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Research Article

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Eco friendly modification of cotton using enzyme and chitosan for enhanced dyeability of curcuma longa

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ABSTRACT

Modification of fabric improves dyeability but the discharge of toxic, non -biodegradable substances as effluent pollute the environment and it is becoming a serious concern for textile industries. In the current study enzymatic and chitosan modification were done on woven cotton fabric in order to enhance the dye ability and pollution load. Cellulase, an eco friendly biodegradable, non toxic and environmentally benign enzyme removes protruding fibers, fuzz on the surface of fabric by the process called bio polishing. It improves fabric hand feel and appearance and also dye uptake. Chitosan is a bio polymer present as chitin in crab shell was prepared and crosslinked with the fabric using citric acid and sodium hypophosphite at 110°C. Modifications are evidenced by morphology changes inferred from SEM analysis. FTIR studies confirmed the fixation of chitosan on fabric. Unmodified and modified fabrics are dyed with natural dye curcuma longa(turmeric) .Dye uptake and K/S values of dyed fabric were evaluated from UV-Visible and CCM analysis. Washing fastness was measured to compare the effectiveness of dyeing. The eco friendly modifiers enzyme and chitosan enhanced the dyeability and washing fastness of dyed fabric.

Keywords: Biodegradable, Biopolishing, Cellulase, Chitosan, *Curcuma longa.*

INTRODUCTION

Cotton is the most widely used textile material because of its properties such as relatively low cost, fine cross section, high strength, durability, thermal stability, good mechanical properties, moisture absorbency and comfort to wear. Cotton can be modified by a number of techniques to improve their performance characteristics such as dye fixation, soil repellency, crease resistance and flame retardant [1]. Chemical modification of cotton will improve their dye ability, but at the same time it will pollute the environment to greater level. Modification can also be possible with the help of biocatalysts (enzyme) and biopolymers like chitosan is an environmentally benign route.

Enzymes are high molecular weight proteins secreted by microorganism. They are preferably used in textile industry due to their bio-degradability, non- toxicity and consume less energy and chemicals. The application of enzyme on cotton materials gained popularity after the commercial success of cellulase enzyme launched by Novo Nordisk in Japan in1986. Cellulase is derived from both fungal and bacterial sources and they find extensive application in the field of food, pharma, paper and textile industries and used for bio-polishing of cellulose [2]. Cellulase is a complex mixture of three major components such as endoglucanase, cellobiohydrolases and β-glucosidases or cellobiases. Endoglucanase cleaves randomly internal bonds in the amorphous sites and break long polymer chains into shorter chains. Cellobiohydrolases which has tunnel shape showed more pronounced effect on the hydrolysis of glucose chains at the end to produce cellobiose. Finally β-glucosidases convert the cellobiose into glucose. Enzymatic hydrolysis of cellulosic fabrics using cellulase and enhancing ofdyeability was also investigated [3, 4]. Recently enzyme immobiliziation technology has been used in different applications [5-7].

Chitosan [(1-4)-2-amino-2-deoxy-D-glucose] is a water insoluble amino polysaccharide obtained from chitin by deacetylation process. It is a copolymer of N-acetyl glucosamine and glucosamine units and generally contains more than 90% glucosamine units and found in the shell of crabs and shrimps [8]. Chitosan contains two main functional groups, namely hydroxyl and amino groups as well as ether linkages. Chitosan and cellulose have similar structure with the same β-glucosidic linkages and the main difference is the presence of primary amino groups at most of the C-2 position in chitosan, in place of the hydroxyl groups in cellulose. Most of the characteristic properties of chitosan are due to the high content of primary amino groups at C-2 position and it is also possible for antimicrobial property [9]. It is an inexpensive biodegradable, non-toxic compound and useful in many areas of applications such as waste water treatment, food and textile industry and recently in drug industry as a hydrating agent in cosmetics [10].However, it was reported that chitosan as an auxiliary in dyeing and printing of textile materials and leathers [11]. Chitosan blended beads are used for removal of copper, cadmium lead and nickel ions from aqueous solution [12] Chitosan treated wool showed a better dyeability [13]. It was investigated that pretreatment of cotton with chitosan eliminates the difference in colour between dyed immature and mature cotton fiber in the dyeing process with direct dyes and it was also confirmed by other researchers [14, 15]. Chitosan fixation on cotton by crosslinker citric acid and sodium hypophosphite was established by researchers [16]. Natural dyes are used for food coloring, painting, and textile dyeing [17-20]. They have shown a greater interest in textile dyeing because they are more ecofriendly than synthetic dyes. Curcumin (1, 7-bis (4-hydroxy-3-methoxy phenyl)-1, 6-heptadione-3, 5 - dione) is a yellow pigment, present in rhizome of Curcuma Longa and which is widely used in food industry. The present work is aimed to enhance the dye ability of cotton fabric with eco-friendly modifiers enzymes and chitosan. SEM images proved the surface morphology change. FTIR studies on fabric, chitosan and chitosan treated fabric confirmed the binding of chitosan on fabric. UV-Visible Spectrophotometer and computer color matching analysis were done to study percent of dye uptake and K/S of all modified dyed fabric. Dye ability and washing fastness was enhanced in modified fabrics compare to unmodified fabric.

EXPERIMENTAL SECTION

Materials

Bleached woven cotton fabric was purchased from Tirupur Industries, India. Acid cellulase and other auxiliary chemicals such as sodium acetate, hydrochloric acid, sodium hydroxide, and acetic acid were purchased from Hi Media, India. Turmeric was purchased in local market. Chitosan was prepared in the laboratory from crab shell collected from local market.

Apparatus

Characterization of samples was done using UV- Visible spectrophotometer, Scanning electron microscope (Hitachi-S-3000N Model). FTIR (Perkin Elmer make Model Spectrum RX1 (Range 4000 cm^{-1} - 400 cm^{1}) spectrophotometer and Computer color matching (Premier color Scan SS6200A) instruments.

Preparation of chitosan

Crab shells are well powdered and demineralized by treatment with 5% hydrochloric acid. Chitin is insoluble in water, which was deacetylated by treatment with 40 % sodium hydroxide at 120°C for 2 hours under constant stirring. Chitosan, as colloidal suspension was centrifuged and the pasty mass was dried. Chitosan was obtained as off white powder with 70% deacetylation.

Modification of fabrics

Well bleached woven cotton was subjected to four types of treatments, such as enzyme treatment, chitosan treatment, and enzyme and chitosan treatment and finally with chitosan and enzyme to produce four types of modified fabricssuch as Enzyme modified fabric (M_1), Chitosan modified fabric (M_2), Enzyme and chitosan modified fabric (M_3), Chitosan and enzyme modified fabric (M_4). After each treatment the effect of modification was assessed by comparing dyeability of modified fabrics with unmodified fabric. Wash fastness of all dyed samples were measured by the (ISO 105-C03; 1989, Geneva), testing method.

Modification of fabric by enzyme

A weighed quantity of fabric was immersed in a bath containing 3 % enzyme at pH 4.5 and temperature 55°C under agitation for one hour by keeping material liquor ratio(MLR) 1:10. The optimized condition was obtained after evaluating parameters (a)concentration of enzyme(1.0, 2.0, 3.0, 4.0, & 5.0 %), (b) temperature(40, 45,50, 55 & 60°C) (c) pH (4.0, 4.5, 5.0, 5.5 & 6.0) (d) time (60, 120, 180, 240 & 300 minutes) and (e) MLR(1:05, 1:10,1:15, 1:20 & 1:25) parameters. The pH of the bath was maintained at 4.5 using sodium acetate acetic acid buffer. Finally the temperature of the bath was raised to 80°C to deactivate the enzyme activity and the fabric was washed with water and dried at 110°C in hot air oven and weighed. Weight loss percentage (WL %) was calculated as per formula.

$$(WL\%) = \frac{(W_1 - W_2)}{W_1} \times 100$$

W_1 and W_2 are the weight of fabric before and after enzyme treatment**.**

Modification of fabric by chitosan

Fabric was soaked in 1 % chitosan solution (dissolved in 1 % acetic acid (V/V) containing 6 % citric acid and 6 % sodium hypophosphite and squeezed in padding mangle for uniform fixing and dried at 80°C for 10 minutes followed by fixing at 110°C for 5 minutes. Chitosan was crosslinked with cotton through citric acid. The optimized concentration required for modification was evaluated by varying concentration of chitosan from 0.5 to 3.0 % and dye uptake of the fabric.

Modification of fabric by enzyme and chitosan

Enzyme modified fabric (M_1) was treated with chitosan and chitosan modified fabric (M_2) was treated with enzyme as per above said procedures to get enzyme and chitosan modified fabrics (M_3) and chitosan and enzyme modified fabrics (M_4).

Dyeing of modified and unmodified fabrics

Unmodified and modified fabrics (M_0, M_1, M_2, M_3 and M_4) were dyed with 6 % turmeric dye using material liquor ratio 1:10 at 75°C for 30 minutes. Absorbance maximum of dye liquor before and after dyeing was measured using UV-Visible spectrophotometer.

Characterization method

Scanning Electron Microscopic analusus were done to study surface morphology of unmodified and other modified fabrics. Prior to examination, modified textile samples were coated with a thin layer of sputtered gold, using an ion sputter JEOL JFC 1100 device. Samples were analyzed using a scanning electron microscope JEOL JSM 6390 at 15kV. Dye exhaustion was calculated from absorbance maximum of dye liquor before and after dyeing using UV-Visible spectrophotometer (JASCO V-530). The dye uptake or exhaustion was calculated as follows

% of dyeuptake = $(1-A_1/A_2) \times 100$

A_1 and A_2 are absorption maximum of dye liquor before and after dyeing.

FT-IR spectral anlysis were done for a) Cotton (M_0), (b) Chitosan, (c) Chitosan modified fabric (M_2) in order to confirm the fixation of chitosan on fabric. Computer Color Matching studies of unmodified and modified dyed fabrics helped to arrive K/S values. Washing fastness of all dyed samples was measured by the ISO 105-C03 testing method. Dyed samples were taken, stitched with one of the shorter side of the adjacent bleached fabric and put in to the bath containing 3 gpl of soap, 2 gpl of sodium carbonate and 1:30 MLR ratio at 60°C for 30 minutes. Then the specimen was washed with hot water, cold water and dried. The change in shade and stain was compared for both modified and unmodified fabric.

RESULTS AND DISCUSSION

Effect of enzyme treatment

The parameters such as concentration of enzyme (A), Temperature (B), pH (C), Time (D) and Material liquor ratio (E) play a significant effect on surface modification. It is depicted in (Table 1). Weight loss percent determines the extent of bio polishing. Weight loss percent increases with the raise of enzyme concentration, but strength loss occurs at higher concentration. Therefore 3 % concentration is sufficient to produce effective surface smoothening. Each enzyme has an optimum temperature to exhibit maximum activity. Acid cellulase shows maximum enzyme activity at 55°C above which activity decreases and still at higher temperature the activity is stopped. Weight loss percent increases when the pH of bath was raised but beyond 4.5 there is gradual decrease due to loss of enzyme activity. Hence the optimum pH required for maximum activity is 4.5. When treatment time was increased weight loss percent increased to a greater level but at the same strength loss occurs due to rupture of normal fibers. An optimum duration of 60 minutes exhibits maximum activity. Material liquor ratio has marginal effect on enzyme activity therefore 1:10 ratio is enough to bring better surface modification, above which effect was diminished due to dilution of concentration. Dye uptake of the modified fabrics for each parameter proves that better dye ability for the above conditions.

Table: 1 Weight loss percent of fabric

S.No	**A (%)**	**WL %**	**B (°C)**	**WL (%)**	**C**	**WL %**	**D (min)**	**WL (%)**	**E**	**WL %**
1	1.0	3.32	40	5.12	4.0	7.23	60	8.62	1:05	8.39
2	2.0	4.92	45	6.33	4.5	7.98	120	9.76	1:10	8.84
3	3.0	8.71	50	7.96	5.0	8.47	180	10.22	1:15	8.24
4	4.0	9.26	55	8.97	5.5	9.03	240	11.04	1:20	7.79
5	5.0	10.45	60	8.41	6.0	7.11	300	12.00	1:25	7.16

(A-Concentration of enzyme, B-Temperature, C- pH, D-Time, E-Material Liquor Ratio, WL – Weight loss)

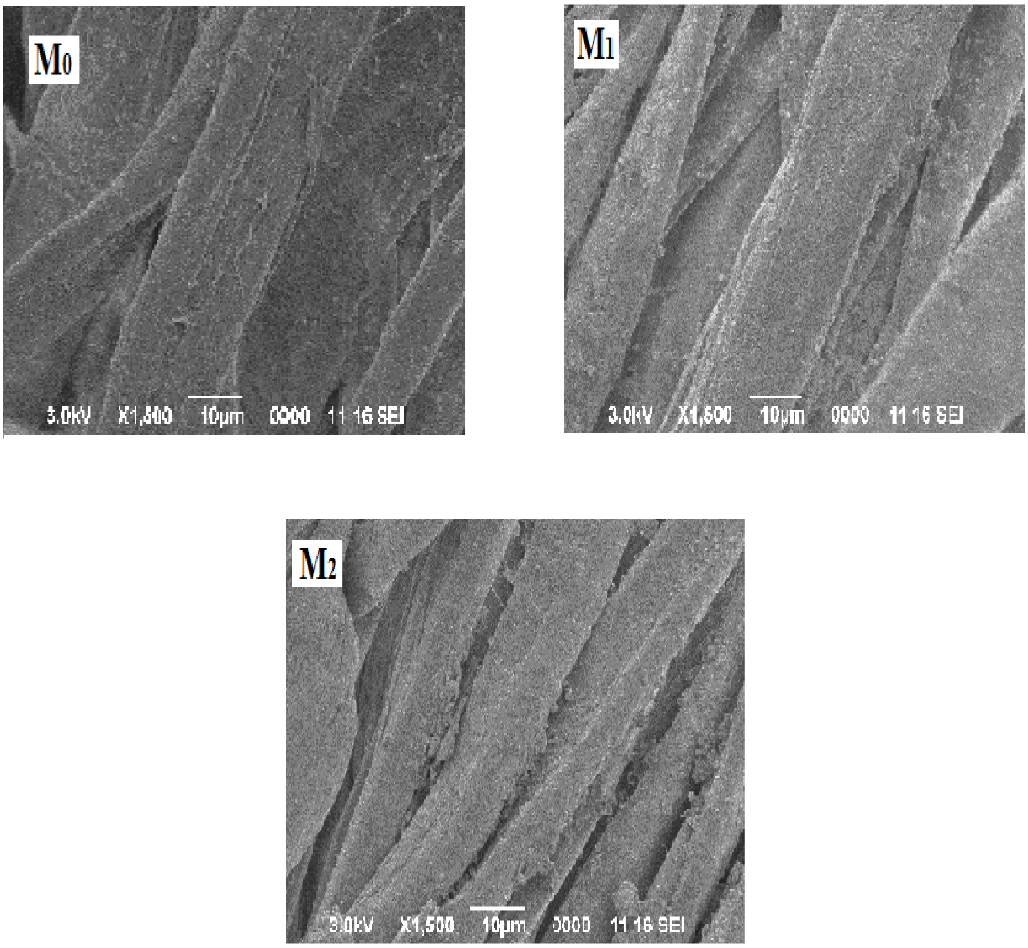

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Fig. 1.SEM images of unmodified (M_0), enzyme modified (M_1) and chitosan modified (M_2) fabrics

Effect of chitosan treatment

The impact of chitosan modification on woven cotton fabric (Table 2) was evaluated from their dye uptake with turmeric. Out of the three different concentrations of chitosan the 1.0 % concentration of chitosan produced comparatively better dye uptake. Therefore higher concentration of chitosan is not necessary to bring better dye ability.

Characterization

Scanning Electron Microscopic studies on unmodified fabric (M_0), enzyme modified fabric (M_1) and chitosan modified fabric (M_2) are depicted in (Fig. 1).Unmodified fabric has uneven surface due to protruding fibers, but enzymed treated fabric shows smooth surface by the removal of fuzz. Chitosan modified fabric shows slight changes on the surface appearance as result of fixation of chitosan.

FT-IR spectrum of a) Cotton (M_0), (b) Chitosan , (c) Chitosan modified fabric(M_2) was depicted in Fig.2. The spectrum of cotton shows a broad peak for OH stretching of cellulosic hydroxyl group in the range 3300-3500cm^{-1} and a complex band between 1000- 1420 cm^{-1} due to OH in plane bending of cotton. Chitosan shows broad peak at 3390 cm^{-1} for stretching vibration of –OH group and a band at 1590 cm^{-1} characteristic of the free -NH_2 of glucosamine unit. Fabric ($M_{2)}$ produces a broad peak characteristic of –OH stretching vibration of cellulose and chitosan at 3371 cm^{-1} and free NH_2 group of chitosan at 1583 cm^{-1} respectively.

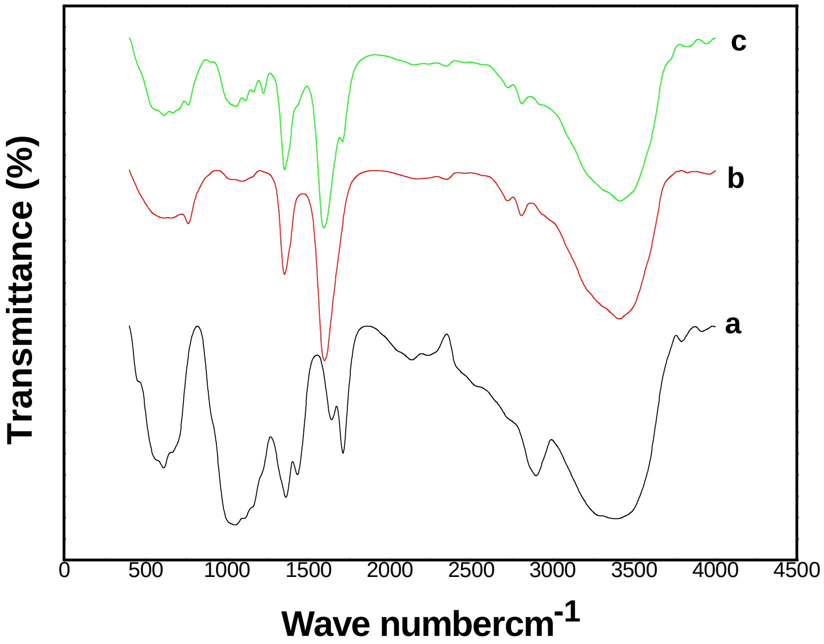

Fig.2. FT-IR spectrum of a) Cotton (M_0), (b) Chitosan, (c) Chitosan modified fabric (M_2)

UV-Visible spectrophotometer analysis of dye liquor produces absorption maximum of dye .The dye uptake of unmodified and modified fabrics are shown in (Table-2). Unmodified fabric has low dye uptake than all other modified fabrics. Enzyme modified fabric shows higher percent, because of surface smoothening. But chitosan modified fabric exhibits still higher uptake than fabric (M_1). The free amino group of chitosan provides cationic environment to fabric thereby more dye molecules are hydrogen bonded with the nitrogen atom of amino group. Modified fabric (M_3) shows still more dye uptake, the cause for this raise is biopolishing and the presence of free NH_2 of chitosan. But modified fabric (M_4) has comparatively less dye uptake than fabric (M_3). Chitosan presence influences inhibition effect to enzyme and biopolishing was not happened, thereby the dye uptake level decreased, but not as poor as unmodified fabric. Hence chitosan modification produces predominant change than biopolishing process. Modification process enhanced the dye uptake of fabric higher percent than unmodified fabric.

Computer colour matching provides still clear evidence for enhancement of dye ability from the K/S values as in (Table-2). While comparing the unmodified fabric with all other modified fabrics, chitosan modified fabric (M_2) shows high K/S, due to more dye absorption. Enzyme treated fabric also produces better K/S since surface smoothening enhances the dye uptake but it is not so high as in fabric M_2 .Fabric M_3 shows higher K/S value next to fabric M_2 but it was less in fabric (M_4).

Washing Fastness

Washing fastness is usually poor for natural dyes.The washing fastness of all fabrics is depicted in (Table-2). All the four modified fabric produces better wash fastness than unmodified fabric. Chitosan based modified fabrics shows better result than enzyme modified and unmodified fabric. Dye molecules are strongly hydrogen bonded with free amino group of chitosan and strongly retained on the fabric

Table: 2 Measurement of dye ability and washing fastness

Fabrics	**Dye uptake**	**K/S**	**Washing fastness**	
			Change in shade	**Change in stain**
Unmodified (M_0)	72.20	6.46	1	1
Enzyme modified (M_1)	82.20	7.86	2	2
Chitosan modified (M_2)	87.50	9.24	4	3
Enzyme and Chitosan modified(M_3)	85.00	8.78	3	3
Chitosan and Enzyme modified(M_4)	83.50	8.18	3	3

CONCLUSION

Dyeability of cotton fabrics can be improved in better way using chemicals, but the pollution load increases due to non-biodegradability and toxic nature of the chemicals. Hence in this work an ecofriendly modifiers enzyme and chitosan are used to improve dyeability. Modifiers enzyme and chitosan are non-toxic, biodegradable and biocompatible substance therefore environment is protected. Fabrics are modified with enzyme and chitosan individually and also combined together to check the effect of dye uptake. All modification is effective, of which chitosan modification and chitosan involved other modification showed higher dye uptake with better washing fastness. Enzyme and chitosan modification was proved by SEM analysis and FTIR spectrum confirmed the existence of chitosan. Improvement in dyeability was well established from UV-Visible spectrophotometer and Computer colour matching analysis. Washing fastness was satisfactory in modified fabrics than unmodified fabric. It can be further improved if ecofriendly mordants are used. Hence enzyme and chitosan modification played a remarkable role in enhancement of dye uptake and washing fastness of natural dye turmeric in greener route.

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