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ENZYMATIC PRETREATMENT OF GREY COTION FABRIC FOR IMPROVING DYE UPTAKE, LUSTUR AND HAND FEEL USING FUNGAL CELLULASE

Gumel, B. U.,[1] Gumel, S.M., [1]Bawa, A. A.[2] and Auwal, A. S.[1]
[1]Department of Pure and Industrial Chemistry, Faculty of Physical Sciences Bayero University Kano, P.M.B. 4011, Kano State, Nigeria.
[2]Chemistry Department, College of Art and Sciences P.M.B. 3145 Kano state, Nigeria.
Corresponding Author: bashirgumel69@gmail.com; Tel: +2348066606828

ABSTRACT
Cellulase enzyme was extracted from pineapple peel substrate using Aspergiluss niger. Because enzymes are sustainable alternatives to harsh toxic chemicals used in the Textile Industries. Cotton fabrics were treated with cellulase at variable concentrations at a pH of 5.5 and 55°C. Changes in various properties of the treated fabrics like weight loss, lusture, soft touch and overall dyeing properties were investigated. The results obtained show that cellulase have successfully removed staple fibres from the fabrics and thus, yield a glabrous appearance and soft touch of the treated fabrics; furthermore, it was established that percentage dye uptake and fastness properties of the fabrics were greatly improved as confirmed by the FTIR spectral analysis and UV- visible spectrophotometric analysis of the absorbance maximum of the dye liquor before and after dying.
Key Words: Cellulase, Aspergillus niger, pre- treatment, cotton fabric and dye uptake.

INTRODUCTION

Enzymes are friendly alternative to the harsh toxic chemicals used in textile industries. Cellulase is the most popular and versatile enzyme used in textile wet processing for biopreparation, biopolishing and softening of cellulosic fibres (Muhammad, 2015). Cellulases can also be used in so many industrial applications, such as paper and pulp, food, animal feed, fuel, chemicals and waste management and pharmaceutical industries, to mention but few. Cellulases are widely applied to cotton, flax hemp, ramie and lyocell fibres in order to improve touch and looks (Isah, 2014). They are used for anti-filling of cotton, defibrillation of lyocell, creating surface effects and super softness. The biopolishing is achieved as a result of the ability of the cellulase to degrade fuzz-fibres of cotton, flex and viscose by hydrolysing the repeat unit of B-1,4-glycosidic bonds in cellulose molecules and has been used for different cellulosic textile (Ping *et al.,* 2015).

Cotton is the most widely used natural fiber and the king of fibres used for the world's apperals (Mohammad, 2015). It is also used in household and industrial products due to its fairly good strength moisture absorption and wicking properties. Thus provides comfort to wear (Sunita and Shahnaz, 2014). However, raw cotton fibre yarn or fabrics contains various kinds of impurities like motes, dirt, chemical residues, metallic salts and immature fibres which affect the quality of the finished textile products (Ping *et al.,* 2015).

In this study, cotton fabric was modified using eco- friendly cellulase which is effective in removal of such impurities and protruding fibers (Shah, 2013).

Cellulase was best qualified for enzymatic pre-treatment of cotton due to the fact that it requires relatively low energy which allows the modification to be done in a controlled manner, mild processing temperature, low energy consumption and without excessive damage to the fabric (Mohammad, 2015; Bashir, 2018).

Cellulase treatment or cellulase- catalysed modification of cellulose is strongly influenced by factors like, pH, temperature, time and agitation. However, the optimum pH for a particular cellulase treatment depends on its origin. For fungal cellulase of *Aspergillus niger* origin (acid cellulase) worked best at pH 4.5-5.5, Temperature of 45-55°C (Shah, 2014). This study is aimed to measure the cellulase producing ability of *A. niger* from pineapple substrate and investigate the effects of enzymatic modification of grey cotton fabrics on the surface smoothness, softness, dye uptake and the fastness properties of the dyed samples.

MATERIALS AND METHODS

The substrate used in the production of Cellulase was pineapple peel obtained from a local fruits vendor at Old Campus Beyero University Kano.

The reagents used for the study were, Sodium hydroxide, Sodium hypochlorite, Sodium sulphate (Glaubal salt), Sodium trioxocarbonate (IV) *Aspergillus niger,* congo red solution, C.I. reactive red 22 (Remazol Red B), C.I. Direct Yellow 6Gwhich were analytical grade reagents.

Extraction of Cellulase From Pineapple Peel Waste

The pineapple peel substrate was washed thoroughly with running tap water and then rinsed with distilled water several time to remove the surface dirt and then oven dried at 50°C for 24 hours. The dried sample was size reduced and then weighed. The weighed sample was treated with 5% NaOH, with material to liquor ratio of (1:20) for 30 minutes. The pasty mixture was then autoclaved at 121°Cfor 1 hour. It was then washed to neutrality after cooling and then oven dried for 24 hours (Kannahi and Elangeswari, 2015).

Media Preparation

The media used for the study was (Zapek dox; it was prepared from the following chemicals, all per litre of distilled water).

2g of $NaNO_2$, 1g of KH_2PO_4 $7H_2O$, 0.5g of $MgSO_4$ $7H_2O$, 0.5g of KCl, 0.01g of $FeSO_4$ $7H_2O$, 0.5g of pepton and 0.5g and yeast extract (Ajayi and Adedeji, 2015).

500ml of the media was added into 1 litre conical flask and 15g of the pre treated sample (pineapple peel carbon source) was added to the flask and labelled property.

1g of carboxy methyl cellulase (C.M.C) was used as control in 250ml conical flask and the pH of the media was adjusted to

The media was sterilized in an autoclave at 121°Cfor 15 minutes as reported by (Milala *et al.,* 2015), the experiment was carried out in triplicates.

Media Fermentation

The media was inoculated with a disc of *Aspergillus niger* using 6mm cork borer and incubated at 30°C in an orbital shaker at 120 r.p.m, the culture was allowed to grow for the period of nine days with the harvest of the cells at every 48 hours intervals by centrifugation at 6000g for 15 minutes.

After incubation, the cell free culture supernatant was filtered with N0- 1 Whatman filter paper (185mm) and used as crude enzyme (Bhat, 2000).

Screening of *Aspergillus niger* for cellulase activity; A loopful of the grown culture of *Aspergillus niger* was inoculated on the media plates and amended with 1 % C.M.C as carbon source. The inoculated plates were incubated for three days at 25°C and then the fungal growth appeared on the plates; after incubation the plates were stained with 10ml of 1% congo red solution and allowed stand for 15 minutes at ambient temperature. It was then de- stained with 1M NaCl for 15minutes. Zone of hydrolysis was observed around the colony and recorded when the enzyme had utilized the cellulase (Kannahi and Elangeswari, 2015). The crude cellulase was purified using Ammonium sulphate precipitation method (Kannahi and Elangeswari, 2015). Crystal Ammonium sulphate (analytical grade) was added to the supernatant at (30% saturation, 222g/ Litre) with stirring to a final saturation of 80% (592g/litre) so as to precipitate the enzyme (Kannahi and Elangeswari, 2015). The purification process was carried out at 4°C.The suspension was then stirred for 1 hour and kept at 4°C for 24 hours and then the resulting precipitate was removed by centrifugation 4000 rpm at 10 minutes interval. The yield was recorded and the pH of the precipitate was recorded (4.71) which shows that the enzyme was acid cellulase.

Modification of Grey Cotton Fabrics Using Cellulase

1g each of grey cotton fabrics was soaked in a bath containing variable concentration of the cellulase (0.5,1.0,1.5,2.0 & 2.5%) at constant pH of 5.5 and temperature of 55°C with constant agitation for one hour with material to liquor ratio of 1:10. The temperature of the bath was raised to 100 °C to stop the activity of the enzyme. The fabrics were washed to neutrality and oven dried at 70°C and reweighed. The percentage weight loss of the fabrics after modification was calculated using equation (1)

$$\%\ WL = \frac{W - W_2}{W_1} \times 100 ....(1).$$

Where,

W_1, & W_2 are weights of the fabrics before and after enzymatic treatments and WL is the weight loss

Dyeing of Cellulase Modified and Unmodified Cotton Fabrics

The modified along with the unmodified grey cotton fabrics were dyed using direct yellow 6G and reactive red 22 and the absorption maximum of the dye liquor before and after dyeing were measured using UV- Visible spectrophotometer.

Dyeing with C. I. Direct Yellow 6G

Cellulase modified and unmodified fabrics were dyed using the method adopted by (Abdul-Rahaman *et al.,* 2017). The fabrics were soaked in a bath containing (6% O.W.F) direct dye, at 40°C for 15 minutes, (20% 0.W.F) NaCl was added to the dye bath in two portions at 15 minutes intervals. The temperature of the bath was gradually raised to boil for 15 minutes. The dyeing process was continued for 40 minutes. The dyed fabrics were removed from the bath and washed to neutrality and air dried.

Dyeing with C.I Reactive Red 22

C.I Reactive Red 22 was applied to cellulase modified and unmodified cotton fabrics at (6% O.W.F) 80g/L glaubers salt and 20g/L sodium trioxocarbonate (iv) with materials to liquids ratio of 1:50 the dyeing was carried out at 30°C for 10 minutes and the temperature of the bath was raised to 60°C for 60 minutes with constant agitation. The fabrics were removed and rinsed in cold water and air dried.

Characterization

The spectral analysis of cellulase modified and unmodified fabrics were achieved suing FTIR spectroscopy (carry 630) as follows: A drop of the cellulase suspension was placed on diamond plate of the spectroscopy to obtain the spectrum of the enzyme.While cellulase modified and unmodified fabric samples were analyzed by placing each of the sample directly on the diamond plate to obtain the spectrum of each sample.

Physical Test of Modified Fabrics

Cellulase modification on grey cotton fabrics led to a change in some properties of the fabrics. Hand feel (softness, flexibility and smoothness) test and moisture absorption test were used to asses these changes.

Hand feel test (luster)

Both modified and unmodified cotton fabrics were examined visually and touch with hand to ascertain the change in softness, flexibility and smoothness (Luster) and rated according to the procedure of American society for testing materials (AST, 1991) and the American association of textile chemists and colorists (AATCC, 1991).

Measurement of Dyes Exhaustion

The amount of the dye absorbed by both modified and unmodified fabrics for C.I direct yellow 6G and C.I reactive red 22 was measured by calculating the difference in the absorbance maximum of the dye liquor before and after dyeing using UV-Visible spectrophotometer (Model Lamda 35). The absorbance values for reactive and direct dyeing were recorded and the percentage dye exhaustion was calculated using equation (2).

$$\%\text{ dye uptake} = \frac{A_1 - A_2}{A_1} \times 100 \quad \text{...............(2)}$$

A, & A_2 are the absorbance maximum values for the dye bath before and after dyeing.

Measurement of Fastness Properties

The fastness properties of the both modified and unmodified fabrics was assessed according to the standard procedures

Wash- Fastness

The dyed fabrics were soaked in a bath each containing 3g/L of anionic soap, 2g/L Na_2CO_3 and material to liquor ratio of 1:50 at 60°C for 30 minutes (Rahman *et al.,* 2007) the fabrics were washed in running tap water and then rinsed in distilled water and air dried. Change in shade was assessed using grey scale (Model: 150 105 AO_2) and (150 105 A03, BS 100 –A03 1978) respectively.

Light - Fastness

The dyed fabrics were exposed to artificial light along side with dyed standard blue wool fabrics for 96 hours using tungsten filament (Burkinshaw and Kumar 2009). After the exposure the test samples and the standard were checked to determine the fading characteristic of both the sample and the standards. The exposed and the unexposed portions of the samples were compared with standard blue wood; the rating given is the number of standard that exhibits the same degree of contrast.

RESULTS AND DISCUSSION

Percentage yield of cellulase obtained from pineapple peel. The percentage yield of cellulase obtained from the alternative treatment and fermentation of the substrate is depicted in Table 1.

Table 1: % yield of cellulase extracted from pineapple peel substrate.

Weight of the substrate (g)	**150g**
% weight after alkaline treatment	15.33%
% weight after fermentation	66.1%
% weight of the product	7.04%

From the Table 1, it was observed that cellulase extraction from pineapple peel substrate is cost effective, although it is time consuming. It was established that out of 150g of the substrate used for the extraction only 10.5g was recovered as required cellulase as confirmed by the FTIR analysis. The pH of the fruit extract revealed that the extract is acid cellulase.

Production of Cell Wall Degrading Enzymes

The extract obtained from the pineapple waste has showed favourable cellulase activity, while the control indicates no detectable enzyme activity. This further confirmed that the enzyme obtained is of fungal origin (Ajayi and Adedeji 2015).

Effects of pH on the Activity of The Enzyme
Cellulases are pH sensitive as such the pH of the reacting mixture during process has against the activity of the enzyme. Because the activity of cellulose increase with increase in pH and then gradually decrease after the optimum pH was attained (pH 5.5 – 6.0).

Fourier Transform Infrared Spectroscopic Analysis
The FTIR spectral analysis of the cellulase extracted from pineapple peel substrate and the cellulase treated cotton fabrics revealed that the enzyme is of fungal origin and effectively removed the staple fibres and enhanced excellent dyeing. The results are depicted in table 2.

Table 2: FTIR spectra data of cotton, fabrics, cellulase and cellulase modified fabrics

Absorption peaks of cotton	Absorption peaks of cellulase (cm^{-1})	Concentration of cellulase and their absorption peaks (cm^{-1})					Functional groups
-	-	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**	
3373	3239	3338	3291	3337	3274	3270	0H
-	(3275)	3275	3275	3281	3287	3289	NH
2892	2898	2800	2898	2898	2892	2902	CH_2
1657	1637	16391	1639	1639	1639	1639	C=0
1539	-	-	-	-	-	-	NH_2
1317	1320	1337	1335	1335	1365	1317	CH-stretching
-	1428	1428	1428	1428	1428	1428	C-0 stretch vibration

From Table 2, it was established that both cotton fabrics, cellulase and cellulase modified fabrics yield absorption at 3393, 3239, 3338, 3340, 3337 and 3350 cm^{-1} which indicate the presence of O-H stretching vibration in the fabrics. The decrease in intensity of absorption peaks in the cellulase and the cellulase modified shows that the cellulase has effectively removed the staple fibres from the fabrics. While peaks at 1600 cm^{-1}1650cm^{-1} indicates the presence of CH_2 stretching in the peptide bond in the amino acids of the enzyme and the hemicellulases of the cotton fabrics (Shah, 2013). Peaks at 2800cm^{-1} – 2920cm^{-1} were due to CH_2-stretching vibration in glucopyranose of both the cotton, cellulase and cellulase modified fabrics. However, absorption bands at 1337, 1365 and 13117cm^{-1} appeared on the enzyme modified fabrics which shows variation in the intensive due to the variation in insensitive and the pH of the modifier. Absorption bands at 1428 cm^{-1} throughout cellulase and cellulase modified fabrics further confirmed the action of cellulase in enhancing dyeability of cotton and hence conferring optimum surface something effect.

Effects of Enzymatic Treatments on Cotton Fabrics
The pH of the cellulase extracted from pineapple was found to be 4.71 which show that the cellulase is an acid cellulose, the concentration of the extract (cellulase) temperature and the duration of the treatments have great effect on the surface modification of cotton fabrics (Sheila *et al.,* 2013) such effect can be explained in terms of hand feel, weight loss and the moisture absorption of the treated fabrics.

Effect on hand feel: Cellulase modified fabrics have show high degree of softness than the unmodified fabrics. These results could be due to effective removal of the staple fibres by the action of the enzyme.

Effects on weight loss: It was established that the concentration of cellulase and the duration of the treatments have great effect on the surface modification of cotton fabrics the result are depicted in the Table 3:

Table 3: Change percentage weight loss of cellulase modified fabrics

Duration of the treatments (minutes)	Concentration of cellulase and their corresponding percentage weight loss.				
	0.5	**1.0**	**1.5**	**2.0**	**2.5**
60	3.6	5.5	6.0	7.2	10.2
90	6.7	7.4	8.0	10.0	11.8
120	7.1	8.7	9.0	10.2	12.4

From table 3, it was observed that percentage weight loss increases in concentration dependant manner which is proportional to the duration of the treatment. However, at a concentration above 2% per gram of the fabrics leads to strength loss of the fabrics. Thus, 2% is the optimum concentration of cellulase required to give effective surface smoothness on grey cotton fabrics at 55°C, pH 5.5, and 60minutes. At higher temperature (70-100 °C) variation of the enzyme activity further confirm the effectiveness of these conditions.

Effects of cellulase modification on percentage dye uptake

The UV-visible spectrophotometric analysis of the absorption maximum of the dye liquor before and after dyeing confirm that the dye uptake of cellulase modified fabrics is much higher than the unmodified fabrics. This is due to the effective removal of the protruding fibres by the action of cellulase. Yet, dyeing with reactive red 22. Yields better dye uptake than the direct yellow 6G as shown in table 4

Table 4: percentage dye exhaustion of cellulase modified and unmodified cotton fabrics.

Dyes	Concentration of cellulase on the fabrics and their percentage exhaustion					
	0.5	**1.0**	**1.5**	**2.0**	**2.5**	**Unmodified cotton fabrics**
C. I. Direct yellow 6G	`48.36	56.61	74.80	63.86	62.60	54.00
C. I. reactive red 22	7.5.50	82.15	85.64	78.93	70.24	78.00

Table 5: Effects of Cellulase Modification on Fastness Properties

Dyes shade (6%)	Concentration of cellulase (%)	Wash fastness: Change in colour	Wash fastness: Colour stain	Light fastness
	0	4	4.5	6
C.I Reaction Red 22	**0.5**	4	4.5	7
	1.0	5	5	7
	1.5	5	5	7
	2.0	5	5	7
	2.5	5	5	7
C.I Direct Yellow 6G	**0**	3	3-4	3
	0.5	3	3-4	4
	1.0	4	3-4	5
	1.5	4	4	5
	2.0	3	3-4	4
	2.5	4	4	5

Properties of grey cotton fabrics dyed with C.I Direct yellow 6G and C.I reactive red B

From table 5, it was observed that cellulase modified fabrics were found to have excellent fastness to bath light and washing compared to unmodified fabrics. The best performance could be as a result of the effective removal of the protruding fibers and surface smoothening effect by the enzyme.

CONCLUSION

Pineapple waste was used in the production cellulase enzyme. The substrate is one of the examples of domestic and industrial Agro waste that produces large amount of cellulase when hydrolysed by cellulolytic microorganism and instead of being left to degrade naturally, it can be utilized effectively to produce enzyme.

Results obtained from this work revealed that the great potentials of the substrate as a possible raw material for cellulase production using aspergillus niger. Among the agro waste, pineapple peel is more suitable for cellulase production due to high yield and support more cellulase activity than other agro waste like, orange Peel and banana Peel (Bashir, 2018).

The result of this research have shown that application of cellulase extracts on grey cotton fabrics have wonderfully enhance the uptake of the fabrics by effective removal of the staple fibers and hence improved readily available and cheaper substrate that yields optimum quality holds promise for the future.

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