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〈Research Paper〉

Reactive Dyeing of Bio Pretreated Cotton Knitted Fabrics

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Abstract: This study describes the feasibility and optimization of reactive dyeing on bio treated cotton knitted fabrics. For this, cotton knitted fabrics distinctly with two different enzymes, alkaline Pectinases(Scourzyme L®) and Pectate lyases(Bactosol Co. ip liquor®). In this way by increasing the concentration and processing temperature, the access of enzymes towards the fatty and waxy substrate was found to be accelerated. To achieve higher absorbency and whiteness index, a series of experiments was carried out to assure that Pectate lyases enzymes possesses high access towards the fats and waxes at high temperature. To this end, cotton knitted fabrics was dyed without oxidative bleaching step. The Pectate lyases scoured and dyed fabrics showed less color difference when 2% dye shade is used. The fabrics pre-scoured with Pectate lyases showed good the light and washing fastness properties, compared to the conventional and Pectinases dyed fabrics. However pectinases enzymes showed lower activity at high temperature, caused poor wettability and whiteness index of fabrics. The improvement of the accessibility of enzyme to the pectin at higher temperature Pectate lyases treatment before dyeing was found to be useful for subsequent pectin degradation in cotton knitted fabrics.

Keywords: *pectate lyases, alkaline pectinases, cotton knitted fabric, reactive dyeing, wettability*

1. Introduction

Raw grey cotton fibers contain some non-cellulosic impurities which mostly are located on the outer surface of the fibers. The surface layer which contains fats and waxes, organic acids, proteins is responsible for hydrophobic property of cotton fabrics[1]. To obtain better absorbency and wettability, the removal of those impurities present in raw cotton is an essential step for subsequent dyeing and finishing processes[2,15,16]. If this pectin wall can be partially hydrolyzed, then a higher hydrophilic property of the fiber can be obtained without fibers deterioration[3]. Scouring with sodium hydroxide is conventionally carried out at higher temperatures to hydrolyze these waxy compounds, but this treatment requires an extensive rinsing process, thereby cellulose fabrics may also be subject to oxidative damage[4] which reduces their tensile strength. Alkaline scouring may also cause fabric shrinkage and changes in physico-mechanical properties on fabrics, e.g. their handle[5].

Bio scouring with enzymes is one of the most promising alternatives to conventional scouring process. Although a few enzymes such as pectinases[6], cellulases[7], proteases[8], xylanases, and lipases[9] were screened and evaluated for bio scouring.

Pectinases have been proven to be the most effective for cotton fabric scouring treatment[5]. Pectinase is a multi-component enzymatic preparation highly effective in depolymerizing vegetable pectin's with varying degrees of esterification, having several enzymatic activities and differing in substrate preference, reaction mechanism, and action pattern[10].

Pectin lyase(EC 4.2.2.10) catalyzes cleavage of α-1,4-glycosidic linkage in pectin whereas Pectate lyase(EC 4.2.2.2) catalyzes cleavage of α-1,4-glycosidic linkage in pectic acid. These two enzymes cleave linkages by β-elimination and generate products with 4,5-unsaturated residues at the non-reducing end. polygalacturonase(EC 3.2.1.15) catalyzes cleavage of α-1,4-glycosidic linkage in pectic acid by hydrolysis[11]. Lyases have optimal pH around 8.5 and(except for

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pectin lyase) require divalent cations[12].

Nowadays the most commonly used commercial pectinase is Bio prep 3000L from Novozyme, an alkaline pectinase with a standard activity of at least 3000 APSU(alkaline pectinase standard unit). However, the industrial scale application was greatly restricted because of its high cost and inadaptability for the cotton fabrics with inferior quality.

Therefore we have successfully used Bactosol Co. ip liquor®(Pectate lyases) enzyme showed better stability at high temperature and remarkably higher absorbency of cotton knitted fabrics. Pectate lyases enzymes shows great application potential in bio scouring of cotton knitted fabrics.

Adequate absorbency and whiteness index are the necessary elements to ensure better dye evenness and exact color of fabrics.

Reactive dyeing of cotton knitted fabrics treated at their optimum conditions is carried out at two different shade percentages. For color matching per oxidative bleaching of bio pretreated was also done. A systematic approach was conducted to explore the possibilities of improving the dye evenness and reduce color difference through exhaust technique on fabric materials with or without oxidative bleaching.

2. Experimental

2.1 Chemical and auxiliaries

For bio scouring, cotton knitted fabrics(weft knitted single jersey fabric, 150g/m^2, yarn count of 40/1Ne) and a new bio catalyst(Bactosol Co. ip liquor, Clariant®) based on selected pectate lyases and alkaline Pectinases (ScourzymeL, Novozyme®) were used. Nonionic surfactant (Imerol JSF liquor, Clariant®), sequestering agent(Sirrix ANT OX IN liquor, Clariant®) and soda ash were also used. For conventional alkaline scouring and bleaching of cotton knitted fabric sodium hydroxide, hydrogen peroxide, surfactant(Sandopan DTC), sequestering agent(sirrix AK) and stabilizer SIFA were used. For dyeing of scoured and bleached fabrics, Reactive dye Drimarene Cl(Blue HF-CD), leveling agent(Drimagen E2R), sodium chloride, soda ash, Detergent(Ladipur RSK) and acetic acid were used.

2.2 Bio pretreatment of cotton knitted fabrics

Cotton knitted fabrics(~15g each) were subjected to enzymatic pretreatment prior to the dyeing. The bio scouring was carried out in an enzyme bath with (1-5g/l) concentration and a liquor ratio of 10:1 under alkaline pH 8.5. The samples were refluxed in the enzymatic buffer solution for 15min. To enhance the accessibility of enzymes towards pectin and waxes substrates, 1wt.% nonionic surfactant, and sequestering agent were also added into the bath. The samples were then washed in boiling water for 2min to deactivate enzyme followed by washing with distilled water for several times. The treated cotton knits were air dried in the end.

2.3 Conventional scouring of cotton knitted fabrics

The cotton knitted fabrics were also subjected to conventional alkali scouring treatment with 2% caustic soda 0.5% sandopan DTC, 2g/l Sirrix AK under reflux for 60min using material to liquor ratio of 1:10 at 100°C. After alkaline scouring, the fabrics were washed three times with warm water and cold rinse. Then the pH of the alkali treated fabrics is neutralized with 0.25g/l acetic acid for 10min at 60°C. Then they are washed with hot water and then cold water.

2.4 Oxidative bleaching of bio pretreated and conventionally treated fabrics

Both the conventional and bio pretreated fabrics were treated with 3.0ml/l hydrogen peroxide, 1.5g/l Sirrix ANT OX IN liquor, 3.0ml/l caustic soda, 0.5g/l stabilizer(SIFA) and 2g/l imerol JSF liquor under reflux for 30min using material to liquor ratio 1:10 at 100°C. After bleaching, the fabrics were washed thoroughly with hot water followed by a cold water rinse.

2.5 Reactive dyeing of cotton knitted fabrics

The objective of this study was to ensure the utilization of bio pretreated fabrics for dyeing and to replace the harsh chemical treatment sequence. For evaluation of better dyeing results, two different enzymes were used and their conditions were optimized to get better even dye uptake. Therefore we dyed only those test samples treated at optimized conditions. The enzymatically scoured(pectinases and pectate lyases) and caustic scoured fabrics were dyed with Drimarene Cl reactive dye(0.5 and 2% dye shade), 2g/l Drimagen E2R, 60g sodium chloride. The fabrics were refluxed in high temperature dyeing machine using 1:10 material to liquor ratio for 30min at 60°C. After that 15g/l soda ash was added into the bath and fabrics were again processed for additional 30min. After then fabrics were thoroughly washed with hot water and cold rinse respectively followed with a detergent wash and acetic acid neutralization step. In the end the fabrics were subsequently washed and air dried.

2.6 Testing and analysis

Degradation of the pectin and waxes impurities is characterized by weight loss of the substrates, being determined by weighing the fabrics with the help of digital weighing balance before and after the treatment following 24 hours of conditioning at 20°C temperature and 65% relative humidity. The following equation was used to calculate the weight loss percentage(Wt. %) by using the equation(1).

$$weight\ loss(\%) = \frac{(w1 - w2)}{w2} \times 100 \quad \cdots\cdots\cdots\cdots (1)$$

Where, W1 and W2 are the weights of the fabric before and after treatment, respectively. Wettability of cotton fabric was characterized by the wetting time(in seconds) and evaluated by means of the drop test(AATCC Test Method 39-1980). Less than 5 seconds of the wetting time is considered good wetting property. One second or less is judged as the fabric having adequate wettability. The whiteness of grey and different pretreated fabrics was evaluated with whiteness index measured in x-rite color eye 7000A spectrophotometer. The color difference(ΔE) between conventionally dyed and bio pretreated dyed, bio pretreated bleached and dyed was evaluated with the help of color x-rite eye 7000A spectrophotometer. The total color difference was assessed by using the equation(2).

$$\Delta E(CMC) = \sqrt{\left(\frac{\Delta L}{lSL}\right)^2 + \left(\frac{\Delta C}{csC}\right)^2 + \left(\frac{\Delta H}{SH}\right)^2} \quad \cdots\cdots\cdots\cdots (2)$$

whereas ΔE is the total color difference, ΔL=lightness difference, ΔC=chroma difference, ΔH=hue difference, and l is the luminance factor=chroma factors, SL semi sphere of light, SC=semi sphere of chroma, SH=semi sphere of hue.

Fastness properties of dyed samples of different treatment were checked in terms of washing and rubbing fastness. The test method of color fastness to washing(ISO 105-CO3) was used to check the washing fastness of conventional and bio scoured (bleached) dyed fabrics, for this purpose Roaches Washtec was used. The test method of color fastness to rubbing (ISO 105-X12) was used to check the rubbing fastness of fabric. Crock meter was used to check the rubbing fastness of the fabrics.

3. Results and Discussion

3.1 Effect of enzyme on cotton knitted fabric

The grey cotton knitted fabrics contain hydrophobic cuticle impurities forming a three-dimensional network where other amorphous waxy materials are embedded, having melting temperature of above 90°C. The cuticle of the cotton fibre is cross-linked to the primary cell wall by esterified pectin substances, which hinder pectinase action on the pectin backbone in cotton scouring. Usually pre-rinsing in hot water above 90°C helps to reduce the wax load, and a subsequent pectinase treatment in the presence of surfactant is more effective towards primary wall destabilization. It was found that by increasing the concentration and temperature of pectate lyases enzyme, waxes and pectin removal in terms of weight loss was increased(Figure 1 and Figure 2). Increase in enzyme dose and temperature had an antagonistic

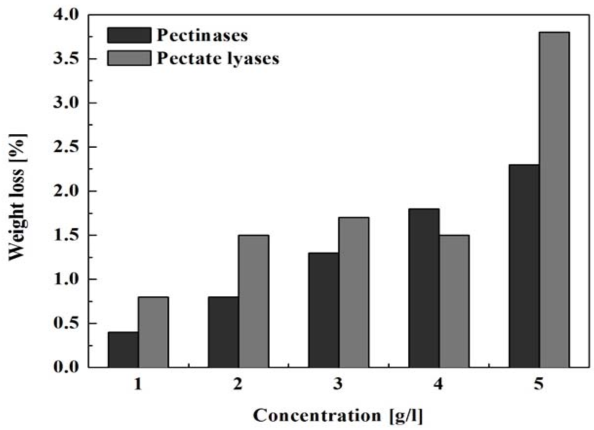

Figure 1. Effect of enzyme dosage on weight loss % of cotton knitted fabrics.

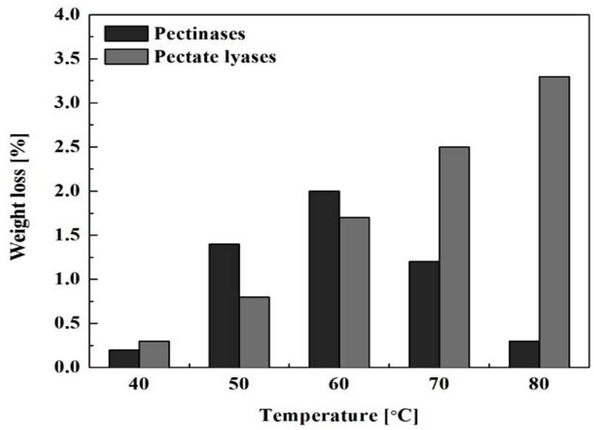

Figure 2. Effect of incubation temperature on fabric weight loss.

effect on the waxy compounds(Table 1 and Table 2). Effect of temperature on fabric was concentration dependent. Furthermore, the gradual increase in weight loss was appeared as the treatment done at higher temperature for 15min. With an optimal enzyme dose(5g/l) caused the maximum degradation of impurities (Figure 1). The fact that temperature affected the effect of enzymes[14)] and wettability properties of the fabrics confirmed that treatment at high temperature(80°C) increased the water absorbency and significantly reduced the wetting time of the fabrics when treated with pectate lyases enzymes. This is because at higher temperature, interaction of thermo-stable Bactosol Co. ip liquor with hydrophobic constituent gets facilitated since the majority of the hydrophobic constituents are above their melting temperature[13,14)].

Pectate lyases was found to be equally efficient in terms of improved absorbency as high temperature caused to swell the cotton fibrils, and swelling improved the accessibility of enzymes, which in turn resulted in higher weight loss values and better absorbency. Pectinases have temperature limitation because they tend to be denatured at high temperature.

Therefore the remains of some pectin and waxes cause wetting property to be lowered. It is observed that alkaline scouring treatment greatly reduces the weight as much as 4.5%. We can also observe high absorbency when water droplet rapidly disappears from the fabric surface pretreated with pectate lyases enzyme. Thus, it is concluded pectate lyases scoured fabrics, showed better wetting, penetration properties giving much better dye uptake. Enzymatic treatment caused the lower weight loss and reduced the consumption of hydrogen peroxide in subsequent bleaching step.

The experimental results showed that the pectate lyases enzymes are thermo stable enzymes compared to the weight loss of fabrics treated with pectate lyases alkaline pectinases enzymes.

As seen in Figure 2, the enzyme is significantly

Table 1. Effect of enzyme dosage on fabric absorbency

Concentration(g/l)	Alkaline pectinases	Pectate lyases
1	120 sec	98 sec
2	70 sec	66 sec
3	48 sec	<10 sec
4	<10 sec	<1 sec
5	<10 sec	<1 sec

Table 2. Effect of incubation temperature on fabric absorbency

Temperature (°C)	Alkaline pectinases (Absorbency time)	Pectate lyases (Absorbency time)
40	65 sec	>60 sec
50	<10 sec	45 sec
60	<10 sec	24 sec
70	75 sec	<10 sec
80	>100 sec	<1 sec

higher when raising the temperature from 40°C to 80°C. Since the melting temperature of pectin is around 100°C due to the complex distribution of waxes present in cotton, the reason that absorbency of the fabrics treated with pectate lyases at high temperature is abruptly increased could be because of the high accessibility of enzymes to the pectin substrate. The pectinases enzymes tend to denature after 60°C temperature, therefore low absorbency and low weight loss was observed.

3.2 Effect of peroxide bleaching on cotton knitted fabrics

To evaluate the effect of enzymes on fabrics for subsequent dyeing, bio pretreated and bleached fabrics was subjected to whiteness index measurement. For comparison, grey cotton and alkali treated samples were tested. Whiteness index of grey cotton knitted was 11.1. The bio and alkali treated fabrics were bleached with hydrogen peroxide(pH 10) at 100°C for 30min.

In Table 3, results show that alkaline scoured samples are whiter than bio pretreated fabrics. The degree of whiteness significantly increased after peroxide bleaching and the differences in whiteness from previous scouring visually disappeared. With pectinases scoured and bleached samples, a high degree of whiteness was not achieved and the differences in whiteness from bleached samples remained visibly clear. This behavior was due to because scouring of pectinases at a low temperature where the impurities remain after scouring are not be fully oxidized.

Table 3. Whiteness index of fabrics

Test samples	After scouring	After bleaching
Alkali treatment	47.5	75.45
Pectinases pretreatment	15.24	55.66
Pectate lyases pretreatment	29.23	70.54

Bio scoured fabrics, if not treated at high temperature and more waxes or other impurities are contained, hindered the successful oxidation, and reduced the fabric whiteness.

3.3 Color difference between conventional and bio pretreated dyed samples

In order to evaluate the dyeing of cotton knitted fabrics, the fabrics are pretreated with enzymes and dyed with reactive dye(reactive blue Drimarene Cl) before and after peroxide bleaching in order to evaluate the color difference between the samples.

Fabrics were dyed with different concentration(0.5 and 2%). Before dyeing it is necessary to ensure a good absorbency and whiteness to get actual dye shade. Therefore we choose samples treated with enzymes having higher absorbency and whiteness index. The results shown in Table 4 proves that color difference between chemically treated and pectate lyases treated dyed fabrics is lower than the pectinases treated dyed fabrics. This may be attributed to the lower absorbency and whiteness index of the pectinases fabrics which increase the color difference between the dyed fabrics.

On the other hand, at lower dye concentration 0.5%, the color difference between enzymatic treated fabrics was rather big and perceptible, and there is a significant difference occurring between the pretreated and bleached dyed fabrics. Therefore it is clear that for lighter shades, bleaching step is necessary to

Table 4. Color difference(ΔE) between different treated samples

Samples	0.5% Shade	2% Shade
Color difference b/w alkali and pectate lyases scoured fabrics	2.7 %	1.7 %
Color difference b/w alkali and pectate lyases bleached treated fabrics	1.7 %	0.8 %
Color difference b/w alkali and pectinases scoured fabrics	4.5 %	3.2 %
Color difference b/w alkali and pectinases scoured fabrics	2.5 %	1.2 %

Table 5. Washing fastness of dyed fabrics

Test samples	0.5% Shade		2% Shade	
	Change in color	Staining on white	Change in color	Staining on white
Alkali treated fabrics	4-5	4-5	4-5	4-5
Pectinases scoured/dyed	4	4	3-4	3-4
Pectinases bleached/dyed	4-5	4-5	4	4
Pectate lyases scoured/dyed	4-5	4-5	4-5	4-5
Pectate lyases bleached/dyed	5	5	4-5	4-5

reduce the color difference between the fabrics. Visual assessment of the fabrics at dyed 2% dye concentration shows that without bleaching, the color difference was acceptable and quite lesser. Therefore bio scoured fabrics can be dyed without bleaching at higher dye concentrations.

3.4 Fastness properties of dyed fabrics

Even dyeing of fabrics may be rendered worthless if the washing fastness properties of the fabrics are poor. Fastness properties are dependent upon the adequate dye exhaustion of the fabrics. Dye penetration is directly proportional to the fabric absorbency. Staining on adjacent material and change in color was assessed by five step gray scale.

Table 5 and Table 6 shows the fastness properties of pectinases dyed/bleached and pectate lyases dyed /bleached fabrics respectively. Pectinases scoured and dyed fabrics which show less fastness properties at high dye concentration due to less absorbency dye molecules left onto the surface show poor fastness properties. Therefore it is clear that pectinases scoured fabrics cannot be dyed without peroxide bleaching, whereas pectate lyases scoured ones can be dyed when higher dye concentration is used.

4. Conclusion

We have investigated two enzymes, pectinases, and pectate lyases, for their effectiveness in fabric wettability and dye uptake properties. Untreated raw cotton knitted fabrics is hydrophobic with low absorbency and whiteness index. Pectate lyases are the enzyme that, when applied under high temperature, produces higher absorbent and good whiteness index for the fabrics. Pectinases do very little improvement in absorbency because of lower temperature stability. Oxidative bleaching enhances the whiteness index of cotton knitted fabrics and lowers the color difference between samples even though lower dye shade % was used. In this study, it is concluded that pectate lyases, when treated at 80°C at optimum dosage, can be used as an alternative to alkaline scouring. Using high temperature stable enzyme removes the non-cellulosic compounds of

Table 6. Rubbing fastness of dyed fabrics

Test samples	0.5% Shade		2% Shade	
	Wet rubbing	Dry rubbing	Wet rubbing	Dry rubbing
Alkali treated fabrics	5	5	5	5
Pectinases scoured/dyed	4	4	3-4	3-4
Pectinases bleached/dyed	4-5	4-5	4	4
Pectate lyases scoured/dyed	4-5	4-5	4-5	4-5
Pectate lyases bleached/dyed	5	5	5	5

cotton fibers and offers many potential benefits in the course of the reactive dyeing. In dyeing, lower color difference and good to excellent washing and rubbing fastness properties were observed when treated with pectate lyases enzyme and can be comparable with alkali treated and dyed fabrics.

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