10,000×).

1984). The images of fuzz fibres protruding from the cotton surface were obtained using a microscope with digital camera and shown in Fig. 6. It is shown that the amount of fuzz fibres existing on the untreated cotton fabric is obviously fewer than that on cationised cotton (10%, owf of cationic agent), suggesting a more powerful polishing towards untreated cotton.

Scanning electron microscopy was also done on the bio-polished cotton fabrics, and the images shown in Fig. 7. Examination of cotton under lower amplification (1000×) in Fig. 7a and b shows typical cotton fibres with twisted, wrinkled surfaces and occasional breaks (Hebeish et al., 2009), but no obvious difference was observed for untreated and cationised cotton (10%, owf of cationic agent). Further investigations on fibril of bio-polished cotton under higher amplification (10,000×) were made in Fig. 7c and d, where a smoother fibril surface for untreated cotton was observed. As discussed previously, the enzyme possesses higher hydrolytic activity towards untreated cotton, so it can peels off the cellulose in untreated cotton more efficiently (Hebeish et al., 2009; Li & Hardin, 1998), resulting in a smoother fibril surface.

4. Conclusions

From the above discussion, the conclusion can be reached that the cationisation of cotton by cationic agent can produce obvious influences on the adsorption of cellulase and its following enzymatic performance. The amount of cellulase protein bound on cotton is obviously increased with the increasing concentration of cationic agent because of the improved electrostatic attraction between oppositely charged cellulase protein and cationised cotton. By using the Langmuir equation, the adsorption parameters were calculated. K_A for cationised cotton is higher than that for untreated one, suggesting a higher affinity after cationisation. But, it is found the increased adsorption capacity cannot result in the improvement of enzymatic hydrolysis towards cationised cotton. Both the concentration of reducing sugars released and weight loss of the cotton decrease with the increasing cationic agent concentration. One reason is the improved adsorption affinity restricts the movement of non-productively bound enzyme to find a new productive position, and the other is the polar NH_4^+ introduced by cationic agent may cause dysfunction of enzyme bound on the cotton.

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References

Al-Zuhair, S. (2008). The effect of crystallinity of cellulose on the rate of reducing sugars production by heterogeneous enzymatic hydrolysis. *Bioresource Technology*, *99*, 4078–4085.

Banka, R. R., & Mishra, S. (2002). Adsorpton properties of the fibril forming protein from *Trechoderma reesei*. *Enzyme and Microbial Technology*, *31*, 784–793.

Bradford, M. (1976). A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein–dye binding. *Analytical Biochemistry*, *72*, 248–254.

Buschle-Diller, G., & Zeroniam, S. (1994). Enzymatic and acid hydrolysis of cotton cellulose after slack and tension mercerization. *Textile Chemistry Coloration*, *26*, 17–24.

Carrillo, F., Colom, X., Lopez-Mesas, M., Lis, M. J., Gonzalez, F., & Valldeperas, J. (2003). Cellulase precessing of lyocell and viscose type fibres: Kinetics parameters. *Process Biochemistry*, *39*, 257–261.

Cavaco-Paulo, A., Almeida, L., & Bishop, D. (1996a). Effects of agitation and endoglucanase pretreatment on the hydrolysis of cotton fabrics by a total cellulase. *Textile Research Journal*, *5*, 287–294.

Cavaco-Paulo, A., Almeida, L., & Bishop, D. (1996b). Cellulase activities and finishing effects. *Textile Chemistry Coloration*, *28*, 28–32.

Cavaco-Paulo, A. (1998). Mechanism of cellulase action in textile processes. *Carbohydrate Polymers*, *37*, 273–277.

Cavaco-Paulo, A., Almeida, L., & Bishop, D. (1998). Hydrolysis of cotton cellulose by engineered cellulases from *Trichoderma reesei*. *Textile Research Journal*, *68*, 273–280.

Choe, E. K., Park, S. Y., Cha, H. C., & Jeon, B. D. (1997). Effect of pre-existing dyes and fabric type on cellulase treatment of cotton fabrics. *Textile Research Journal*, *67*, 155–162.

Cortez, J. M., Ellis, J., & Bishop, D. P. (2001). Cellulase finishing of woven, cotton fabrics in jet and winch machines. *Journal of Biotechnology*, *89*, 239–245.

El-Shishtawy, R. M., & Nassar, S. H. (2002). Cationic pretreatment of cotton fabric for anionic dye and pigment printing with better fastness properties. *Coloration Technology*, *118*, 115–120.

Eriksson, T., Borjesson, J., & Tjerneld, F. (2002). Mechanism of surfactant effect in enzymatic hydrolysis of lignocellulose. *Enzyme and Microbial Technology*, *31*, 353–364.

Fang, K., Wang, C., Zhang, X., & Xu, Y. (2005). Dyeing of cationised cotton using nanoscale pigment dispersions. *Coloration Technology*, *121*, 325–328.

Gusakov, A. V., Sinitsyn, A. P., Berlin, A. G., Markov, A. V., & Ankudimova, N. V. (2000). Surface hydrophobic amino acid residues in cellulase molecules as a structural factor responsible of their high denim-washing performance. *Enzyme and Microbial Technology*, *27*, 664–671.

Haroun, A. A., & Mansour, H. F. (2007). Effect of cationisation on reactive printing of leather and wool. *Dyes and Pigments*, *72*, 80–87.

Hebeish, A., Hashem, M., Shaker, N., Ramadan, M., El-Sadek, B., & Hady, M. A. (2009). Effect of post- and pre-crossliking of cotton fabrics on the efficiency of biofinishing with cellulase enzyme. *Carbohydrate Polymers*, *78*, 953–960.

Ibrahim, N. A., El-Badry, K., Eid, B. M., & Hassan, T. M. (2011). A new approach for biofinishing of cellulose-containing fabrics using acid cellulases. *Carbohydrate Polymers*, *83*, 116–121.

Jiang, Y., Ju, B., Zhang, S., & Yang, J. (2010). Preparation and application of a new cationic starch ether–starch–methylene dimethylamine hydrochloride. *Carbohydrate Polymers*, *80*, 467–473.

Kamel, M. M., El-Zawahry, M. M., Ahmed, N. S. E., & Abdelghaffar, F. (2009). Ultrasonic dyeing of cationized cotton fabric with natural. Part 1: Cationization of cotton using Solfix E. *Ultrasonics Sonochemistry*, *16*, 243–249.

Kan, C. W., Yuen, C. W. M., & Wong, W. Y. (2011). Optimizing color fading effect of cotton denim fabric by enzyme treatment. *Journal of Applied Polymer Science*, *120*, 3596–3603.

Kim, D. W., & Hong, Y. G. (2000). Ionic strength effect on adsorption of cellobiohydrolases I and II on microcrystalline cellulose. *Biotechnology Letters*, *22*, 1337–1342.

Koo, H., Ueda, M., Wakida, T., Yoshiura, Y., & Igarashi, I. (1994). Cellulase treatment of cotton fabrics, Parts I & II. *Textile Research Journal*, *64*, 219–222.

Li, Y., & Hardin, I. (1998). Treating cotton with cellulases and pectinases: Effects on cuticle and fiber properties. *Textile Research Journal*, *68*, 671–679.

Linder, M., & Teeri, T. T. (1997). The roles and function of cellulose-binding domains. *Journal of Biotechnology*, *57*, 15–28.

Ma, W., Zhang, S., Tang, B., & Yang, J. (2005). Pretreatment of cotton with poly(vinylamine chloride)for salt-free dyeing with reactive dyes. *Coloration Technology*, *121*, 193–197.

Morris, H., & Hauser, P. (2003). The effects of a cationic reagent on typical finishes. *AATCC Review*, *11*, 17–19.

Paralikar, K. M., & Bhatawdekar, S. P. (1984). Hydrolysis of cotton fibers by cellulase enzymes. *Journal of Applied Polymer Science*, *29*, 2573–2580.

Paul, R., & Teli, M. D. (2010). Swelling of cotton as a tool to enhance the response of cellulase enzymes. *Coloration Technology*, *126*, 325–329.

Paul, R., & Teli, M. D. (2011). Effect of swelling and reactive dyeing on the accessibility of cotton to cellulase enzymes. *Journal of Applied Polymer Science*, *121*, 1946–1950.

Pazarlioglu, N. K., Sariisik, M., & Telefoncu, A. (2005). Treating denim fabrics with immobilized commercial cellulases. *Process Biochemistry*, *40*, 767–771.

Ran, J., Jia, S., Liu, Y., & Wu, S. (2009). Charaterization of cellulase under various intensities of static magnetic fields. *Catalysis Communications*, *11*, 91–95.

Rastegari, A. A., Bordbar, A. K., & Taheri-Kafrani, A. (2009). Interactions of cellulase with cationic surfactants: Using surfactant membrane selective electrodes and fluorescence spectroscopy. *Colloids and Surfaces B: Biointerfaces*, *73*, 132–139.

Rattanaphani, S., Chairat, M., Bremner, J. B., & Rattanaphani, V. (2007). An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan. *Dyes and Pigments*, *72*, 88–96.

Saravanan, D., Vasanthi, N. S., & Ramachandran, T. (2009). A review on influenctial behaviour of biopolishing on dyeability and certain physico-mechanical properties of cotton fabrics. *Carbohydrate Polymers*, *76*, 1–7.

Sariisik, M. (2004). Use of cellulases and their effects on denim fabric properties. *AATCC Review*, *1*, 24–29.

Sarkar, A. K., & Etters, J. N. (2001). Kinetics of the enzymatic hydrolysis of cellulose. *AATCC Review*, *3*, 48–52.

Schimper, C. B., Ibanescu, C. I., & Bechtold, T. (2006). Technical aspects in enzymatic hydrolysis of cellulosics. *Lenzinger Berichte*, *85*, 107–112.

Schimper, C. B., Ibanescu, C. I., & Bechtold, T. (2011). Surface activation of dyed fabric for cellulase treatment. *Biotechnology Journal*, *6*, 1280–1285.

Sild, V., Stahlberg, J., Pettersson, G., & Johansson, G. (1996). Effect of potential binding site overlap to binding of cellulase to cellulose: A two-dimensional simulation. *FEBS Letters*, *378*, 51–56.

Traore, M. K., & Buschle-Diller, G. (1999). Influence of wetting agents and agitation on enzymatic hydrolysis of cotton. *AATCC Review*, *12*, 51–56.

Valjamae, P., Sild, V., Pettersson, G., & Johansson, G. (1998). The initial kinetics of hydrolysis by cellobiohydrolases I and II is consistent with a cellulose surface-erosion model. *Europe Journal of Biochemistry*, *253*, 469–475.

Vascocelos, A., & Cavaco-Paulo, A. (2006). Enzymatic removal of cellulose from cotton/polyester fabrics blends. *Cellulose*, *13*, 611–618.

Vishnu Vardhini, K. J., & Selvakumar, N. (2006). Biopolishing enzymes and their influence on the properties of cotton materials – A review. *Colourage*, *53*, 45–52.