

OPTIMIZATION OF ENZYMATIC PRE-TREATMENT AND DYEING OF COTTON WITH SELECED NATURAL DYES

Dissertation

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By

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CERTIFICATE – I

This is to certify that the dissertation entitled, **“OPTIMIZATION OF ENZYMATIC PRE-TREATMENT AND DYEING OF COTTON WITH SELECTED NATURAL DYES”**, submitted for the degree of **Ph.D.** in the subject of **Clothing and Textiles (Minor subject: Sociology)** of the Punjab Agricultural University, is a bonafide research work carried out by **Sandeep Sandhu (L-2002-H.Sc.-64-D)** under my supervision and that no part of this thesis has been submitted for any other degree.

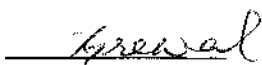
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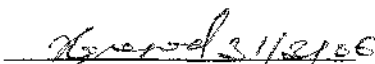
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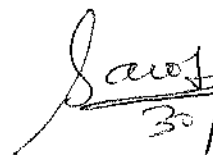
CERTIFICATE – II

This is to certify that the dissertation entitled, **"OPTIMIZATION OF ENZYMATIC PRE-TREATMENT AND DYEING OF COTTON WITH SELECTED NATURAL DYES"**, submitted by **Sandeep Sandhu (L-2002-H.Sc.-64-D)** to the Punjab Agricultural University, Ludhiana in partial fulfilment of the requirement for the degree of Doctor of Philosophy in the subject of **Clothing and Textiles (Minor subject: Sociology)** has been approved by the Student's Advisory Committee after an oral examination on the same, in collaboration with an External Examiner.


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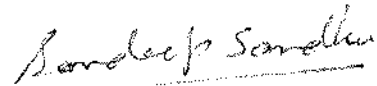
With profound privilege, I express deep sense of my gratitude and heartfelt thanks to my Major Advisor, Dr. (Ms) Neelam Grewal, Professor and Head, Department of Clothing and Textiles, Punjab Agricultural University, Ludhiana for her able guidance, patience, constructive criticism and constant involvement throughout the course of this research work. Her uncompromising attitude for quality in work made the present pursuit a success.

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ABSTRACT

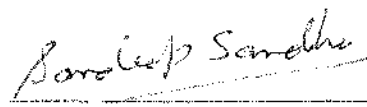
The present study was carried out to optimize the conditions of enzymatic pre-treatment using cellulase enzyme (Neutrox BDN 100 Powder) and dyeing of cotton with four natural leaf dyes - *bansa*, (*Uricalum indacom*), bottle brush (*Callistemon lanceolatus*), *duranta* (*Duranta vr. goldeana*) and mango (*Mangifera indica*). Four natural mordants selected on the basis of high tannin content namely, *arjun* bark (*Terminalia arjuna*), *babool* bark (*Acacia nilotica*), eucalyptus bark (*Eucalyptus sp.*) and pomegranate fruit rind (*Punica granatum*) were used for dyeing.

The optimized pre-treatment conditions were pH level 7, enzyme concentration 5 percent (o.w.f) and treatment time of 75 minutes. The optimum dye extraction pH for all the dyes was 9 or 10, dye extraction time was 60-75 minutes, dyeing pH 9 or 10, dye concentration was 3 or 4 g/g of cotton, dyeing time 60-75 minutes. All the mordants extracted best at 10 pH with mordant extraction time of 60-90 minutes and 0.3-0.5 percent (o.w.f) mordant concentration. The best mordanting method was found to be simultaneous-mordanting. The CIE LAB values revealed that enzymatic pre-treatment led to an increase in dye absorption. The colour fastness properties also showed an improvement when the samples were enzymatically pre-treated.

Therefore, it was recommended that the cotton may be pre-treated at the optimized conditions for quality dyeing with *bansa*, bottle brush, *duranta* and mango dyes using selected mordants.

Key words : Cellulase, Cotton, Natural dyes, Natural mordants, Optimized conditions, Pre-treatment, Dyeing.


Signature of the Major Advisor


Signature of the Student

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CHAPTER I

INTRODUCTION

Natural dyes have been in use since the times immemorial. All the dyes, which were known till the early 19th century and before were natural in origin. They were mainly extracted from roots, stems, leaves, flowers and fruits of various plants and some of them were also of animal and mineral origin.

Natural dyes are considered as very good for their soft and, lustrous colours and endurance. Even after a long period they retain a great beauty and charm. Originating from natural sources, these do not create any pollution problem and in some cases like *harda*, indigo etc., the 'waste' obtained in the process becomes an ideal fertilizer for use in agricultural fields. Another very important factor in favour of natural dyes is their aesthetic appeal. Compared to synthetic colours, natural dyes are very soothing to the human eyes.

However, the hereditary craft of vegetable dyeing, could not survive the competition offered by the introduction of synthetic dyes in 1856. The reason for this was, the ease of availability in standard form and a shorter, simplified and easier process of dyeing with synthetic dyes. The discovery of many more synthetic dyes followed quickly and flooded the markets not only in Europe but in India, Japan, Egypt and other countries, which were dependent on India for natural dyes. The soft delicacy and harmony of natural colours, which formerly

characterized Indian fabrics have given place to brilliant tints produced by synthetic dyes. In fact, even the Indian dyers and printers found that the imported synthetic dyes were cheaper to use and offered a greater variety of shades. The conservative nature of craftsman community was also responsible for the decline of the use of natural dyes. At times, financial returns for the labour put in were not adequate and thus, the younger generation lost interest in the craft and thus the number of people having knowledge of the craft went on declining (Gulrajani 2001).

The synthetic dyes are made from chemical compounds, some of which have been found to be carcinogenic, mutagenic and sensitizing. Therefore, an attempt is being made to revive the vegetable dyeing industry. The use of natural dyes has increased substantially during the last couple of years. These dyes are mainly being used by hobby groups, designers, traditional dyers and printers, non-government organizations, museums, academic institutes, research associations / laboratories and industry. Designers have very effectively utilized natural dyes as a design tool. The non-reproducibility and non-uniformity of shades make each creation a unique piece. The handicraft industry in many countries has evolved around local talent in the art and craft of dyeing yarn with natural dyes and weave them to produce special fabrics (Gulrajani 2001).

There is a growing trend all over the world for the natural colourants, and in the present context of eco-preservation these have tremendous commercial potential. There is also a growing awareness of their non-hazardous nature. On the other hand synthetic dyes evolve many carcinogenic chemicals which are

discharged as effluents in rivers or into the environment, which result in pollution. (Verma 1994)

The popular perception is that the industrial practices in general and the chemical industry in particular is responsible for declining standards in our global environment, which is altering the natural balance within the world. This in turn leads to returning to a traditional or more natural way of life. Biological farming, natural foods and the belief that all things natural are good for us. As a part of this trend, there is now a lobby promoting the use of natural colouring matters to dye textiles. Today the protection of environment has become a challenge for the chemical industry world wide. The water pollution caused by synthetic dyes, especially, the control of effluent continues to be a problem. All over the world, environment regulations are becoming more strict and forcing the shift of technology towards less polluting or non-polluting areas of technological development. Although attention has mostly been paid to modifying synthetic dyeing processes, the need to realize the importance and explore the technology of natural dyes is more urgent. Any effort to reassess and promote the use of natural dyes deserves encouragement (Chawan 1995).

Natural dyes are either substantive, needing no mordant or adjective requiring mordant. The majority of natural dyes need a chemical in the form of metal salt to create an affinity between the fibres and the pigment. These chemicals are known as 'mordants' - the name being derived from Latin word 'mordere' meaning to bite. It was thought that metallic salts being corrosive in nature, make the fabric rough and more recipient to colouring matter. A mordant

is now regarded as a chemical, which can itself be fixed on the fibre and combines with dyestuff also. A link is therefore formed between dyestuff and fibre, which allows certain dyes with no affinity for the fibre to be fixed. When the fibres are capable of being dyed directly, the mordants help to produce faster shades by forming an insoluble compounds of mordant and dyestuff within the fibre itself (Paul 1996).

There are several different mordants, but five most effective ones are alum, copper, chrome, iron and tin. The natural dyes can form metal complexes with these and give different colours. According to the eco-standards, out of these, copper and chrome are red listed. While dyeing with natural dyes, a substantial proportion of mordant remain unexhausted in the residual dye bath and thus pose serious effluent problem when synthetic mordants are used.

Thus, the use of natural dyes alone does not help the environment much because some of the mordants are deadly poisonous by themselves. Keeping in view the environmental conditions, the anionic and cationic sites can also be created on cotton fibres by tannins. Tannins are also called 'natural mordants'. These are naturally occurring compounds of high molecular weight (about 300-5000⁵) (Gulrajani *et al.*1992d), containing phenolic hydroxyl groups (1-2 per 100 Mw) to enable them to form effective cross links between proteins, cellulose and other macromolecules (Gulrajani 2001).

In dyeing, natural mordants are significant for several reasons. These are most important eco friendly ingredients in the dyeing with natural dyes, producing yellow, brown, grey and black colour (Gulrajani 2001) and are primarily used in

the preservation of leather. They are also used in glues and stains. A number of tannin containing substances are employed as mordants in the dyeing of textile fibres. Some of these are used as a substitute for tannic acid in mordanting on account of their lower price. Among the tannins, myrobalan and sumach are most important (Paul 1996). A back tanning process improves the wash fastness of some dyes. However, the treatment with tannins make the dyeing dull (Gulrajani 1992).

Cotton, whether present as fibre, yarn or fabric, requires some form of pre-treatment to make it suitable for dyeing and finishing. During the pre-treatment, natural as well as added impurities are removed using basic chemicals and textile auxiliaries. The basic function of pre-treatment is to impart uniform and good absorbency and whiteness, without chemically damaging cotton. The natural impurities in cotton are pectin, protein, wax and minerals, whereas added impurities could be lubricating oils, sizes, etc. (Alat 2001).

Traditionally, alkaline scouring using caustic soda at high temperature had been used for removal of impurities all over the world. During the alkaline scouring treatment, up to 8% caustic soda is consumed, which after neutralization, exists as a salt load in waste water and also forms 75 percent of the total organic load (Achwal 1993). In recent years efforts are being made to develop a mild and environment friendly process. Thus, enzymatic pre-treatment has assumed more importance due to present concern of clean and eco-friendly environment (Alat 2001).

The term 'enzyme' is derived from the Greek word 'enzymos' meaning in the cells or ferments (Pardeshi 2002). These are naturally occurring high molecular weight proteins capable of catalyzing specific chemical reaction of biological processes and hence known as 'bio-catalyst'. Chemically, enzyme is defined as a protein composed of about 200-250 amino acids. The molecular weight of these ferments is very high and is of the order of 10^4 - 10^5 . Enzymes can bring about hydrolysis, oxidation, reduction, coagulation and decomposition (Das 2000).

Enzymatic treatment of cotton fibres has led to the development of non-toxic, eco-friendly desizing scouring, bleaching, bio-stoning and bio-polishing processes. The application of enzymes in industrial textile processes began way back in 1857, when malt extract was used to remove amylaceous sizes from some textile materials before printing (Das 2000). Around 1900, Diastafor was found more efficient for starch desizing and prevented the damage caused by the older treatment with sulphuric acid (Pardeshi 2002). The concept of treating fabric with enzyme to improve their surface properties was first developed in Japan in 1989 (Raje 2001).

Today enzymes have become an integral part of the textile processing. Their applications have widened with the introduction of new products only in the recent years. With the increased awareness and regulation about the environment concerns, the enzymes are emerging as the obvious choice for wet processing (Doshi 2001). Since these are biodegradable, work under mild conditions and save precious energy (Raje 2001). Being biocatalyst and very

specific, even in small quantities these have direct consequences of lesser packing material and lower transportation impact. In an overall consideration, the enzymes are the wonder products (Doshi 2001). By the use of suitable application techniques, enzymes have resulted in the achievement of specialized effects on textiles, which are certainly new and exciting.

Enzymes have come to forefront in the textile processing and due to their intrinsic environmental friendly nature they have made it more eco- friendly than conventional processing. These do not produce toxic effluents and can be easily deactivated and disposed off. The use of the enzymes is found to be safer, more efficient and very specific in nature (Nishkam 2002).

Effect of enzymatic pre-treatment on dyeing and colour fastness is relatively a new concept which may yield unexpected positive benefits on the resulting colour yield and fastness properties. Keeping in view the emerging trend of bio-processing and

dyeing with natural dyes in mind the present study was planned with the following objectives:-

1. To optimize the conditions for enzymatic pre-treatment of cotton.
2. To optimize the dyeing conditions of enzymatically pre-treated and untreated cotton with four natural dyes obtained from leaves using natural mordants.
3. To evaluate the colour fastness of the dyed samples.
4. To study the effect of enzymatic pre-treatment on dyeing and fastness properties of cotton.

Limitations

- The study was limited to the use of only cellulase enzyme for pre-treatment.
- The study was limited to the use of only for natural dyes namely, *bansa*, bottle brush, *duranta* and mango.
- The study was limited to the use of only for natural mordants namely, *arjun*, *babool*, eucalyptus and pomegranate.

REVIEW OF LITERATURE

The review of literature related to this study has been amassed from libraries of Punjab Agricultural University and CCS HAU, Hissar. Some studies have also been culled from the internet. In this chapter the literature related to application of natural dyes on cotton and other fibres, use of natural mordants and use of enzymes has been reviewed under the following subheads.

2.1 Dyeing of cotton with natural dyes and synthetic mordants

2.2 Dyeing of other fibres with natural dyes and synthetic mordants

2.3 Dyeing of cotton and other fibres with natural dyes and natural mordants

2.4 Enzyme treatments

2.1 DYEING OF COTTON WITH NATURAL DYES AND SYNTHETIC MORDANTS

Bhattacharya *et al.* (1996) carried out dyeing of cotton fabric with naturally occurring *Katha (Acacia catechu)* in an automatic jigger, at levels of 0.5 to 3 per cent. The resulting brown fabrics, when assessed for colour strength, wash fastness, acidic and alkaline perspiration fastness, light and rubbing fastness showed that these were good with respect to the ISO 4 test methods.

Chattopadhyay *et al.* (1997) studied the effect of mordants and mordanting techniques on dyeing of jute and cotton fabric with *Adula* extract, a

natural dye. In the case of cotton, the depth of shades was found to be too light and pre and post-mordanting gave comparatively better results with cotton but for jute, simultaneous mordanting was found to be better. With both jute and cotton, the colour depth was found to be higher with ferrous sulphate than with alum.

Sexana *et al.* (1997) developed the methods of application of *lac* dye on cotton pretreated with chitosan (a naturally occurring polymer). The pretreated cotton fabric was dyed using alum, ferrous sulphate and tannic acid as mordants. The dyed samples exhibited medium light fastness, good rubbing and perspiration fastness but poor wash fastness. The wash fastness improved considerably when the dyed fabric was treated with DMDHEU.

Kalyani and Jacob (1998) used *gulmohar* dye extracted from red *gulmohar* flowers for dyeing cotton. The aqueous and alkaline method of extraction gave the best results. Pre-mordanting method was adjudged the best. Different colours produced using different mordants were olive green, brownish black and biscuit. The dyed samples showed poor to good wash fastness, fair to excellent fastness to dry rubbing and poor to good wet rubbing fastness. Light fastness after 40 hours of exposure ranged from poor to fair. The samples exhibited poor to excellent fastness to alkaline perspiration and good to excellent fastness to acidic perspiration.

Katyayini and Jacob (1999) optimized the dyeing conditions to dye cotton with a vegetable dye extracted from mesta calyx (*Hibiscus sabdariffa*). The optimum dye material concentration (3%) was extracted for 60 minutes and myrobalan pretreated cotton fibre and fabric was dyed for 60 minutes. Various

shades were obtained with use of different mordants. Fastness properties were found to be fair to good for dyed samples.

Padamaja and Jacob (1998) standardized different dyeing parameters of dyeing cotton with red *Hibiscus* flowers. Acid method of dye extraction was found best. Optimum dye material concentration was 3 per cent; extraction and dyeing time was 60 minutes. Post-mordanting gave the best results with different mordants. The wash fastness was found to be the best for ferrous mordanted and copper mordanted samples, light fastness for samples mordanted with zinc chloride and rubbing and perspiration for cobaltous sulphate mordanted samples.

Devi *et al.* (1999) studied dyeing of cotton fabric with turmeric (*Curcuma longa*) using synthetic mordants with special reference to colour fastness properties; general fabric appearance, including luster; texture and fabric count, weight, thickness, breaking strength and elongation. Approximately 63 per cent of judges rated the general appearance of untreated samples as good, whereas 60 per cent evaluated the samples treated with alum as fair and samples treated with ferrous sulphate has a poor appearance.

Gaba (1999) extracted dyes from the flowers of *jatropha* and *pili kaner* to dye cotton fabric. The optimum values for *jatropha* and *pili kaner* were 3 per cent dye concentration, 90 and 75 minutes extraction times, respectively and 60 minutes dyeing time. Pre-mordanting method was adjudged the best method of mordanting. In both the dyes the tensile strength increased in almost all the cases in warp direction but decreased in weft direction. Elongation percentage

showed increase in some cases while decreased in others. Flexural rigidity in all the dyed samples showed increase in both the directions.

✓ Khanna and Dedhia (1999) dyed pineapple leaf fibres (PALF) with two natural dyes, namely *ratanjot* and *eucalyptus* leaves, using mordants and their various combinations. When the pretreatment with *harda* and pomegranate rind compared regarding the strength, reflectance and fastness properties, it was inferred that in some cases *harda* treatment was better whereas in others pomegranate rind showed comparable results. It was also found that the type of mordant or mordant combination had an effect on the reflectance, strength as well as fastness properties of PALF dyed with respective dyes.

✓ Radhika and Jacob (1999) developed a dye from *jatropha* seeds for dyeing cotton pretreated with myrobalan and indicated that alkaline method was the best method of extraction with dye concentration 15g and dyeing time and extraction time 60 minutes. It was found that *jatropha* seeds gave a range of bright, even and soft colours on cotton fabric using different mordants. All the dyed samples showed fair to excellent colour fastness to various agencies.

✓ Ghorpade *et al.* (2000a) used ultrasound energy assisted extraction for the red dye from sappan wood and dyed cotton in sonicator using eco-friendly mordants. Aqueous extraction of dye in sonicator yields dark red dye. This dye when dyed in sonicator showed medium fastness to washing, rubbing and perspiration. With the aid of tannic acid and eco-friendly metallic mordants, the fastness properties improved in the sonicator that was earlier considered as fugitive.

Ghorpade *et al.* (2000b) exploited a natural colouring material from canna flower extract to dye cotton and concluded that dyed samples had good fastness properties. The colour range was from pinkish purple to dark purple by pre-mordanting in stannic chloride, sap green with alum, dark green and yellow mustard with ferrous sulphate with pre and post mordanting, respectively.

A one-bath process of dyeing using sonicator and simultaneous antimicrobial finish by methanolic extract of tulsi leaves (*Ocimum sanctum*) was investigated and very encouraging results were observed. As evaluated by the fabrics fastness properties one bath dyeing proved to be very effective. Similarly, the antimicrobial activity evaluated by soil burial test of both treated and untreated fabric exhibited the resistance of microbial growth on the treated fabric after soil burial for 3 days (Ghorpade *et al.* 2000c)

Moses (2000a) dyed JUCO fibres using natural dyes extracted from turmeric, tamarind and *majitha* and obtained different colours with the use of metallic mordants. Colours obtained in the jute/cotton blend by the natural dyes showed good washing as well as light fastness.

In another study, Moses (2000b) dyed JUCO fibres with myrobalan, catechu, pomegranate rind, red creeper and *parijatham*. Results revealed that with the use of tannic acid, ferrous sulphate, tartaric acid and alum, these natural dyes produced a wide range of colours with good washing and light fastness properties.

Rastogi *et al.* (2000) used *lac* dye on cationised cotton fabric. Maximum colour yield was obtained in fabric treated with 5 per cent Discofix DBA at pH 4.0

and exhibited good fastness to washing and perspiration, fair to good fastness to light excellent fastness to dry and wet.

In another study, Tiwari *et al.* (2000a) undertook ultrasonic dyeing with *tulsi* leaves (*Ocimum sanctum*) for cotton using eco-friendly mordants. It was observed that the dye did not give much variation in colour. However, the colour adherence to fabric was good. The colours obtained were light green, fluorescent green, green shades, dark green khaki with stannic chloride, stannous chloride, alum and ferrous sulphate, respectively. All the dyed samples exhibited fair to good fastness to rubbing and good fastness to light and washing.

Aqueous extract of *bougainvillea* was used for dyeing cotton in sonicator Tiwari *et al.* (2000b). The dye showed a full gamut of colours from dark magenta in acidic medium to yellow in alkaline medium. Alkaline extract gave *mehandi* green with alum. The washing and light fastness of dyed samples were fairly good.

A natural dye from *pinus roxburghii* bark and needles was extracted by Dayal *et al.* (2001) for dyeing cotton fabric using different metallic mordants. Different colours ranging from light brown, brownish peach to dark brown were obtained. The dyed samples had very good wash fastness; good light, crocking and perspiration fastness except stannous chloride treated samples, which had poor wash and light fastness.

Eom *et al.* (2001) cationized the cotton fabric for improving its dyeability before dyeing with natural colourants, namely redwood, gromwell, cochineal, goldthread and *amur* cork tree. The K/S values of cationized cotton fabric dyed

with redwood and cochineal were higher than that of untreated ones. In the case of gromwell, though the K/S value of the cationized fabric was higher than that of untreated one, the fabric showed poor levelness. Cationization of cotton had no effect on the dyeability of goldthread and *amur* cork tree. It was observed that, when the concentration of sodium hydroxide exceeds beyond a certain level, NaOH hydrolyzed the cationizing agent and the K/S value of dyed materials decreased.

Gaba *et al.* (2001) dyed cotton fabric with a dye from *pili kaner* (*Thiveta peruviana*). The fabric was pre-mordanted with different concentrations of tin and iron. It was found that the general appearance, luster and texture of dyed fabric was good and fabric count, weight and thickness increased after dyeing.

Sengupta (2001) conducted a study on dyeing cotton fabric with tea liquor with or without synthetic mordants. It was observed that the K/S values of the dyed samples increased with the increased depth of shade in all the cases, even with the sample dyed without mordant. All the dyed samples without mordant or with the addition of mordants exhibited good washing and rubbing fastness properties.

Tiwari *et al.* (2001) reported the dyeing properties of cotton fabric and hosiery material with alkanet roots by using sonicator. A variety of shades were produced ranging from light peach to brown, light green to dark brown to black. Best results were obtained with stannic chloride as mordant for cotton as well as for hosiery. The dyed samples exhibited good to very good fastness properties to all agencies.

Tiwari and Vankar (2001a) extracted a dye from alkanet root bark and dyed pretreated cotton with acetic acid in sonicator and microwave. The naphthaquinone based chromophore dye exhibited high affinity for cotton and a variety of shades were obtained with different mordants. All the dyed samples showed good colour fastness.

Bains *et al.* (2002a) extracted arjun dye in aqueous solution to dye cotton fabric. The dye produced shades of bright pink brown with alum, pinkish brown and mud brown with chrome, light and pinkish brown with copper sulphate and dirty brown with ferrous sulphate. The test samples exhibited excellent fastness to washing and perspiration; good to excellent fastness to rubbing and poor to fair fastness to light.

In another study Bains *et al.* (2002b) undertook dyeing of cotton fabric with extracted goldendrop dye in aqueous solution. The dye produced shades of slate grey with alum, chrome and copper sulphate and steel grey with ferrous sulphate. The test samples exhibited fair to excellent fastness to washing and perspiration; good to excellent fastness to rubbing and poor fastness to light.

Bhattacharya and Lohiya (2002) dyed cotton with four vegetable dyes viz. turmeric, pomegranate rind, catechu and nova red (mixture of *magistha* and betel nut) using conventional and HTHP method of dyeing. The colour data as well as wash, light and perspiration fastness characteristics were investigated. The results indicated improved fastness with most of the dyes when dyed with HTHP method as compared to conventional method.

2.2 DYEING OF OTHER FIBRES WITH NATURAL DYES AND SYNTHETIC MORDANTS

Verma and Gupta (1995) carried out a study on wool dyeing with wattle bark using alum, chrome, copper and ferrous sulphate as mordants. Light fastness of the dye at different pH values was at par with light fastness of many synthetic dyes. The wash fastness was also found to be very good. Tenacity of the woollen yarn was adversely affected by the wattle bark colour. Use of mordants produced a deteriorating effect on the tensile properties of woollen yarn.

Katti *et al.* (1996) studied the dyeing of silk fabric with mango leaves (*Mangifera indica*), *majishta* roots (*Rubia cardifolia*) and French marigold flowers (*Tagetes crecta*). It was observed that dyeing with mango leaves had poor wash fastness and colour faded considerably. It was also noted that with the increase of dye material concentration, the wash fastness got reduced. The colour fastness of dyed fabrics with 100 per cent *majishta* and marigold towards washing, perspiration and sunlight were fair to good except that of wash fastness of marigold which was graded poor. With combination of 75 per cent *majishta* and 25 per cent marigold, the fastness to both washing and perspiration was low but the sunlight fastness for the same was high. With 25 per cent *majishta* and 75 per cent marigold, the wash and perspiration fastness had increased and the light fastness remained the same.

Singh *et al.* (1996a) carried out a study to standardize the dyeing process of silk with *kamala*. The thirty minutes of dyeing time was found to be optimum.

Dyed samples mordanted with alum, chrome and stannous chloride were fast to light. The light fastness of samples mordanted with copper sulphate and ferrous sulphate was rated slightly good. It was also reported that all the samples had fair to good fastness to washing.

Singh *et al.* (1996b) conducted a study to standardize the parameters for dyeing of silk from natural dyes of leaves of *nargis* (*Setareasea pellida*). The 60 minutes of extraction time and 30 minutes of dyeing time were found to be optimum. With the optimum concentrations of selected metallic mordants, a good range of colours was produced.

Lac dissolved in hydrochloric acid was able to dye wool directly and gave beautiful orange-red shade, which was fast to light (Agarwal 1997). The amount of mordant to be used varied from 2 to 5 per cent (owf) depending upon amount of dye used and shade required.

Ahmed *et al.* (1997) examined the physical properties of silk fabrics dyed with natural dyes. The samples were dyed with *kamala*, *indigo*, *turmeric* and *henna*. The findings concluded that the dyed samples exhibited increased fabric count, fabric thickness and fabric weight as compared to original samples. An increase in the tensile strength was also noted.

Chinchwade *et al.* (1997) dyed jute and jute cellulosic blends with turmeric and catechu. Pure jute dyed with turmeric or catechu showed higher K/S values than jute cellulosic blends. Tannic acid, ferrous sulphate, citric acid and their combinations were used as mordants. A combination of 5 per cent tannic acid and 10 per cent citric acid gave best results on jute and its blends dyed with

turmeric. In case of catechu dye, only citric acid or ferrous sulphate gave better results regarding K/S value and fastness properties of jute and jute cellulosic blends.

Gogoi *et al.* (1997) studied the colour and fastness of natural dyes namely, *kamela*, indigo, turmeric and *henna*. Results revealed that all the four silk dyes dyed silk evenly. Samples dyed with *kamela*, turmeric and *henna* were found to be good, but indigo dyed sample rated fair in general appearance. Colour fastness to washing of *kamela* dyed sample was the best. All the dyed samples showed good fastness to perspiration. As regards to rubbing fastness, turmeric dyed sample had good fastness to crocking in dry and wet conditions than the other test samples.

Achwal (1998) dyed fabrics of 100% PET, PA, PAN and wool with selected natural dyes covering different dye classes (anthocyanine, betaine, carotenoids and flavonoids). For all the dyes, the dye depth was low and only pastel shades were obtained. Even for wool, deep colours were obtained only for log wood, madder and *henna*. In some cases, the tone of dyeing was different from what it was for polyamide 6, 6 that created problems in dyeing their blends to achieve tone in tone dyeing.

Bhattacharya *et al.* (1998) dyed bleached jute fibres with various natural dyes, namely *Acacia catechu*, *Ornosmas echiodes*, *Indigoferra tinctoria*, *Artocarpus integrifolia*, *Adenanthera pavonina*, *Rubia cardifolia*, *terminalia chebula*. The dyeing procedure was standardised without any mordant except in the case of *Rubia cardifolia*, where aluminium sulphate was used, and

Artocarpus integrifolia where copper sulphate and potassium dichromate were used in small amounts (<0.1%). The fastness properties viz. light, wash and perspiration were found to be good.

Goel and Goel (1998) used *tessu* flower extract for dyeing rabbit hair and rayon blend. Colours produced were golden yellow on rabbit hair yarn and light lemon on pure viscose rayon yarn and different cross-dyed effects were obtained on different blend compositions. Washing fastness of pure blended yarns ranged from good to excellent and light fastness ranged from fair to good.

Lokhande *et al.* (1998) dyed polyester with onion, *lac* and turmeric extracts with or without mordants using two dyeing techniques namely, open bath and high temperature high pressure (HTHP). A good range of shades was obtained by using different mordants. All the dyed samples exhibited good fastness to washing and sublimation and light fastness ratings were higher for copper and iron mordanted samples.

Pant (1998) dyed woollen knitting yarn with African marigold, *kethula* flowers and oak tree bark at different concentrations, temperatures time periods, using different mordant concentrations and mordanting methods. 1 per cent concentration of marigold, 2 per cent of *kethula* and 4 per cent of oak bark was found to be optimum. Optimum temperature of dyeing was found to be 80-100° C and wide range of colours was obtained with different mordants. The colour fastness properties of the dyed samples were from fair to excellent with all three dyes.

Verma *et al.* (1998) used eucalyptus and wattle bark for dyeing of wool. Different chemical mordants namely, tin, iron, chrome, alum were applied using all the three mordanting methods and a wide range of shades was obtained. A complete colour range of dark brown to dark grey was produced. Washing fastness of the dyed samples was at par with many synthetic dyes while light fastness was in the range of 4-5, which is acceptable for many woollen products.

Wakida *et al.* (1998) treated woollen fabric with oxygen, carbon tetra fluoride and ammonia low temperature plasmas and dyed with several natural dyes - Chinese cork tree, madder and gromwell. The dyeing rate of plasma treated wool increased considerably with Chinese cork tree and madder but not with gromwell. Furthermore, plasma treated wool fabrics dyed with Chinese cork tree had increased brightness as compared to untreated wool.

Bhattacharya and Shah (1999) carried out a study on dyeing of wool with two natural dyes, namely tea leaves (*Thea sinensis*) and *poi* fruits (*Basella rubra*). Iron, tin and potassium dichromate were used as mordants. Pre-mordanting was found to be good in both the cases. Between the two dyes, tea produced very attractive and soothing colours. In the case of tea dyeing, light, wash and rubbing fastness were very good whereas with *poi*, the light fastness was poor but wash and rubbing fastness were good.

El-Zawahry and Kamel (1999) used *Terminelia bellerica* fruit extract to dye the wool cloth. Different parameters of dyeing like dye extraction time, dye material concentration, dyeing pH, duration and temperature were standardized. The results were evaluated as colour strength and colour shade/hue. Mordants

i.e. potassium dichromate + lactic acid, chromic chloride + lactic acid, copper acetate, ferrous sulphate and ferric chloride were used at low concentration to produce a variety of shades. Fastness properties were not altered markedly by the mordants. Rubbing fastness of pre-mordanted samples was lower than that of unmordanted samples. Light fastness increased in the increase of duration of exposure to light from 35 to 58 hours. It was concluded that at longer exposure to light cyclization of the pigmented colour occurred with higher colour strength.

Gogoi and Kalita (1999) dyed silk fabric with *henna* leaves (*Lawsonia alba*) and studied the effect of mordants on colourfastness and physical properties of dyed fabrics. The study concluded that silk fabrics dyed with mordant at different concentrations showed better results with respect to physical as well as colourfastness properties. Fabric mordanted in 3% concentration of aluminum potassium sulphate performed better than the other two concentrations (1% and 2%).

Gulrajani *et al.* (1999a) dyed nylon and polyester with annato dye and results revealed that annato dye has high affinity for both nylon and polyester fibres. The process of dyeing was found to be endothermic as the dye uptake increased at higher temperature. It was observed that the carotenoid based annato dye (bixin) was capable of dyeing ionic and non-ionic fibres by different mechanism. The colours obtained on nylon and polyester fibres were considerably fast to washing, though not so soft to light.

Acrylic fibre was dyed with berberine by Gulrajni *et al.* (1999b). Results of study revealed that process of dyeing was endothermic. *Barberine* dye was

found to have high affinity for acrylic fibres and was capable of dyeing bright yellow shades. The colour obtained, however were susceptible to light fading but were fast to washing.

In another study Gulrajni *et al.* (1999c) used *ratanjot* dye to dye nylon filament yarn and polyester fabric and found that *alkanin* dye present in *ratanjot* exhibited high affinity for both the fibres. Though the mechanism of dyeing was found to be similar for both the fibres, the shade obtained on nylon was black while that on polyester was pink. Results revealed that rate of dye uptake for nylon fibres was much higher than that for polyester but affinity values were comparable. All the dyed samples showed good light fastness and excellent wash fastness on both the fibres.

Kalyani and Jacob (1999) conducted a study on dyeing of silk fabrics with red gulmohar flowers. Acid method of dye extraction was found to be the best. Post mordanting method gave good range of shades. The colours obtained were dark brown, light brown and biscuit colour with copper sulphate, lead acetate and alum respectively. Dyed samples exhibited fair to excellent fastness to dry rubbing, poor to fair fastness to washing, good to excellent fastness to alkaline perspiration and poor in case of acidic perspiration.

Dayal and Dobhal (2000) undertook a study on dyeing wool with poplar bark (*Populus deltoides*). Different variables of dyeing were optimized. Acid medium was used for dyeing, as the electrostatic forces between the positively charged side of the protein fibre and dye molecules would be expected to play a

major role in dye absorption. All mordants increased the L* value of the dyed samples. Further, except alum and iron, all increased a* and b* values also.

Ghorpade *et al.* (2000d) used *lac* dye for dyeing terrycot and cotton fabric using ultrasound energized dyeing technique. The fabric pretreated with mild acids, followed by dyeing and mordanting gave very good fastness properties to the fabric. For maximum dye utilization cotton fabric was dyed in the same bath after terrycot fabric dyeing. It was observed that the *lac* dye had good fastness to light and excellent fastness to rubbing as well as to alkaline and acidic perspiration. Alum mordanting had slight stone wash effect on the fabric similar to that when the fabric was mordanted with stannous chloride. However, stannic chloride gave a very uniform peach colour and ferrous sulphate gave gray colour on both types of fabrics.

Gupta (2000) conducted a study to investigate the dyeing characteristics of synthetic fibres with natural dyes. It was concluded that nylon, polyester and acrylic fibres could be dyed with selected natural dyes. The dyes had high affinity for the synthetic fibres and bright and deep shades could be obtained. The quinone based dyes exhibited exceptional fastness properties though dyes based on other chromophoric groups were not be so fast.

Kiranmai *et al.* (2000) used *Ixora singaporensis* flowers to dye wool. Mordants used were alum and myrobalan. Acidic method of extraction was found to be best because of maximum dye extraction and pre-mordanting method was adjudged best. The best results were obtained with, 15% alum and 20%

myrobalan (owf). All the samples showed excellent fastness to light and rubbing. Fastness to washing was good to very good and good to perspiration.

Mishra *et al.* (2000) carried out a study on dyeing silk fabric with a natural dye-lac. Samples were mordanted with potash alum or tartaric acid before dyeing. The dyed samples became redder, less yellow, darker and more saturated after mordanting with potash alum or tartaric acid. However, the samples became more yellow and lighter when simultaneously mordanted with potash alum or tartaric acid. Mordanting either with potash alum or tartaric acid enhances K/S values and it indicated that dye uptake increased with the mordanting treatment.

Patel and Agarwal (2000) used babool bark for dyeing nylon substrate by open bath (exhaust) and HTHP dyeing techniques. Different synthetic mordants were applied by pre-mordanting and meta-mordanting techniques. Colours obtained were golden-yellow to brownish black without mordant while mordants produced a variety of shades ranging from dark brown and copper brown to brownish black. The fastness ratings of all the dyed samples were acceptable and at par with unmordanted sample.

Shah *et al.* (2000) studied dyeing behaviour of catechu and turmeric on wool with respect to dye exhaustion and fastness properties. In both the dyes, dye exhaustion values increased, with the percentage increase in shade. The results of colourfastness properties of catechu were encouraging except for light fastness. While for turmeric dye light, washing and wet rubbing fastness showed inferior results.

Shirata *et al.* (2000) isolated a bacterium, namely *Janthinobacterium lividum* from wet silk thread whose colour became bluish-purple. The bacterium produced large amounts of bluish-purple pigment on some media containing amino acids. The pigment was extracted with methanol and was identified as a mixture of violacein and deoxy-violacein. Dyeing could be performed by a simple procedure consisting of either dipping in the pigment extract or boiling with the bacterial cells. By changing the contact time and temperature of dye bath, shades ranging from light purple to deep bluish-purple could be obtained, the colourfastness of dyed material was almost the same as that of material dyed with vegetable dyes, but the colour faded easily when material was exposed to sunlight.

Bansal and Sood (2001a) conducted a study on dyeing of wool with eupatorium leaves. Optimum concentrations of dye material were 1.5% and 3.0% for light and dark shades. Optimum extraction and dyeing time was 45 minutes and the maximum extraction was obtained in alkaline medium. The range of colours obtained were light olive green, greenish yellow and ochre with alum; light leaf green, yellow ochre and brown with copper; light greenish umber, greenish sienna with chrome and greenish umber, light umber with ferrous while using simultaneous method of mordanting.

The wool yarn when dyed with litchi leaves, gave the best colours with 75 minutes extraction time, 60 minutes dyeing time and 2 per cent dye material concentration in alkaline medium of extraction. Colours obtained were light burnt sienna, burnt sienna, dark burnt sienna and burnt umber with alum, copper,

chrome and ferrous, respectively. All the dyed samples exhibited excellent colourfastness properties (Bansal and Sood, 2001b)

Bhattacharya *et al.* (2001) standardized the extraction conditions of some natural dyes, namely *arjun* bark, *babool* bark and pomegranate rind. Various extraction conditions like pH of the extraction media, extraction time, extraction temperature, material to liquor ratio and yield percentage of the dye were optimized. It was observed that in all the cases time, temperature, MLR, pH of soaking and pH of the extraction were similar to get optimum yield percentage. The extracted dye was characterized by its solubility with different solvents i.e. water, methyl alcohol, ethyl alcohol, ethyl acetate, hydrochloric acid and sodium carbonate.

Dayal *et al.* (2001) optimized the dyeing conditions of wool and silk with *Pinus roxburghii* bark and needles. It was indicated that best extraction of dye from the bark was at 6 per cent concentration for 90 minutes at 95-98°C. Maximum dye absorption was obtained in 0.8% dye solution at 70-85°C for 45 minutes (MLR 1:60) for bark dye. Extraction of dye from pine needles was found to be more in alkaline medium than the neutral medium. After observing the darkness of the shades, dyeing trials with pine needles were carried out using 3 per cent dye solution at 80-90°C for 45 minutes. Post-mordanting method was suitable in both the dyes. Colours obtained ranged from yellowish brown to dark brown.

Gulrajani (2001) reported that wool can easily be dyed with yellow dye extracted from Himalyan rhubarb (*Rhuem emodi*), which is an important

anthraquinone based yellow dye. It was reported that about 11,000 kg of rhizome are collected annually from Kullu and Kangra valley of Himachal Pradesh. Rhizomes and roots are dug up from 3-10 years old plants, washed, cut into small pieces, dried and stored in airtight containers. Roots contain a number of anthraquinone derivatives. The most prominent among them is chrysophanic acid, the main source of natural dye. Colours obtained were fast to light and washing.

Gulrajani *et al.* (2001) undertook a study to dye nylon with natural dyes, namely, *ratanjot*, annato and berberine. It was observed that K/S values and dye absorbancy increased with the increase in the dye concentration. Best dyeing were obtained at pH 4, 6 and 9 for *ratanjot*, annato and berberine, respectively. The dyed samples exhibited moderate to good light and wash fastness

Pan *et al.* (2001) used *deodara* and eucalyptus leaves for dyeing of bleached jute fabrics. The fabric was pre-mordanted with potash alum and dyeing was carried out using extract of *deodara* and eucalyptus leaves. Results revealed higher dye uptake and slightly higher brightness values. Wash fastness rating was found to be almost the same for all.

Shukla and Patil (2001) dyed wool using natural dyes and mordants using singly and in their binary mixtures. Computer colour matching system was used to evaluate these dyeing and generate matching dyeing recipes for synthetic trichromatic acid dyes, which are eco-friendly. After dyeing with acid dyes, the natural and acid dyed samples were evaluated for colour differences and it had been observed that in almost all cases, good matching were there for natural

dyed wool samples. This indicated that selective classes of synthetic dyes, which exhaust to higher levels and have proven non-toxicity, could be used with due concern to ecology and economy.

Singh and Yadav (2001) optimized the conditions for dyeing wool with black *kikar* (*Acacia nilotica*) bark. To obtain light to dark shades 2% and 8% concentration of dye material were used, respectively. The optimum extraction time was 75 minutes and dyeing time 60 minutes. Four synthetic mordants i.e. alum, chrome, copper and ferrous sulphate were used to obtain variety of shades. Fastness properties of dyed samples were evaluated and found to be good to excellent.

Tiwari and Vankar (2001b) dyed blended hosiery material with a number of natural dyes such as sappan wood (a red dye extracted from basil wood), *tulsi* (a green dye extracted from leaves of basil wood), AI (a dark red dye from root of *Morinda citrifolia*), eucalyptus (a yellow dye extracted by supercritical extraction), *tessu*-pomegranate dye (a flower of *Butea monosperma* and *Punica granatum* yellow dye) and alkanet (a purple dye from root of *Alkannin tinctoria*). Dyeing were carried out in sonicator as well as in microwave vessel and results revealed that better dyeing performance on hosiery by sonicator technique. The dyed hosiery materials were tested for the presence of heavy metal, pesticides and fastness properties.

Bhattacharya and Lohiya (2002) used pomegranate rind, catechu, nova red and turmeric for dyeing polyester fibre using conventional and HTHP dyeing conditions. Aluminium sulphate and alum were used as mordants. The dyeing

were carried out in neutral, acidic and alkaline medium. In case of nova red and turmeric, very good fastness to wash and perspiration was obtained whereas poor light fastness rating with turmeric was obtained.

Bhattacharaya and Mathew (2002) reported that woollen fabric can be successfully dyed with two different natural colourants, namely mango and babool at different percentage of shades using various mordants by different dyeing processes. In the case of mango, copper sulphate showed excellent dyeability by pre-mordanting method, whereas ferrous sulphate with babool in simultaneous dyeing method. The fastness properties of all the dyed samples were all around satisfactory.

Devi *et. al.* (2002c) reported that the dye was extracted in alkaline medium to obtain yellowish green shades on silk. Alum, chrome, copper sulphate and ferrous sulphate were used as mordants. Dark shades were obtained by post mordanting method, followed by simultaneous and pre-mordanting methods. The samples exhibited excellent to outstanding fastness to sunlight, perspiration, washing and slight staining was observed in samples subjected to crocking.

Gulrajni and Maulik (2002) investigated the colour fastness and colour value of natural dyes on synthetic fibres. Annato and *ratanjot* were used for polyester and nylon and berberine for acrylic. The results of the study revealed that annato dyed on nylon and ployester had low light fastness rating, but it had moderate wash fastness ratings on those fabrics. The light and washing fastness ratings of *ratanjot* dyed on nylon and polyester were excellent. But berberine dyed on acrylic had poor light fastness rating and moderate wash fastness

properties. For all the dyes except berberine, L^* values decreased. An increase in the percentage shade did not bring any significant change in the L^* value for berberine because yellow colour gets stabilized after a certain percentage shade.

Kaur (2002) optimized the method of dyeing woollen yarn with *kasud* (*Cassia siamea*) bark. The optimized concentration (7%) of dye material was extracted for 45 minutes in all the three mediums (aqueous, alcoholic and acidic). Dyeing was carried out for 45 minutes at pH 4.0 in aqueous and alcoholic media and pH 4.5 in acidic media. Different shades of brown were obtained in all the three media using different mordants and mordanting methods. All the dyed samples showed good to excellent colourfastness to washing, light, crocking and perspiration.

Patel and Agarwal (2002) extracted a dye from *Acacia arabia* wild bark and applied with or without mordant on polyester using open bath and HTHP dyeing methods. Pre-mordanting and meta-mordanting techniques have been used for the study. Ferrous sulphate produced shades varying from gray, pale brown to copper brown colour with different mordanting techniques and at varying concentration levels. A mixed mordant system of ferrous and copper sulphate was capable of giving pale to dark brown/chocolate brown shades on polyester substrate. Fastness properties of samples dyed by open bath as well as HTHP dyeing techniques were adequate for all the dyed samples.

Tomer (2002) extracted banyan (*Ficus bengalensis*) leaves using three methods of extraction viz. aqueous, alcoholic and acidic to dye woollen yarn. The optimum material dye concentration was 7 per cent and optimum extraction and

dyeing time was 45 minutes. A good range of shades from pink to olive green was produced by different mordants and mordanting methods in three media. The colourfastness grades ranged from very good to excellent for washing rubbing and perspiration for all the media. The light fastness grades ranged from fair to very good in aqueous medium, good to excellent in acidic and very good to excellent in alcoholic medium, respectively.

Gulrajani *et al.* (2003) used red sandal wood extract as a dye for wool and nylon. The colouring components were extracted with organic as well as aqueous solutions from the sandal wood. The extracted dye was applied on wool and nylon with and without mordants. The light fastness of the dyed wool samples improved substantially on mordanting with copper sulphate. The wool and nylon samples dyed and treated with mordants, except copper sulphate showed good wash fastness.

Gulrajani *et al.* (2003) dyed coir yarns with different purified commercial natural dye powders. It was observed that almost all the dyes have good wash fastness ranging from 4-5 and some dyes have light fastness rating of ≥ 3 . The $a^* b^*$ plot of the coloured yarn gave the range of shades that can be produced by the given set of dyed yarn.

Devi *et al.* (2002a) extracted a dye from fruit pulp of *amaltas* (*Cassia fistula*) for dyeing cotton. Pre and post mordanting methods were found suitable for application of *amaltas* dye. Even though the absorption values reduced in mordanted cotton, visually the shades produced were darker. All mordanted

samples showed excellent to outstanding sunlight fastness, good to very good wash fastness, excellent resistance to crocking and good perspiration fastness.

Devi *et al.* (2002b) used a natural colourant annatto for dyeing cotton using metallic mordants. Annatto produced a very bright orange shade on cotton. The colour was found to be sensitive to alkaline reagents. By observing the fastness properties of mordanted annatto dyed cotton it could be concluded that the dye was having very fair wash fastness, good to excellent crocking fastness and fair to good perspiration fastness.

Mahale *et al.* (2002) investigated the colour fastness of eco dyed cotton with marigold. Results of the study revealed that the sample pre mordanted with 3 per cent potassium dichromate showed good fastness properties for all agencies followed by 15 per cent potash alum concentration. Among all the simultaneously dyed samples 1 per cent potassium dichromate showed highest grades for all the colour fastness properties. Samples post mordanted with 2 per cent and 3 per cent potassium dichromate showed good colour fastness to washing, rubbing, sunlight and perspiration.

Verma and Venkatachalam (2002) reported that *mangifera indica* (mango) bark dye yield yellow shades on the jute – cotton fabrics with moderate colourfastness. The colourfastness increased by addition of tartaric acid. Pre and post mordanting techniques showed appreciable results.

Patel *et al.* (2003) dyed unmordanted / mordanted cotton fabrics with babool bark dye extract using padding technique. Pre-mordanting and meta -

mordanting techniques were used for mordanting. Fastness properties were adequate for both mordanted and unmordanted dyed samples.

Dhavamoorthi and Selven (2004) used aloe juice from leaves to dye cotton. The samples were dyed for one hour at room temperature 40°C and 50°C. The different shades were developed using ferrous chloride, potassium permanganate and sodium acetate. The samples were treated with these solutions at 50°C for 15 minutes and washed. The samples gave satisfactory results when subjected to rubbing fastness.

2.3 DYEING OF COTTON AND OTHER FIBRES WITH NATURAL DYES AND NATURAL MORDANTS

Dwivedi (1993) reported that among natural mordants tannins form the main category. The word *tannin* came from the early French word *tan*, which means bark of an oak. The term *tannin* was introduced by Seguin in the year 1976 to indicate various plant extracts, which have the capacity to convert hides and skin into leather. The word is also abbreviated as tan.

Tannins are almost universally secreted by plant tissues. Their quantity may be negligible or may be enough for their economic exploitation. However only a handful of plant species secrete *tannins* in concentrations strong enough to make it economically viable (Negi 1992).

Table 2.1: Principal tannin producing plants and their tannin content *

Name of plant	Part used	Tannin content (%)
Acacia catechu (<i>Kikar</i>)	Wood	57-60
A. leucopholea (<i>Hiwar</i>)	Bark	15-17
A. mollissima (<i>Mimosa</i>)	Bark	35-65
A. mearnsii (<i>Black wattle</i>)	Bark	35

<i>A. nilotica</i> (Babool)	Bark	12-18
<i>Anogeissus latifolia</i> (Dhawada)	Leaves	16-18
<i>Anacardium occidentale</i> (Cashew)	Leaves	20-25
<i>Astronium balansal</i> (Urun day)	Wood	10
<i>Caesalpinia brevifolia</i> (Algarobilla)	Pods	50
<i>C. coriaria</i> (Dividivi)	Pods	35-50
<i>Cassia auriculata</i> (Avaram)	Bark	15-20
<i>C. fistula</i> (Amaltas)	Bark	9-12
<i>Castanea spp.</i> (Chesnut)	Wood	30
<i>Casuarina equisetifolia</i> (Casuarina)	Bark	7-18
<i>Ceriops roxburghiana</i> (Goran)	Bark	20-40
<i>C. tahal</i> (Goran)	Bark	20-40
<i>Cleistanthus collinus</i> (Karad)	Bark	23-27
<i>Emblica officinalis</i> (Amla)	Stem bark, Twig bark, Fruit, leaves	8-9 21-24 28 22
<i>Eucalyptus occidentialis</i> (Mallet)	Bark	40
<i>Eucalyptus spp.</i> (Eucalyptus)	Bark and Wood	55
<i>Eugenia jambolana</i> (Jammun)	Bark	13-19
<i>Hopea parviflora</i> (Hopea)	Bark	21
<i>Larix spp.</i> (Larch)	Bark	10
<i>Mangifera indica</i> (Mango)	Bark	17
<i>Peltophorum ferrugineum</i> (Peltophorum)	Bark	20-22
<i>Pithecelobium dulce</i> (Jungli jalebi)	Bark	30-35
<i>Punica granatum</i> (Pomegranate)	Fruit rind	26
<i>Quebracho colorado</i>	Heart wood	20-27
<i>Quercus aegilops</i> (Oak)	Bark	30
<i>Q. marolepis</i> (Valonia)	Cup and beard	25-35
<i>Q. montana</i> (Chesnut oak)	Bark	6-15
<i>Rhizophora mucronata</i> (Mangrove)	Bark	30
<i>Rhus spp.</i> (Sumach)	Leaves	20-35
<i>Rhus pentaphylla</i> (Tizrah)	Roots and wood	30
<i>Shorea robusta</i> (Sal)	Bark	7-9
<i>Terminalia alata</i> (Saja, Laurel)	Bark	15
<i>T. arjuna</i> (Arjun)	Bark	23
<i>T. bellirica</i> (Beheda)	Nut	12
<i>T. chebula</i> (Harar)	Nut	30-55
<i>T. tormentosa</i>	Fruit	10-23
<i>Tsuga canadensis</i> (Hemlock)	Bark	25
<i>T. heterophylla</i> (Western hemlock)	Bark	25
<i>Tamarindus indica</i> (Tamarind)	Fruit	20
<i>Uncaria gambir</i> (Gambier)	Leaves	35-40

(Salt and Sinclair 1951, Dastur 1964, Workman 1997, Negi 1992 and Dwivedi 1993)

2.3.1. Chemistry, Classification and Properties of Tannins

Tannins are simple chemical compounds made of carbon, hydrogen and oxygen. The empirical formula of tannins is $C_{76}H_{52}O_{46}$. These are water soluble polyphenolic compounds, with high molecular weight ranging from 500 to 3000 (Dwivedi 1993). These are bulky powders ranging from light yellow to brown in colour (Nault 1977).

Dwivedi (1993) reported that tannins do not denote a single compound. These include a large class of organic substances, which often differ widely in their chemical composition and reaction. Some varieties are found in diseased vegetable tissues or in abnormal growths while others are present in different parts of healthy plants. Gallotannic acid is present in gallnuts, caffetannic acid in coffee beans, morring-tannin in yellow wood, quercitannic acid in oak bark, egallitannic acid in pomegranate rind, etc.

(Pankaj (2002) has classified tannins into broad categories :-

- i) Condensed or flavonoid (catechol type) tannins based on polymeric flavon.
- ii) Hydrolysable (pyrogallol type) tannins based on esters of gallic acid.

In same plant different parts like bark, nut, leaf and wood may contain different types of tannins. In fact the presence of both hydrolysable (like chebulic acid and terchebin) and condensed tannins (like proanthocynidindimers, trimers and other oligomers) together in the same part of tanniferous plants is generally not found (Dwivedi 1993). These tannins are not by any means identical in all their physical properties and chemical conduct (Dudley 1957).

Cayne (1976) observed that tannins possess some common characteristics. These are usually amorphous, have an astringent taste and dissolve in hot water. These form insoluble products with proteins and thus turn animal skin into leather. However, according to Nault (1977) one important difference among tannins obtained from different kinds of trees is the colour produced in the tanned leather.

2.3.2 Application of Tannins on Textiles

Gupta (1992) reported that decoction of *Iodh* (*Symplocos racemosa*) or *harda* (*Terminalia chebula*) was done to make the colours of *tessu* dyed fabric more lively and fast. Both are quite rich in tannins and can be added to the dye bath by the traditional dyers.

Myrobalan is very widely used tannin in different parts of India as a mordant in dyeing of cotton (Negi, 1992).

Rafai (1992) reported that the fabric to be printed in the *Multani* style is mordanted with myrobalan after removal of starch and treatment with oil. Fine powders of chebulic myrobalan (*harda*) and baileric myrobalan (*baheda*), 40g each, are dissolved in one and a half litre water. Sugar is added to this solution. *Quercus infectoria* (*mazufal*), *Garcinia xanthochymus* (*tamala*), thick cinnamon and cobra saffron (*nagkesar*), 5g each, are ground to fine powder and soaked with *harda* overnight. The mixture is boiled for 15-20 minutes, cooled and filtered through muslin cloth. The fibre is then treated with the filtrate.

Dwivedi (1993) reported that *Divi-divi* (*Caesalpinia coriaria*) fruit is also used as mordanting agent in textile industry. The important feature of pods in

high tannin content and the easy extraction process. The tannin from axle-wood tree (*Anogeissus latifolia*) is also used as a mordant. The bark of *Alnus nepalensis* and *Alnus nitida* are used to improve fastness of the colour of fabric previously dyed with brown dye of *Himalayan madder* (*Rubia cordifolia*).

2.3.2.1 Application of tannins on cotton

Padhye and Rathi (1990) treated pure cotton fabric with different concentrations of myrobalan followed by application of different concentrations of various synthetic mordants and finally dyed with two dyes, i.e. madder and *savalikodi*. It was found that, as the concentration of *harda* increased, the dye uptake on fabric increased.

Nalankilli (1997) reported that tannin is most widely used mordant ever since the colouration of textiles started. People from Rajasthan, Bihar, Andhra, Tamil nadu and maharashtra have been using tannin for dyeing and printing which are still being exhibited in museums. The famous *Kalamkari* works of olden days and printing of *Multani* sarees have been done mostly in tannin. These are largely used for preparing cotton so as to enable it to retain colouring matter permanently.

Deo and Paul (2000) dyed ecru denim with onion extract using natural mordant separately and also in combinations. Ecru denim swatches were dyed with onion extract using natural mordants like *harda*, tartaric acid and tannic acid. Synergistic effect of mordants was observed while using binary combinations of mordants. *Harda*-tartaric acid was found to be the best followed by tannic acid-*harda* and tartaric acid tannic combinations. Meta mordanting showed the best

results for *harda*-tartaric acid combinations. There was an overall improvement in fastness properties of the samples dyed with different combinations over that of the control and single mordanted samples.

Prabu and Premraj (2001) extracted mordant at room temperature from fruit of *Phyllanthus Embilica* and leaves of *Terminalia catappa* to dye cotton. Varied mordant concentration and mordanting time were studied. *Terminalia catappa* showed better results than *Phyllanthus Embilica*.

2.3.2.2 Application of tannins on other fibres

Gulrajani *et al.* (1992a) studied dyeing of wool with turmeric. Seven natural mordants namely alum (10%), iron (3%), potassium dichromate (5%), tin (1%), tannic acid (5%) and *harda* (10%) were employed. The a^* and b^* values of dyed wool showed that all mordants increased yellow as well as red content of the dyed samples. *Harda* mordanted samples has similar wash fastness to iron mordanted samples and had better wash fastness than alum and tin mordanted samples.

Gulrajani *et al.* (1992b) studied wool dyeing with natural dye *kapila* (*Mallotus phillipinesis*), onion (*Allium cepa*) and *tessu* (*Butea monosperma*). Mordants changed the hue, reduced a^* (redness) and b^* (yellowness) values and did not improve fastness properties of the *kapila* dye. All mordants except iron, tannic acid and *harda* increased the yellow content of the colour from onion-skin. All the synthetic mordants increased the L^* (darkness), a^* and b^* values while *harda* and tannic acid decreased them.

Gulrajani *et al.* (1992c) studied the effect of *harda* and synthetic mordants on dyeing wool with *henna* (*Lawsonia inermis*) and *dolu* (*Rheum emodi*). Alum, *harda* and tannic acid increased the redness of henna dyed wool while other mordants reduced it. The mordants did not appear to have effect on the fastness of the dye. In the case of *dolu* dye the light fastness of copper, iron and chrome mordanted samples were good, while it was poor for alum, tin, *harda* and tannic acid mordanted samples. Wash fastness was fair to excellent.

In another study (Gulrajani *et al.* 1992d) conducted a study on dyeing wool with natural yellow dye, namely *Terminalia chebula* and *Punica granatum*. Both dyes gave different shades of yellow and brown with different mordants. *Harda* dyed samples exhibited better light fastness when mordanted with iron, copper and chrome than tin, tannic acid. Pomegranate rind dye showed better fastness with alum, copper, iron and chrome over unmordanted samples.

It has been reported that in dyeing with *harsingar*, *harda* mordant increased the L^* and a^* values and did not alter b^* values of samples (Gulrajani *et al.* 1992e). In the case of safflower *harda* treatment decreased the L^* a^* b^* values. *Harda* reduced the light fastness but improved wash fastness. In case of barberry, *harda* darkened the hue but reduced a^* and b^* values and L^* values were better than alum, tannic acid and stannous chloride mordanted samples. The a^* values of *harda* treated samples were greater than alum, iron, potassium dichromate and tannic acid treated samples with b^* values were greater than potassium dichromate samples. Mordants had no effect on the fastness properties

Rathi and Padhye (1994) treated polyester fabric with *harda* extract in combination with the different synthetic mordants from the same bath before dyeing with one of the five natural dyes viz, *Shavalikodi*, *harda* flower, madder, pomegranate rind and turmeric using carrier and heat set methods. Highest rating of light fastness were conferred for all the dyes with copper sulphate and with heat set method.

Burde and Mehra (1994) dyed the pineapple fibres with turmeric yellow dye and red sandal wood dye using two mordants i.e. *harda* and pomegranate rind and some inorganic mordants. The dye uptake of turmeric dyed fabrics treated with pomegranate rind in absence of other mordants showed good results. In the case of red sandal wood dye uptake was very low, post-mordanting was found better and *harda* treatment gave best results.

Aeron (1999) studied the effect of natural and synthetic mordants. In dyeing wool with *dhavdi* flowers. *Amala*, *harda* and *naspal* were selected as natural mordant, while alum, chrome and copper sulphate as synthetic mordants. It was concluded that *amala* gave lighter shades than *harda* and *naspal*. With synthetic mordants produced brighter shades than natural mordants. Fastness of *amala* and *naspal* treated samples was fair to good, while *harda* treated was very good. The fastness of samples treated with synthetic mordants was better than natural mordant treated samples.

Moses (2002) dyed silk with natural dyes viz. black grape skin, tamarind, onion skin and turmeric using myrobalan as natural mordant. It was observed that increased intensity of colour shades was produced by increasing the dye

material concentration. Results revealed that by incorporating the natural mordant, myrobalan, in the natural dye bath, the wash fastness and light fastness on the silk material increased considerably.

Pankaj (2002) studied the effect of natural mordants on dyeing wool with six natural dyes, namely *ashoka* bark, cassia leaves, lantana leaves, physic nut leaves, rubber plant leaves and *semal* gum. Different eight natural mordants were employed by three methods of mordanting. Premordanting method gave the best results. The effect of natural mordants on hue, value and intensity of the colour was investigated by calculating CIE LAB values. It was concluded that all the natural mordants improved the fastness properties of the dyes, specially the light fastness, followed by washing fastness. These also enhanced the dye uptake in all the dyes.

Ammayappan *et al.* (2003) reported that generally tanning as mordanting is used in dyeing of cellulosic fibres with basic dyes and also in mordanting and weighting of silk fabrics. The investigator studied the effect of back tanning on dyed silk fabrics, which were dyed by acid dyes. The back tanning treatment enhances the fastness property and also the flatness of the colour.

Mathur and Gupta (2003) dried aqueous extract of petaloid of banana flowers and used it as mordant. Bharat Merino sheep wool yarn was dyed with turmeric and subjected to natural mordant and chromium under identical conditions. It was observed that 3.5% (oww) concentration of natural mordant provided just similar results to that of 1.5 % (oww) chromium in terms of colour

fastness, colour shade / tone and K/S values. The natural mordant doesn't damage wool.

Karolia and Dilliwar (2004) dyed sheep leather with marigold to produce earthy colours in shades of brown, green for leather garments with combination of vegetable tanning agents and post-mordanting agents. Leather dyed with marigold showed good fastness properties with few exceptions. Hence, marigold flowers can be effectively used as colouring agent for leather, which is eco-friendly, reduce pollution and is abundantly available and grown as a crop in India.

Banga and Patil (2004) dyed wool fabric with an aqueous extract from the bark of *Acacia pennate* containing tannins as the major colourant. Dyeing with combination of extracts of *Acacia pennate* and banana stem was carried out which improved depth of colour. The dyeing showed moderate to good fastness to washing, light and rubbing.

Dixit and Jahan (2005) used natural mordants (amaltas bark, pomegranate rind) as well as synthetic mordants (ferrous sulphate and potassium dichromate) to dye silk with *euphorbia* leaves. They produced shades of grey, chamios, sandstone and sandalwood. Colourfastness to light, washing, perspiration and crocking of the dyed samples increased with the use of natural and metallic mordants.

2.3.2.3 Natural mordants other than tannins

Gulrajani (1992) reported that the naturally occurring oil-mordants are used mainly in the dyeing of Turkey Red colour from madder. The main function

of the oil mordant is to form complex with alum, which is used as the main mordant.

Venugopal (1993) reported that in addition to metallic mordants, natural mordants like urine, saliva and egg albumin can also be exploited for dyeing with natural colouring matter to ensure fastness. These mordants were in use in ancient times also in our country.

According to Ramakrishna (1999) natural dyes can be used in conjunction with mordants like urine, saliva and egg albumen to improve their substantivity.

Tiwari *et al.* (2001) reported that weavers of Orissa pre-treated the cotton yarn with castor oil, cow dung and alkaline water before dyeing.

Vankar (2002) reported that lichen dyes were dissolved in human urine, and the yarns were immersed in this mixture. Ammonia salts in the urine functioned as mordants to make dye permanent.

2.4 ENZYMATIC TREATMENT

Achwal (1992) concluded that pectinase Boerzyme M. completely removed pectin from chloroform extract. The residual pectin was determined by extraction with ammonium oxalate after the enzyme treatment. The pectinase process can remove the pectin from cotton effectively in a short time which normally requires a severe boil with high concentration of caustic soda for many hours. Sonwalkar and Prabhu (1992) concluded that the twisted mulberry silk can be effectively degummed with 2.5 g/l Biopril – 50 and 1.0 g/l of a non – ionic wetting agent at 50°C for 60 minutes maintaining the pH of bath at 9 without

affecting the tenacity. This process can be carried out in a single bath without and pretreatment or after treatment resulting in saving time and energy.

Kundu *et al.* (1993) treated jute fibres with enzymes, which increased the pore volume (46.2%), lead to increase in capacity to retain peroxide (25.5%) and larger surface area of lignin accessible to the oxidant (~30%). Improved bleaching was therefore achieved. Enzyme treatment increased transverse swelling (14%) and reduced bulk torsional rigidity (12.5%), making the fibre more flexible and therefore softer. The removal of cementing materials such as hemicellulose and lignin by bleaching was enhanced by enzyme pretreatment, resulting in better filamentation and fineness. Scanning electron micrographs confirmed this. Experiments with purified enzyme pretreatment showed that xylanase pretreatment predominated in facilitating bleaching and cellulase in the swelling or softening. An appropriate combination of the two was required to obtain optimal effect.

Diller *et al.* (1994) conducted enzymatic hydrolysis to decrease stiffness, ease stretchability and loosen the structure of all cellulosic fabrics. Retention of strength after 48 hours incubation time increased in the order viscose rayon < cotton < ramie < linen, whereas weight loss increased in the order ramie < linen < cotton < viscose rayon. X-ray crystallinity and moisture sorption of the samples did not change after the treatment.

Koo *et al.* (1994a) reported that both direct and reactive dyes on the substrate apparently inhibited the enzyme catalytic reaction, whereas a vat dye did not. The enzyme treatment significantly reduced both tear strength and dye

uptake of the fabric. Enzyme treated and successfully dyed fabrics showed different colour fading profiles compared to untreated fabrics after laundering.

According to Koo *et al.* (1994b) both anionic and cationic surfactants apparently inhibit the cellulase catalytic reaction, whereas nonionic surfactant do not. The inhibitory actions of the surfactants are similar to that of dyes. The actions have been attributed to the electrostatic interactions between charged inhibitory compounds and the cellulase enzyme in a treatment solution and on the cotton substrate.

Achwal (1995) reported that a pretreatment with enzyme leads to fibre swelling, which is enhanced by alkali boil. If the enzyme also contained pectinase, increased up-take of red dye was observed due to crystallization during the enzyme treatment itself.

Cavaco-Paulo and Almeida (1996) reported that the characterization of enzyme mixtures is essential to control the finishing effect obtained by cellulase enzymes. The fabric structure and the presence of pill on the fabric surface are important factors that determine cellulase activity particularly at high levels of mechanical actions.

Gulrajani and Gupta (1996) degummed the silk with eight different commercially available enzymes viz. Degummase 1000L, Protosol, Trypsin, Alcalase, Protease A, Protease N, Pepsin and Protease M. The degumming conditions with respect to concentrations and time were optimized for each enzyme. Enzyme activity, an important intrinsic property and degumming efficiency were evaluated in terms of weight loss, tensile strength, handle and

lustre. A weight loss of 24.3% was obtained for most of the enzymes at an optimum enzyme concentration of 15% except for Degummase 1000L, which gave this result at 25% concentration. Trypsin and pepsin gave extremely poor results. The increase in treatment time at the optimum enzyme concentration showed no further significant weight loss. There was no significant strength loss in any of the degummed samples but marked improvement was observed in handle and lustre. Scanning Electronic Microscope (SEM) showed that Protosol enzyme gave the best results both with respect to weight loss and smoothness of the fabric.

Gulrajani *et al.* (1997) treated the spun silk fabric with a proteolytic enzyme, degummase. It improved the wettability and whiteness of the fabric without affecting the strength. The enzyme treated fabric absorbs more dye as compared to the untreated fabric. Dyeing of the spun silk fabric under alkaline conditions gave more uniformly dyed fabrics as compared to that obtained on dyeing under neutral conditions. However, the dye uptake and dye fixation are higher under neutral conditions.

Li and Hardin (1997) reported that the enzymatic scouring with cellulases and pectinases was very effective part of preparing cotton for chemical treatment. The change in the water absorbency of cotton was rapidly catalyzed by pectinases, cellulases or their mixtures.

Blanchard *et al.* (2000) chemically modified the cotton with methylolamide or polycarboxylic acid, cross-linking agents and treated with cellulase. Physical properties (tensile strength loss and weight loss) of cotton

were altered by chemical modification with cross-linking agents. Glucose analysis of enzyme solution was useful for determining the effect of enzymatic activity on cellulose. Some reactive dyed cotton fabrics show resistance to enzymatic hydrolysis, but substantially more protection was achieved with low concentration level of conventional finishing agents.

Different types of pectinases, proteases and lipases were used to treat cotton fibre and knitted fabrics by Buchert *et al.* (2000). The effect of enzymatic action was analyzed using high pressure liquid chromatograph and electron spectroscopy. The enzymes improved water absorbency and fabric colour.

Chattopadhyaya and Sharma (2000) finished pure jute fabrics with Biosoft – P (Cellulase enzyme) under different conditions and then tested for physical properties. The image analysis and Kawabata Evaluation System for fabrics (KES-FB) were used to evaluate the extent of modification and fabric hand respectively. It was observed that enzyme treatment caused considerable reduction in protruding surface hairs on the fabric and improvement in softness of the fabric. Samples treated with 4% (owf) enzyme at 50°C for 90 min. were found to be the best as they reached in more than 15% increased in the total hand value of the fabric.

Hartzell and Durrant (2000) demonstrated that the effectiveness of *Aspergillus niger* pectinase increased by incorporating agitation into the treatment procedure. This reduced the duration of the treatment period and reduced the quantity of enzyme used. Shaking agitation increased wettability by more than 50% and fabric to fabric agitation increased wettability by 70%. Fabric

wettability increased further when the rate of agitation was doubled. Added agitation to the treatment process also reduced the treatment time and enzyme amount required for high wettability.

Gusakov *et al.* (2000) developed a small scale method for assaying the abrasive activities of cellulase (the ability to remove indigo from denim during enzyme treatment) and indigo backstaining on cotton fabric in the presence of enzymes. Both the abrasion and backstaining microassays were carried out either with 20-30 ml or with 2-3 ml of enzyme solution. Depending on the scale, the microassay procedures required not more than 10 mg or not more than 1 mg of enzyme protein respectively. Image analysis was performed to evaluate minor amounts of enzyme during strain development and biochemical research.

Liu *et al.* (2000) treated three cellulase compositions for bio-polishing of the cellulosic fabric. An acid cellulase complex, endo-enriched cellulase and a mono-component endoglucanase were compared based on their selectivity and sensitivity to process conditions. All cellulases have similar application pH and temperature ranges. However their sensitivity to liquor ratio and to mechanical agitation differ significantly.

Navarro *et al.* (2000) studied the capacity of chitosan to adsorb Blue Bezanyl 5R. The maximum capacity for chitosan was 30% at pH 4.9 and pH 90% at 3.5, at dyestuff concentration of 0.045g/l at 25⁰C. The adsorption capacity of Chitosan at an acid pH is higher than at neutral pH and that it depends on the initial dyestuff concentration.

Neelima *et al.* (2000) concluded that scouring and dyeing had an effect on yarn properties of UAS sheep breed wool. Yarn count, yarn twist and yarn tensile strength slightly reduced and yarn elongation increased after dyeing.

Niels *et al* (2000) pre-treated the cotton with pectinase enzyme for subsequent bleaching and / or dyeing. The process has many distinct advantages and may be combined with other treatments. The pectinase operates at mild pH condition and a broad temperature range and can be used in a majority of wet textile processes. It replaces the traditionally harsh alkaline chemicals with an environmentally friendly system (lower BOD, COD) while maintaining the quality of cotton. Considerable saving in water, time and chemicals along with excellent dyeing characteristics have been determined.

Pant and Sariya (2000) concluded that 5% concentration of Protosol and 10% concentration of degummase are sufficient for removal of gum. Enzymatic treatment made silk white by decreasing yellowness but when enzyme as well bleaching treatment was given to silk, whiteness and other properties improved. Of all the three methods - first enzyme treatment then bleaching; first bleaching and then the enzyme treatment and simultaneous enzyme and bleaching; the first method with the enzyme treatment then bleaching gave best results. Stiffness of silk decreased and its crease recovery improved. Silk became lustrous and absorbent.

Pant and Tayal (2000) reported that the enzymatic treatment improved crease recovery of wool fabric but decreased its stiffness. It enhanced bleaching efficiency. Good whiteness was obtained when both – bleaching as well as the

enzyme treatment were given as compared to only bleaching or only enzyme the treatment. Wettability increased markedly, but there was some loss in strength of wool. It was also found that the bleaching can be carried out in less time with low concentration of H_2O_2 if combined with enzyme treatment.

Takagishi *et al* (2000) pre-treated the mercerized cotton fibres using ammonia treatment, sodium hydroxide treatment and two combined treatments using ammonia and sodium hydroxide. The physical properties, dye ability and handle of the resultant fibres were investigated after the treatments. Crystalline regions of the mercerized fibres were hydrolyzed in the first step of hydrolysis. In this step, ammonia treatment decreased crystallite size to a great extent due to the hydrolysis of the cellulose III crystalline phase. Cellulase treatment rendered the crystallite surface highly accessible to water molecules. The crystalline phase was closely related to water sorption of cellulase – treated fibres.

Traore and Diller (2000) applied pectinase in combination with lipase and cellulase on cotton. Dyeing with direct dyes yielded uniform results with increased colour strength. The whiteness of fabric was slightly enhanced with and without aqueous pretreatment. All samples showed significantly softer hand with basically unchanged tensile properties.

Yoon *et al.* (2000) reported that there was a significant reduction in backstaining at much lower temperature than the conventional process by using small amounts of protease C compound with soda ash either at the end of the cellulase washing step or during the rinsing step. By adding protease treatment

at the end of the cellulase wash step, one rinse step was eliminated, offering saving in time and energy.

Chattopadhyaya and Sanyal (2001) reported that enhancement of enzyme activity on grey bleached and scoured bleached jute fabric produced substantial loss of weight after the treatment. As a result of the enzymolysis, pore volume increased. Due to their lignin surface exposure also increased. The increase in pore volume allowed large resin molecules enter the pore easily and make a cross link with lignin rapidly on the exposed lignin surface. This increased reactivity of resin on enzyme treated fabric produce a larger crosslinking reaction, which was manifested by a 25 % increase in crease recovery angle. Moisture-regain value and abrasion resistance decreased after resin treatment. Resin treatment caused a substantial drop in tensile strength, but dimensional stability improved appreciably.

Chattopadhyaya *et al.* (2001) reported that the activity of enzyme activity on bleached fabric was in the order: hydrogen peroxide bleached jute fabric > sodium chloride bleached jute fabric > sodium hypochlorite bleached jute fabric. Scouring with 4% (owf) NaOH followed by bleaching and enzyme treatment produced the maximum change in fabric properties due to enzyme treatment. Enzyme treatment on both direct and reactive dyed fabric result in less weight loss due to the inhibition action. Thus weight loss is less in the case of scoured – bleached and dyed fabric than only bleached and dyed fabric, as in the former case, the dye fixation is more.

Raje *et al.* (2001) reported that the smoothness and softness of medium and heavy weight fabrics can be improved to a great extent by treatment with cellulase enzyme. The change in properties of fabric depends not only on enzyme concentration and time of reaction, but also on fabric characteristics such as thickness. Prolonged enzyme treatment leads to more serious fabric damage accompanied by a higher weight loss. Enzyme treatment followed by silicone softener solution treatment enhanced the smoothness and softness of fabric.

Ramkumar and Abdalah (2001) treated the cotton fabric with CellusoftTM AP at 6 different concentrations. The enzyme application process was terminated by soaking the enzyme treated fabrics in water at pH 8, at 80° C for 10 minutes. Fabrics were then rinsed in cold water (five minutes) and dried in air. The results showed that the application of cellulase enzyme on cotton fabric had a positive effect on the surface characteristics. The friction parameters showed that the enzyme enhanced the smoothness of cotton fabric.

Singh and Goel (2001) concluded that the use of enzymes for the treatment of coarse (carpet) wool resulted in improvement of their texture. Extra softness is also imparted, with increase in the lustre but there was slight decrease in weight and strength. The action of enzyme trypsin was found to be more effective in the process of enzymatic treatment as compared to enzyme pepsin.

Chattopadhyaya *et al.* (2002) used two bleaching agents, namely hydrogen peroxide and sodium chlorite. It was found that enzyme treatment before

bleaching resulted in increase in whiteness index, while due to back staining whiteness index decreased if enzyme treatment was done on bleached fabric. There was no effect of enzyme treatment on bleaching of grey jute fabric. For the same degree of whiteness the enzyme pre-treated fabric required 25% less hydrogen peroxide.

Teli *et al.* (2002) subjected the cotton to swelling treatment using three different swelling agents, like sodium hydroxide, ethylene diamine and morpholine. The swollen cotton samples were then treated with acid and neutral cellulase enzyme and similarly pre-enzyme treatment followed by swelling agent treatment. All treated samples were dyed with aqueous extract of tea. The K/S values of the dyed samples indicated that the enzyme treatment followed by swelling showed a higher depth of dyeing as compared to swelling treatment followed by enzyme treatment. The wash and light fastness of the samples with aqueous extract of tea were found to be satisfactory and were independent of the treatment.

Gurumallesh and Arputharaj (2003) reported that the cellulase enzyme modified the properties of both woven and knitted cotton fabrics, the surface area and the fabric structure played an important role in enzymatic action. Some synthetic dyes may inhibit the action of enzyme in cotton. The enzymatic treatment improved the dyeability and water absorbency of both knitted and woven cotton fabrics.

Lipp – Symonowicz *et al* (2003) carried out a research to assess the effect of enzyme treatment on the dyeing behaviour of flax fibre. Wet spun, 120 tex flax

yarn bleached with hydrogen peroxide, preceded by enzyme treatment with two enzymatic agents, Cellusoft Ultra L and Bio-Prep was used in the experiment. The fibres were dyed using a range of dyes. It was found that preceding bleaching with enzymatic treatment increased the exhaustion of the dye in the dye bath, depending on the dye used, increased the colour intensity and the purity of the shade obtained in the dyed yarn and increased colour fastness especially to washing.

Paul *et al.* (2003) concluded that dyeing with acid Red RS, basic Red, metal complex orange G and yellow GR caused reduction in the fibre tenacity. Fibre became finer after dyeing. From the results of colour fastness it was concluded that metal complex dyes gave the best results for all the three parameters of fastness i.e., light, washing and crocking.

Raval and Banerjee (2003) concluded that the enzyme treatment showed weight loss in silk which attributed to removal of residual sizing agents, sericin and surface fibrils. Lowering of strength and elongation attributed to removal of sericin, as well as enzymatic hydrolysis of fibroin content during the treatment. Pretreatment with formic acid and zinc chloride was found to be effective. Formic acid being a weak acid, partially dissolved the fibroin and zinc chloride, leading to fibre swelling and more dye absorption.

Stanescu *et al.* (2003) dyed wool samples with an acid dye, Bemacid Brilliant Blue 2R, after enzymatic pre-treatment organic and inorganic silicates as matrix as catalysts i.e. Na_2SO_3 and Tetraethyl silicate respectively. The dye uptake proved to be related to the enzyme action expressed as weight loss. The

results from the inorganic matrix catalyst differ from those of the organic matrix catalyst. Better results have been obtained with inorganic catalyst, where a lower weight loss generated better dye uptake.

Djordievich and Djordievich (2004) investigated that the lipase enzyme improved dye uptake and water penetration of polyester fibres causing a minimal loss of fibre weight and strength.

Moses and Ramasamy (2004) processed / enzyme treated jute and the bleached materials and dyed with some natural dyes. The jute and jute – cotton material treated with cellulase enzyme enhanced the basic properties, helped to produce uniform, brilliant colours, improved dye uptake and increased wash and light fastness properties.

Pan *et al.* (2004) used enzyme treatment on scoured fabric for 2 hrs. at 55°C using 4% (owf) enzyme concentration and produced better results as far as bleaching and handle property are concerned. The bending length decreased after enzyme treatment. This means that the enzyme treatment leads to improvement of drapability of the jute fabric. Residual shrinkage of jute fabric reached minimum if enzyme treatment was done on scoured jute fabric before bleaching.

Singh and Goel (2004a) concluded that enzymatic treatment improved softness and lustre of the wool, but decreased 3-5% strength and elongation percent of the wool yarn. The decrease in fibre diameter and yarn count of wool pointed towards the fineness of yarn.

Singh and Goel (2004b) treated wool fabric with three proteolytic enzymes – pepsin, papain and trypsin. The fabrics were then dyed with basic, reactive and natural dyes. The effect of enzymatic treatment resulted in significant increase in the dye absorption percent of the wool fabric with slight improvement in the colour fastness properties of the dyed fabric. It was observed that the enzyme treated woollen samples exhibit better dye pick up and gave more colour value and brilliant shades for the same strength of dyestuff as compared with untreated wool fabric. The enzymatic treatment enhanced the surface for the same strength of dyestuff as compared to the untreated wool fabric

Teli *et al.* (2004) subjected cotton to swelling treatment using three different swelling agents, like sodium hydroxide, ethylene diamine and morpholine. These swollen cotton samples were then treated with acid and neutral cellulase enzyme. All treated samples were dyed with aqueous extract of madder. The K/S values of the dyed samples indicate that the enzyme treatment followed by swelling showed a higher depth of dyeing as compared to swelling treatment followed by enzyme treatment. Independent of the treatment, the wash and light fastness of the samples with aqueous extract of madder were found to be good to excellent.

Sahin and Gursoy (2005) optimized pectinase 0.011g/100ml, surfactant 1g/100ml, treatment time 25 min., treatment temperature 40°C, pH 4.2, liquor ratio 1:40 and stirring speed 1000 rpm. The staining results with Ruthenium Red confirmed that pectinase treatment removed the pectins and proteins when compared to unscoured fabric. Microscopic observation showed that cellulosic

structures of cotton fibre did not change after enzymatic treatment. The surfactants improved water absorbency and weight loss was within the range of estimated non-cellulosic weight.

Thilagavathi *et. al.* (2005) concluded that enzyme treatment improved the handle value of cotton fabric in terms of softness, smoothness, and stiffness. Bending rigidity and shear stiffness values were lower for enzyme treated fabric reflecting the improvement in softness and drapability. The lower tensile strength and compressional energy level after enzyme treatment suggested that the energy requirements for extension and compression were lower, indicating the improved softness and smoothness.

From the literature reviewed in this chapter, it is evident that a lot of work has been done on bio processing of textiles. Similarly, research has also been conducted on dyeing with natural dyes using both natural as well as synthetic mordants. However, no work has been done on optimization of enzymatic pre-treatment and dyeing cotton with natural dyes using natural mordants. Therefore, this study on optimization of enzymatic pre-treatment and dyeing of cotton fabric with natural dyes has been undertaken with a view to develop eco-friendly process of dyeing.

MATERIALS AND METHOD

The present investigation was carried out to optimize the conditions of enzymatic pre-treatment and dyeing of cotton with selected natural dyes, obtained from leaves. To facilitate the comprehension of the presentation, this chapter has been divided into following categories:

- 3.1 Materials used for the study
- 3.2 Optimization of variables for enzyme treatment
- 3.3 Optimization of dyeing variables
- 3.4 Colour measurement of dyed samples
- 3.5 Evaluation of colour fastness of the dyed samples

3.1 MATERIALS USED FOR THE STUDY

The materials used to treat and dye cotton fabric in the study include enzyme, natural dyes, natural mordants and various chemicals. The investigator made use of several instruments during the experiment. The details of the material and methods are discussed below:-

3.1.1 Selection of textile Material

Pure white cotton fabric was used for research work, since the fibre is widely used in India and enjoys a good export market as well. It was purchased from the local market. To confirm that the fabric procured for the study is pure

cotton, microscopic, burning and chemical tests were conducted. Its thread count and weight (GSM) was also tested.

3.1.2 Selection of enzyme

Commercial cellulase enzyme (Neutrox BDN 100 Powder) was procured from Rosari Biotech India Private Ltd., Mumbai. It was used for treating cotton fabric prior to dyeing with natural dyes. The enzyme was brownish powder, miscible in water and compatible with non-ionic products. According to Rosari Biotech India Private Ltd., it gave best results at temperature of 50°C and pH ranging from 6.5 - 7.5.

3.1.3 Selection of natural dye material

Four natural dye materials in the form of leaves were selected for the study. Details of these have been given in Table 3.1. The dyes were obtained from the local market as well as collected from the trees grown in Punjab. The leaves were shade dried and ground to form a powder (Plates 1 - 4).

Table 3.1 Natural dyes used in the study

S.No.	English name of the dye	Local name	Botanical name	Cost (Rs. / Kg)
1.	Bansa	Bansoti	<i>Uricalum indacom</i>	50
2.	Bottle Brush	Bottle Brush	<i>Callistemon lanceolatus</i>	Free
3.	Duranta	Duranta	<i>Duranta vr. goldeana</i>	Free
4.	Mango	Amb, Ambi	<i>Mangifera indica</i>	Free

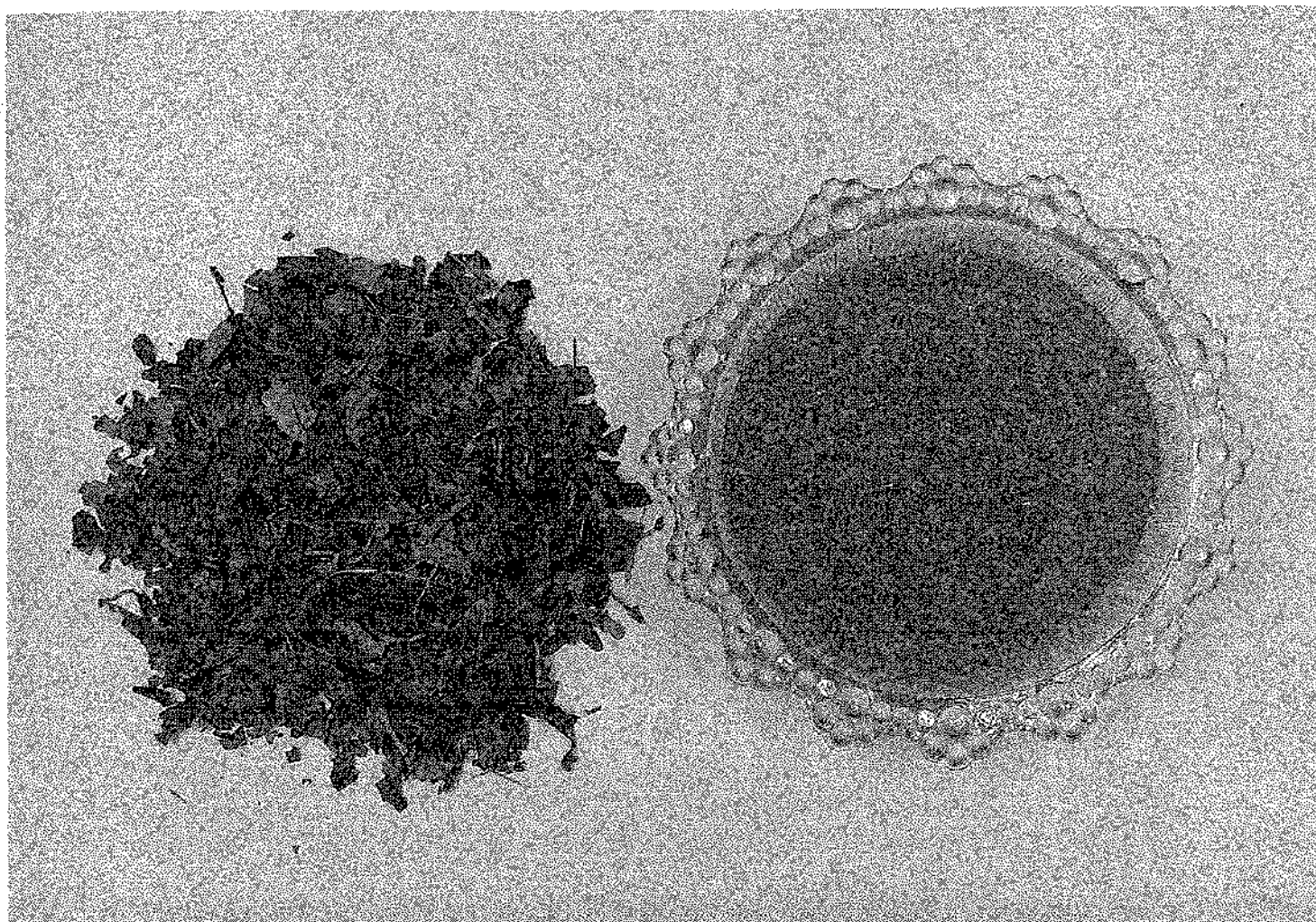
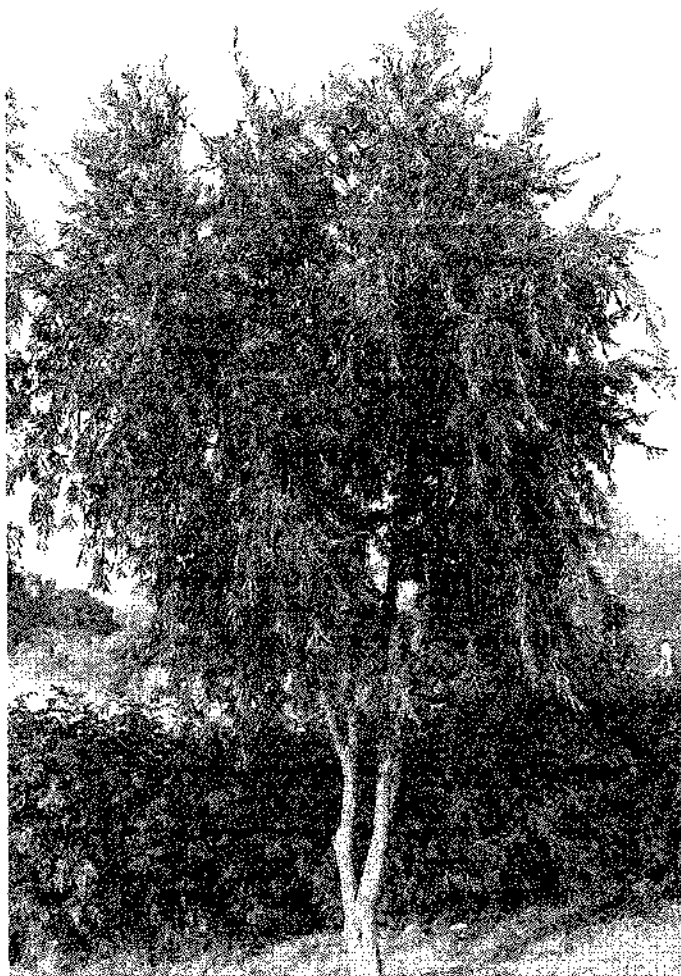
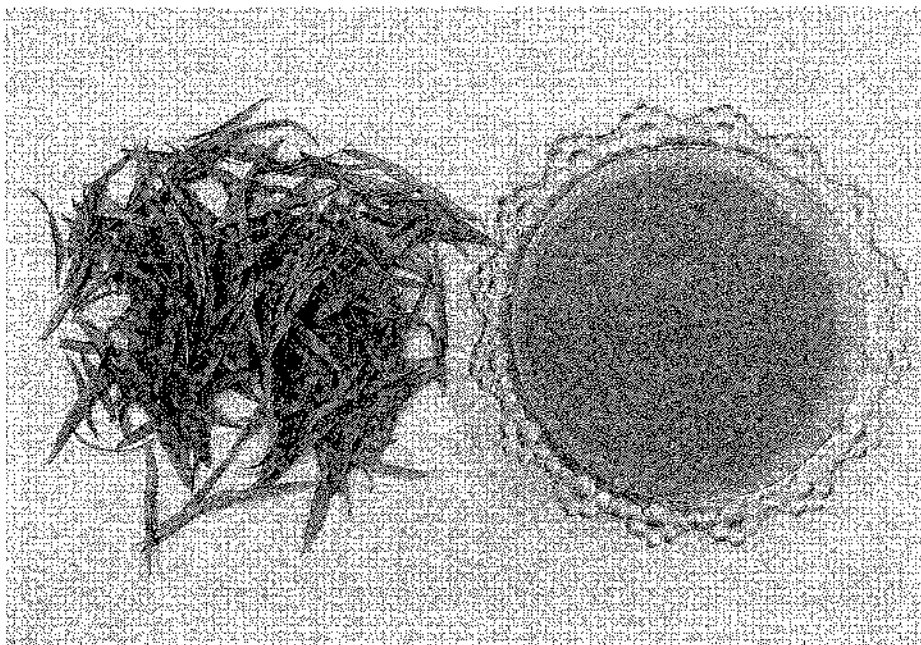


Plate 1 Dried and ground *bansa* leaves



a)

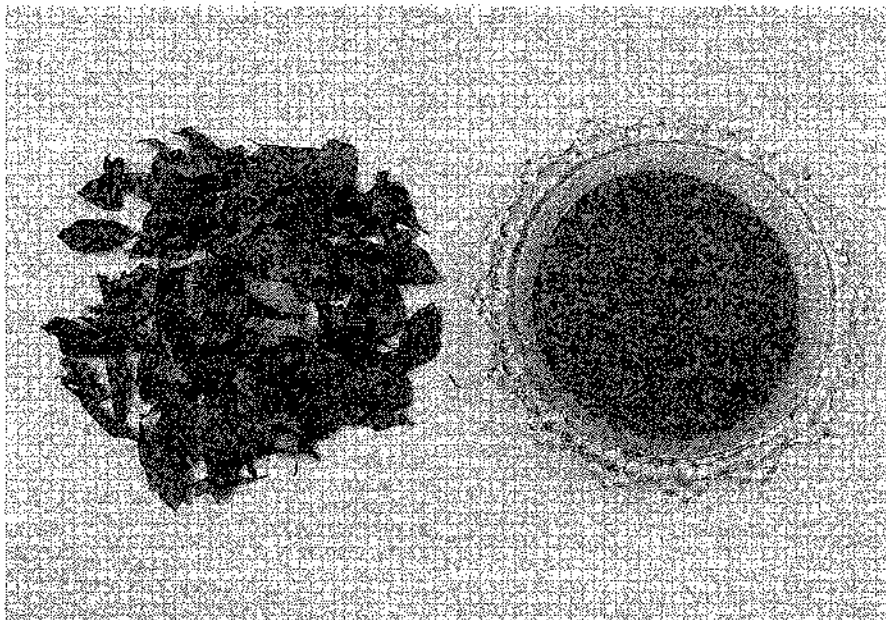


b)

Plate 2 a) Bottle brush tree b) Dried and ground bottle brush leaves



a)



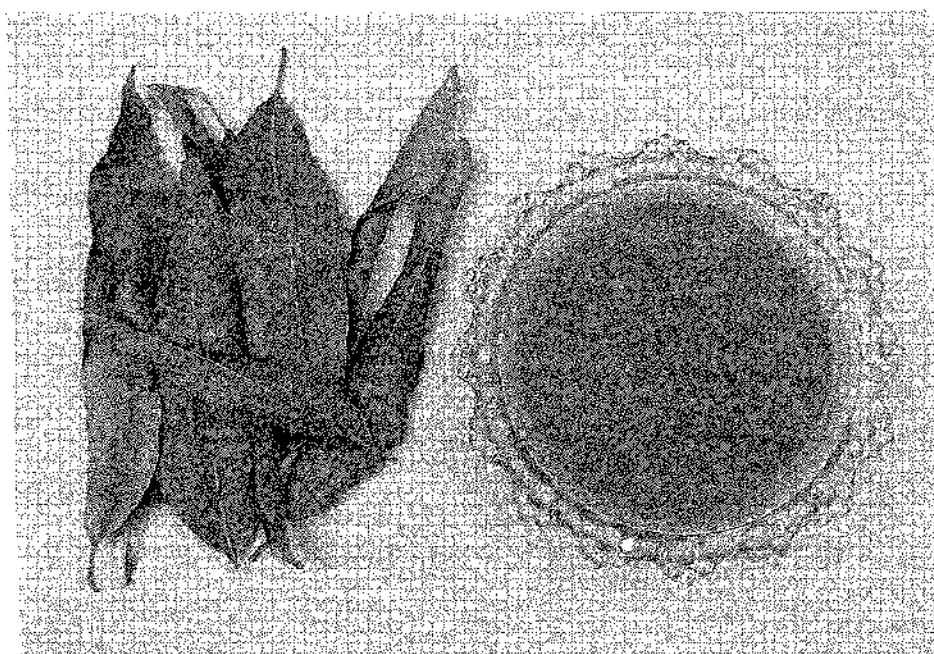
b)

Plate 3 a) Duranta shrub b) Dried and ground duranta leaves





a)



b)

Plate 4 a) Mango tree b) Dried and ground mango leaves

3.1.4 Selection of natural mordants

The four natural mordants used for the study have been presented in Table 3.2. The mordants were selected on the basis of their high tannin content. These were obtained from the local market as well as from the plant sources grown in Punjab (Plates 5 - 8).

Table 3.2 Natural mordants used in the study

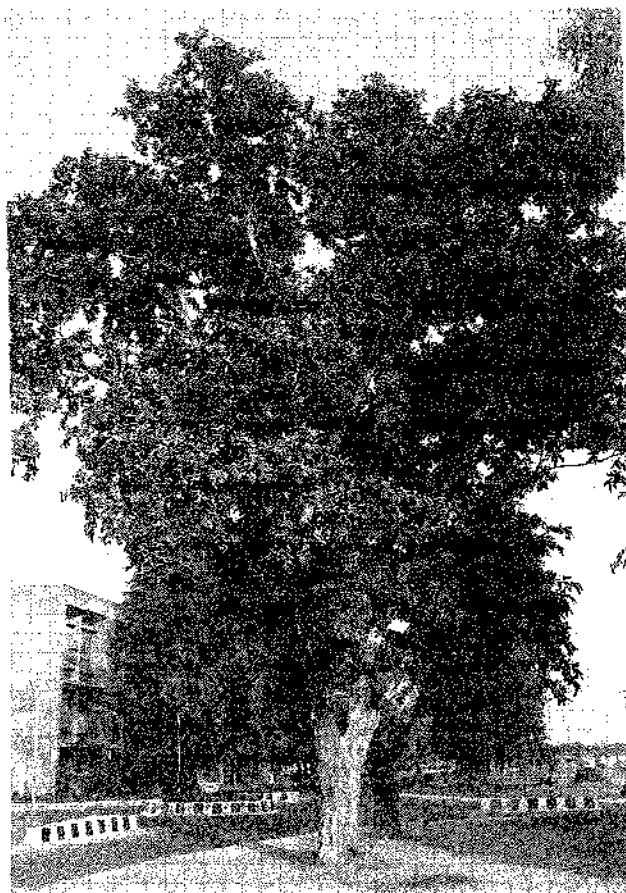
S. no.	English name of the dye	Local name	Botanical name	Source of the dye	Cost (Rs./Kg)
1.	Arjun	Arjun	<i>Terminalia arjuna</i>	Bark	80
2.	Babool	Kikar	<i>Acacia nilotica</i>	Bark	50
3.	Eucalyptus	Safada	<i>Eucalyptus sp.</i>	Bark	Free
4.	Pomegranate	Anar	<i>Punica granatum</i>	Rind	Free

3.1.5 Chemicals used

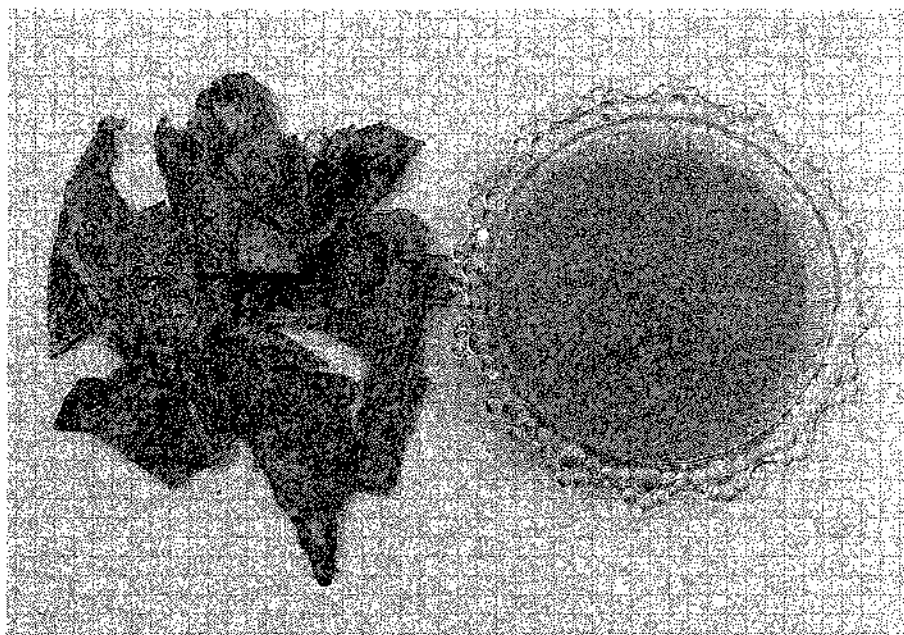
The chemicals used in the study have been given in Table 3.3. These chemicals were supplied by Thames Chemicals, Ludhiana. All the chemicals used were of laboratory grade.

Table 3.3 Chemical used

S. No.	Name of the chemical	Molecular formula	Purpose
1.	Sodium phosphate monobasic dihydrate	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	Buffer solution
2.	Sodium phosphate dibasic anhydrous	Na_2HPO_4	Buffer solution
3.	Acetic acid	CH_3COOH	pH regulator
4.	Sodium carbonate	Na_2CO_3	pH regulator
5.	Sodium chloride	NaCl_2	Perspiration fastness
6.	Urea	Na_2CONH_2	Perspiration fastness
7.	Potassium carbonate	K_2CO_3	Light fastness

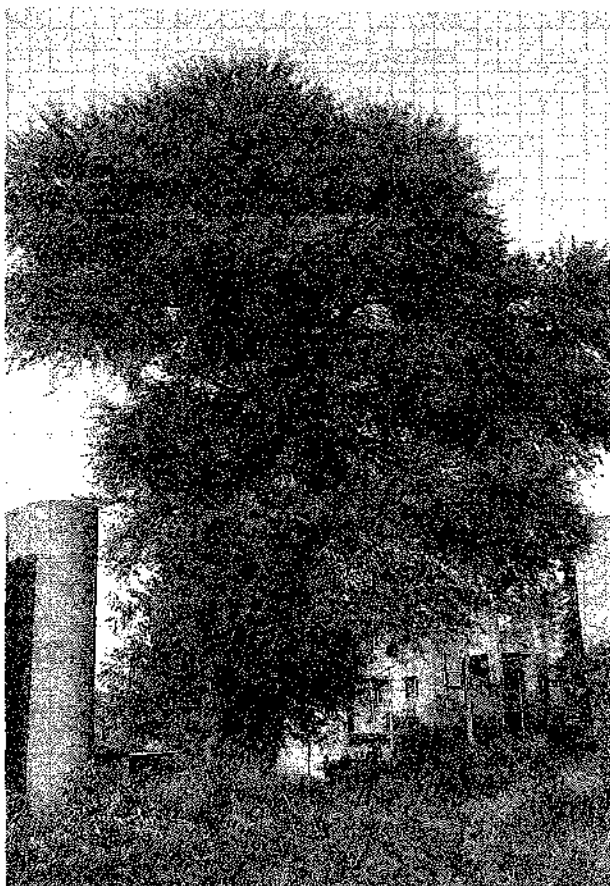


a)

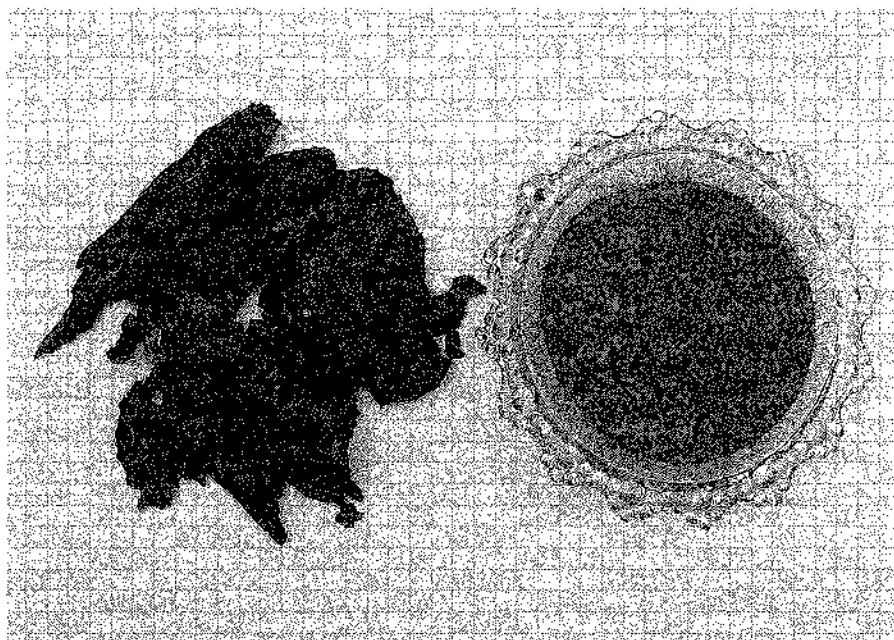


b)

Plate 5 a) *Arjun* tree b) Dried and ground *arjun* bark

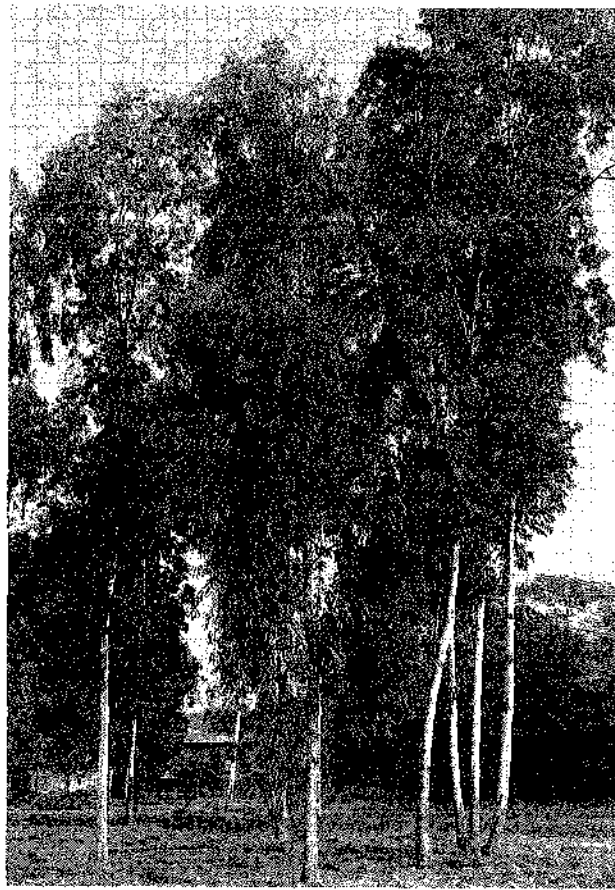


a)

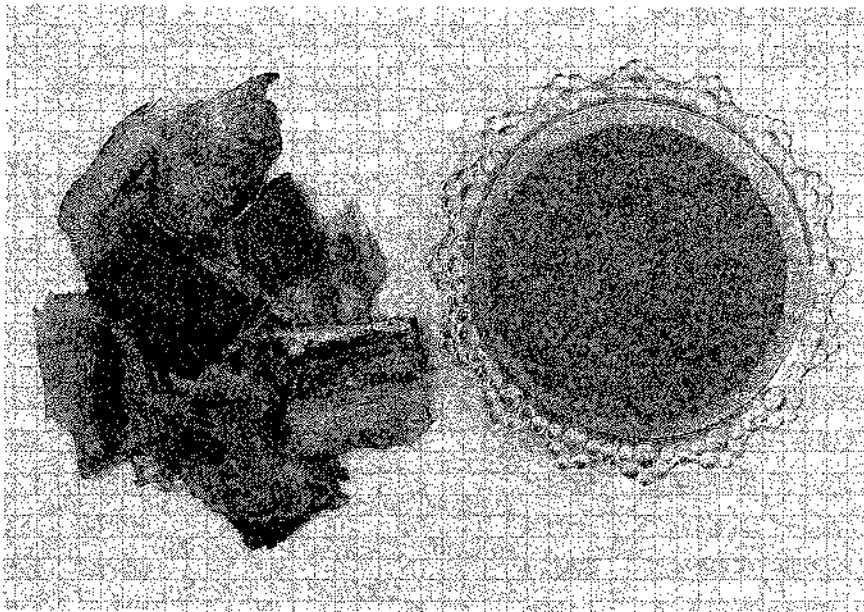


b)

Plate 6 a) *Babool* tree b) Dried and ground *babool* bark

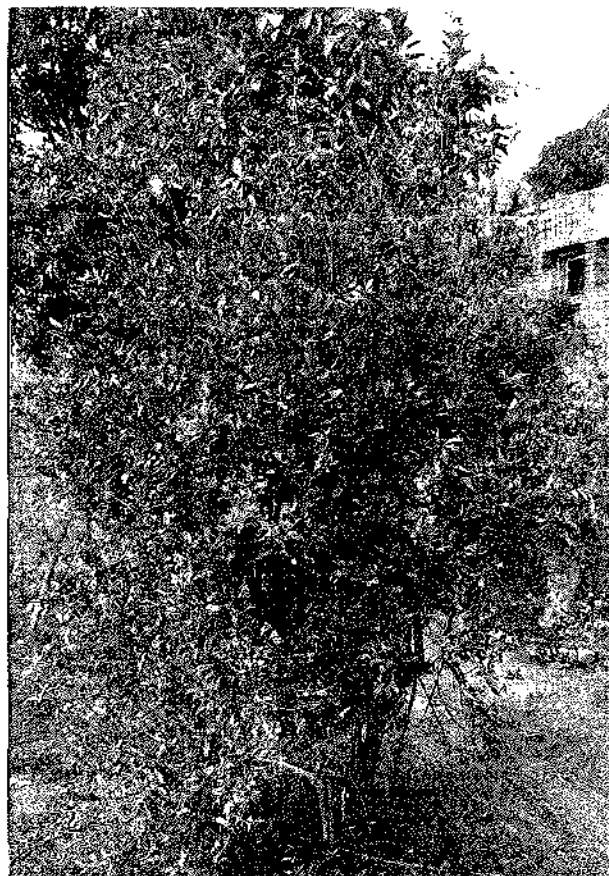


a)

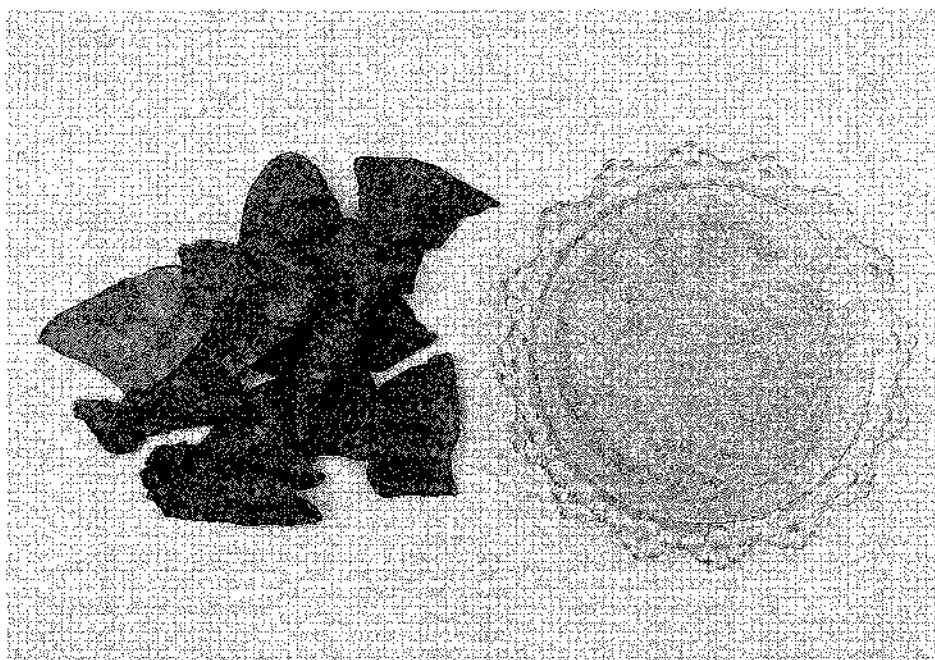


b)

Plate 7 a) Eucalyptus tree b) Dried and ground eucalyptus bark



a)



b)

Plate 8 a) Pomegranate tree b) Dried and ground pomegranate rind

Table 3.4 Instruments used

S. No.	Name of the instrument	Purpose	Manufacturer
1.	Crockmeter	Rubbing fastness test	Paramount Instruments
2.	Digital light fastness tester	Light fastness test	Pvt. Ltd., N. Delhi
3.	Digital pH meter	pH measuring	- do - Lab master
4.	Electronic balance 200B	Weighting test samples, dyes, mordants, chemicals, enzyme	Adair Dutt Instruments
5.	Hot air oven	Drying dye material	Pvt. Ltd., Calcutta
6.	Laundrometer	Washing fastness test	- do - Paramount
7.	Rectangular hot plate	Dyeing	Lab master
8.	Spectrophotometer	Measuring optical density of dye solution	Electronic Corporation of India Ltd.
9.	Spectravide	For colour assessment	Paramount
10.	Stiffness tester	Measuring bending length	- do -
11.	Strength tester	Measuring tensile strength	Cahindzu, Japan
12.	Thickness tester	Measuring thickness of test specimen	Paramount
13.	Computer Colour Matching System	Measuring CIE L*a*b* values	Chromoflash, ASHCO India, Ltd.

3.1.6 Instruments used

The details of the instruments used in the study have been furnished in Table 3.4.

3.1.7 Preparation of samples

- 1) **Scouring:** The cotton fabric was scoured in order to remove impurities. The fabric was samples were soaked in 0.5 percent warm solution of Ezee (liquid detergent) for 30 minutes, keeping MLR 1:20. After kneading and squeezing, it was thoroughly rinsed in tap water and dried in shade.
- 2) **Wetting / Soaking:** The samples were soaked in water to remove air and soften the fabric to facilitate absorption of water.

3.2. OPTIMIZATION OF VARIABLES FOR ENZYME TREATMENT

Trials were conducted to determine the optimum values of three variables, namely pH of the enzyme solution, enzyme concentration and treatment time. For this, an appropriate buffer solution for the selected enzyme was prepared. The procedure followed for optimization of each variable has been discussed below :-

3.2.1 Optimization of pH media

The phosphate buffer solution was prepared for cellulase enzyme by mixing 0.2 M solution each of Sodium phosphate monobasic dihydrate and Sodium phosphate dibasic anhydrous. Since this enzyme is active over a pH range of 6.5 - 7.5, the buffer solution was diluted in deionized water in different formulations to obtain three pH levels, i.e. 6.5, 7 and 7.5. (Malik 1952).

For optimization of pH, 1% enzyme concentration (o.w.f) and non - ionic surfactant (1gm / lt) was added to three different beakers containing buffer solutions at the three specific pH levels. The solution was stirred to mix the enzyme thoroughly. Three scoured cotton samples of a known weight were immersed in different buffer solutions keeping the MLR 1:30. This treatment was carried out in Laundrometer at $50^{\circ} \pm 2^{\circ} \text{C}$ for 45 minutes. The samples were taken out and immediately added to the hot water (80°C) and boiled for 15 minutes to denature the enzyme. The samples were then allowed to cool and thoroughly rinsed in running water. These were dried in shade and tested for weight loss, tensile strength, thickness, moisture absorption and flexural rigidity. The pH at which the samples gave the best results in relation to the physical properties was considered optimum. (Pant and Taya¹ 2000).

3.2.1.1. Weight loss

To study the weight loss due to pre-treatment, weight of the fabric samples before and after the treatment was taken. These fabric samples were conditioned for 24 hours at room temperature using saturated common salt solution in a desiccator and then weighed. Each sample was weighed separately. These were dried and conditioned for 24 hours in a desiccator and again weighted after the enzyme treatment also. The percentage weight loss was calculated using the following formula (Sharma 1995).

$$\text{Weight loss \%} = \frac{W_1 - W_2}{W_1} \times 100$$

Where, W_1 = Weight of the fabric before enzyme treatment
 W_2 = Weight of the fabric after enzyme treatment

3.2.1.2 Tensile strength

Tensile strength is the ability of the fabric to withstand the load of force usually expressed as Kilogram weight or pound weight.

The tensile strength of the fabric samples was determined on Computerized Universal Strength Tester using IS:1969 -1985 test method.

The samples of size 325 x 60 mm were cut from warp and weft direction of the fabric. The yarns were unraveled from both sides to obtain samples of uniform width throughout. For moisture equilibrium from dry side the specimens were conditioned prior to the test. The test was carried out in standard atmosphere of 65 ± 2 % Relative humidity and $27 \pm 2^{\circ}\text{C}$ temperature.

The specimen was held between two clamps of the tensile strength testing machine in such a manner that the same set of yarns were gripped by both the clamps. A continuous increasing load was applied longitudinally to the specimen by moving one of the clamps until the specimen ruptured. Value of breaking strength of the test specimens was read from the indicator of the machine. Tensile strength of the fabric was calculated by taking the mean of the five such measurements. Strength of the control and all the samples treated at different pH values, different concentrations of the enzyme and at different times was tested in this manner.

3.2.1.3 Moisture absorption

Moisture absorption is the ability of the fabric to absorb water.

The moisture absorption of the samples was determined by using simple wetting test by wicking (Booth 1996). In this method, the fabric absorbs water by

wicking or capillary action, observed through timing the rate at which water climbs up a narrow strip of fabric suspended vertically with its lower end dipped in the water.

A square of fabric 2 inches x 2 inches is fully immersed in water at 20°C for 20 seconds, removed and weighted. From its known dry weight the percentage water absorbed was calculated using the following formula

$$\text{Percent regain} = \frac{W_2 - W_1}{W_2} \times 100$$

Where, W_1 = Weight of dry sample

W_2 = Weight of wet sample

Moisture absorption of the fabric was calculated by taking the mean of the five measurements. Moisture absorption of the control and all the samples treated at different pH values, different concentrations of the enzyme and at different times was tested and calculated.

3.1.1.4 Fabric thickness

For optimizing the conditions for enzyme treatment, fabric thickness of the control sample as well as the samples treated with different concentrations of enzyme was studied (Booth 1996).

Under this method, the thickness of the fabric was measured using Thickness Tester, consisting of a graduated dial gauge of 10 mm capacity, with a least count of 0.01 mm. The pressure foot was 5 cm² in area and pressure from 20-100 gm/cm², i.e. a load of 100 gm - 500 gm, was applied. The instrument had a base and a frame that was heavy enough to be stable. A stationary, circular plate or anvil was fixed to the instrument. The sample rests on this plate. A

vertical sliding circular foot with accurate surface rests on the top of the specimen. The latter turns a dial pointer thus, giving the thickness of a sample under measurement, through the distance between the foot and the anvil. The measurement were made at five different positions of the fabric, that had been cut 6 inches away from the selvedge and was free of the creases. Thickness of the fabric was calculated by taking the mean of the five measurements.

3.2.1.5 Bending length and flexural rigidity

Bending length is the length of fabric that will bend under its own weight to a definite extent. It determines the drapability of the fabric. It relates to the quality of stiffness that is appreciated by visual examination of the draped material, in the sense that clothes having a high bending length tend to drape stiffly.

Samples of size 6" x 1" were cut from warp and weft direction with the aid of a template and conditioned (Booth 1996). Both template and samples were transferred to the platform with the fabric underneath, coinciding the zero mark of the scale and zero line engraved on the side of platform. The template was moved slowly over 41.5° slope alongwith the strip till the top of the specimen viewed in the mirror cut both the index lines. The bending length was read from the scale, which coincided with the front edge of the top plate. Each sample was tested four times at each edge.

Reading from the scale was noted in mm and average of the four readings was calculated for both the directions. All the test samples were weighted and their length as well as width was measured. Their areas were calculated and their weight per unit area in mg/sq. cm was determined.

Calculation

$$\text{Flexural rigidity (G)} = C^3 W$$

$$\text{Average bending length (C)} = L/2$$

Where,

$$L = \text{Mean length of overhanging portions}$$

$$W = \frac{\text{Average Weight of samples}}{\text{Average area of samples}} \text{ g/cm}^2$$

Flexural rigidity in warp direction (G_1)

$$G_1 = C^3 \times W_1 \text{ g cm}$$

Flexural rigidity in weft direction (G_2)

$$G_2 = C^3 \times W_2 \text{ mg cm}$$

$$\text{Overall flexural rigidity (G}_0\text{)} = G_1 \times G_2 \text{ g cm}$$

3.2.2 Optimization of enzyme concentration

For optimization of enzyme concentration, 1 - 5 % of enzyme was taken in five beakers. Buffer solution having optimum pH as discussed in section 3.2.1. was prepared. This stock solution was poured in five beakers along with non-ionic surfactant. The solution was stirred to mix the enzyme thoroughly. Five scoured cotton samples of approximately same weight were entered in different buffer solutions maintaining the MLR 1:30. Enzyme treatment was carried out in Laundrometer at $50^0 \pm 2^0\text{C}$ for 45 minutes. The enzyme concentration at which the sample gave the best results with regard to physical properties was selected for the final treatment.

3.2.3 Optimization of enzyme treatment time

For optimization of enzyme treatment time, buffer solution having optimum pH was prepared as described in section 3.2.1. This stock solution was poured

into four beakers maintaining MLR 1:30. Enzyme dosage as optimized in section 3.2.2 and non ionic surfactant (1g/l) were added to each beaker and mixed thoroughly. Scoured cotton was immersed in each beaker containing solution. The treatment was carried out for three different time durations, i.e, 45, 60 and 75 minutes in the Laundrometer at $50^{\circ} \pm 2^{\circ}\text{C}$, following the method described in section 3.2.1. The time duration at which the sample gave the best results with regard to physical properties was selected for the final treatment.

3.2.4 Final pre-treatment of fabric with enzyme

The final enzyme pre-treatment was carried out by treating the required amount of fabric, at optimized pH of enzyme solution, optimized enzyme concentration and optimized treatment time (as decided after studying its effect on selected physical properties). The samples were dried and then used for final dyeing with natural dyes.

3.3 OPTIMIZATION OF DYEING VARIABLES

Experiments were conducted to determine optimum values of nine variables, namely dye extraction pH, dye extraction time, dye concentration, dyeing pH, dyeing time, mordant extraction pH, mordant extraction time, mordanting method and mordant concentration. The procedure followed for optimization of each variable is as under :-

3.3.1 Optimization of dye extraction pH

For optimization of dye extraction pH, 1 gm each of dye material was taken in seven beakers and 50 ml of deionized water was poured in each beaker. The pH value of each dye extract was varied ranging between 4 - 10. The

solution was boiled for 60 minutes, maintaining the liquor volume constant. Each extract was then strained through four layers of muslin cloth to obtain clear filtrate. The optical density of each dye solution extracted at different pH values and wavelength was then measured with the help of a spectrophotometer. The dye solution giving maximum optical density at a particular wavelength was taken as the optimum pH for the extraction.

3.3.2 Optimization of dye extraction time

For optimization of dye extraction time, 1 gm each of dye material was extracted in deionized water in five beakers, at optimized pH as described in section 3.3.1, The dye extract was boiled for 30, 45, 60, 75 and 90 minutes separately, maintaining constant dye liquor ratio of 1:50. The optical density of each dye solution was measured with the help of a spectrophotometer. The dye solution giving maximum optical density was taken as the optimum dye extraction time.

3.3.3 Optimization of pH dyeing

For optimization of pH for dyeing, 1 gm each of dye material was extracted in four beakers at optimum pH for optimum time. The pH value of the dye solution was changed i.e., 7, 8, 9 and 10. Four pre-soaked samples of 1 gm each were entered separately in the dye solutions having different pH values. The temperature of the dye baths was gradually raised to 90°C. The dyeing was carried out at this temperature for 45 minutes, taking care that the samples were frequently and gently stirred. The material liquor ratio was maintained at 1:50 by adding hot, deionized water. After dyeing, the baths were allowed to cool down

for some time to avoid sudden temperature change during rinsing. The samples were then taken out, washed in mild detergent solution and rinsed under tap water to remove the superfluous dye. After thoroughly rinsing, the samples were finally dried in shade.

Just before dyeing process, 0.2 ml of each dye solution was taken out from each dye bath and diluted 100 times. This dye solution was then centrifuged at 3000 rpm for 20 minutes. Then the optical density of the dye solution was measured with the help of spectrophotometer. At the end of dyeing also, the optical density was again measured after giving the same treatment.

The percentage dye absorption of each sample at different dyeing pH values was calculated with the help of the following relationship :-

$$\text{Percentage dye absorption} = \frac{\text{O. D before dyeing} - \text{O. D after dyeing}}{\text{O. D before dyeing}}$$

Where, O. D. is the Optical Density

The dyeing pH value giving maximum dye absorption was taken as optimum dyeing pH value.

3.3.4 Optimization of dye concentration

For optimization of dye concentration, 1, 2, 3, 4 and 5 gm each of the dye material were extracted separately at optimum pH for optimum time. Five pre-soaked fabric samples of 1 gm each were entered separately in dye bath of optimum pH value and dyed following the method described in section 3.3.3.

Percentage dye absorption was calculated for all the dye concentrations as described in section 3.3.3. The dye material concentration giving maximum dye absorption was taken as the optimum dye material concentration.

3.3.5 Optimization of dyeing time

For optimization of dyeing time, the optimum concentration of dye material was boiled at the optimum pH to extract the dye. Dyeing was carried out at optimum pH for five different samples separately, for 30, 45, 60, 75 and 90 minutes each and the percentage dye absorption was calculated for each of these as described in section 3.3.3. The dyeing time giving maximum dye absorption was taken as the optimum dyeing time.

3.3.6 Optimization of mordant extraction pH

For optimization of mordant extraction pH, 0.1 gm of each mordanting material was taken in seven beakers and 50 ml of deionized water was poured in each beaker. The pH value of the mordant extract varied ranging between 4 - 10. The solution was boiled for 60 minutes, maintaining the liquor volume constant. The liquors were allowed to cool down a room temperature and strained through four layers of muslin cloth to obtain clear filtrates. The optical density of each mordant solution extracted at different pH values was then measured with the help of a spectrophotometer. The mordant solution giving maximum optical density was considered as the optimum pH for the extraction.

3.3.7 Optimization of mordant extraction time

For optimization of mordant extraction time, 0.1 gm of each mordant material was extracted in deionized water in five beakers, at optimized pH as described in section 3.3.6. The mordant extract was boiled for 30, 45, 60, 75 and 90 minutes separately, maintaining the liquor volume constant i.e., 50 ml. The optical density of each mordant solution was measured with the help of a

spectrophotometer. The mordant solution giving maximum optical density was taken as the optimum mordant extraction time.

3.3.8 Selection of mordanting method

The fabric was mordanted by three mordanting methods, namely pre-mordanting, simultaneous mordanting and post mordanting, with the mordant extracted at optimum pH, for optimum time. Mordanting time for each of these was 30 minutes. The mordanted samples were dyed employing dye extraction pH, dye extraction time, dye material concentration, dyeing pH and dyeing time, optimized earlier in section 3.3.1 - 3.3.5.

The mordanting method was decided on the basis of colour obtained. To select the best colour, the samples were observed in Spectraaide. The method, which gave best and different shade was selected as best mordanting method.

3.3.9 Selection of mordant concentration

For selection of mordant concentration, 0.1, 0.2, 0.3, 0.4 and 0.5 gm of each mordant material were extracted separately at optimum pH, for optimum time. Five samples were mordanted with five different concentrations using mordanting method selected in section 3.3.8. The mordanted samples were then dyed using dye extraction pH, dye extraction time, dye material concentration, dyeing pH and dyeing time, optimized earlier in sections 3.3.1 - 3.3.5.

The dyed samples were observed in Spectraaide to select the best colour. The mordant concentration which gave the best shade was selected as best mordant concentration.

3.3.10 Final dyeing of cotton samples

To study the effect of enzyme pre-treatment on dyeing and assess the fastness properties, both control and the enzyme treated cotton fabrics dyed were with four different mordants. The dyeings were carried out using dyeing parameters optimized earlier. The colours of all the dyed samples were assigned the names according to the colours given by Methuen. The names were named according to the nearest possible matching colour from the book.

3.4 COLOUR MEASUREMENT OF THE DYED SAMPLES

The methods of measuring colour numerically was established by the Commission Internationals del' Eclairage (CIE) in 1931 and 1976. These methods provide uniform colour differences in relation to visual differences. The measurement is precise and colour is specified by a set of numbers, which can be used to re-create the original colours at any time and place, i.e. reproduction is possible. This method extends the use of computer in colour matching prediction, i.e. to correct the colour of a recipe obtained by the use of the computer. The use of computer in measurement of colour thus, increases the objectivity of experimental results of dyeing.

The colour of the dyed samples both control and enzyme treated was measured numerically through computerized colour matching system. This system uses CIE Lab (76) colour space, D65 illuminant (International standard for day light published by CIE for the purpose of colour matching and appraisal) and 420 nm wavelengths to measure the actual colour and changes in colours. The CIE Lab colour space uses L^* , a^* , b^* , h^* and C^* scales to describe colour.

The L^* is a measure of lightness / darkness of colour of an object and ranges from 0 (black) to 100 (white), a^* is a measure of redness (+ve a^*) or greenness (-ve a^*), b^* is a measure of yellowness (+ve b^*) or blueness (-ve b^*), h^* is the hue and C^* is a measure of dullness / brightness.

The L^* , a^* , b^* and C^* for all the dyed samples were calculated and the enzyme treated samples were compared with untreated samples to see the effect of enzyme treatment on the colour obtained.

3.5 EVALUATION OF COLOUR FASTNESS OF THE DYED SAMPLES

All the dyed samples were evaluated for colourfastness to washing, light, rubbing and perspiration by the methods prescribed by the Bureau of Indian Standards to compare enzyme treated samples with untreated samples

3.5.1. Evaluation of colour fastness to washing

For determining the washing fastness of dyed samples, Test - 2 described in the Indian Standard IS:3361-1979 was used.

For preparing a composite specimen, two fabric pieces, each measuring 10 cm x 4 cm, were taken. One of the fabric pieces taken was wool and the other cotton. The dyed fabric to be tested was placed between these two pieces. The sample was sewn on all the four sides.

All the composite specimens were prepared as above were weighed and the required quantity of soap solution of 5 g/litre of water was prepared for keeping the material to liquor ratio of 1:50. One composite specimen was placed in each of the eight containers of a laundrometer along with 10 steel balls and soap solution previously heated to $50 \pm 2^\circ\text{C}$ was added to it. The composite

specimen were treated for 45 minutes at $50\pm 2^{\circ}\text{C}$ in the laundrometer. The composite specimen were removed and rinsed in cold water. The samples were squeezed and the stitching along two long sides and one short side was removed. The composite samples were then opened and dried in air with three pieces (one test specimen and two adjacent pieces) in contact along the remaining line of stitching.

The samples were evaluated for colour change. A piece of original dyed fabric and the test specimen were placed side by side on the same plane. Care was taken to keep the surrounding field neutral grey in colour. The visual difference between the original and the test specimen was compared and fastness rating was given with the help of a grey scale for assessing change in colour. The fastness grade given was that number of the grey scale which corresponded to the contrast between the original and washed specimen. If the contrast was judged to be nearer to the non-existing half step, the approximate half step rating was given.

The different grades of grey scale indicated the following level of fastness:

Grey scale rating	Colour change	Colour staining
5	Excellent	Negligible or no staining
4	Good	Slight staining
3	Fair	Noticeable staining
2	Poor	Considerable staining
1	Very poor	Heavy staining

3.5.2 Evaluation of colour fastness to light

For determining the colour fastness of dyed samples to light, the test prescribed by the BIS in the IS : 2454-1985 was employed.

The test samples were exposed to the light of MBTL fading lamp for standard time period (at least 5 hours). The exposure was continued until specimen faded to a contrast equal to grade 4 on the grey scale. The approximate number of hours required to fade each blue wool standard to a contrast equal to grade 4 of the grey scale on such exposure are given below:

Blue wool standard no.	Number of hours	Fastness level
1	5	Very poor
2	10	Poor
3	20	Fair
4	40	Fairly good
5	80	Good
6	160	Very good
7	320	Excellent
8	640	Outstanding

3.5.3 Evaluation of colour fastness to rubbing

The colour fastness of all the dyed samples against dry and wet crocking was determined using the test prescribed by the BIS in the IS:766-1988 .

For testing fastness to dry rubbing a test specimen was prepared, in the form of a layer the dyed fabric attached lengthwise on rectangular cardboard of size 14 cm x 5 cm. The undyed cotton sample of size 5 x 5 cm was fixed to the finger of rubbing device of crockmeter and test specimen was fixed at the base of the rubbing device. The test specimen was rubbed to and fro with undyed pieces,

times in 10 seconds. Similarly, fastness to wet rubbing was tested by rubbing wet undyed cotton sample on the test specimen. The dry and wet crocked samples were assessed against standard grey scales for colour change and colour staining. The different grades in the grey scale for change in colour and staining of colour were given as described in section 3.6.1.

3.5.4 Evaluation of colour fastness to perspiration

The fastness to perspiration was tested by the test IS:971-1983 prescribed by the BIS.

The acidic test liquor was prepared by dissolving 2.65 g of sodium chloride and 0.75 g of urea / litre and adjusting the pH of the solution to 5.6 with addition of acetic acid. The alkaline test liquor was prepared by dissolving 3 g of sodium chloride / litre and adjusting the pH of the solution to 7.2 with addition of sodium bicarbonate.

A composite specimen was prepared by placing the test specimen of 5 cm x 4 cm between the two adjacent fabrics of 5 cm x 5 cm size, one being wool and the other cotton. The test specimen was stitched along all the four sides. The test specimens were soaked in the acidic and alkaline test solutions as prepared above separately with material to liquor ratio 1:50 for 30 minutes at room temperature. Then the treated samples were kept between two glass plates of perspirometer under a force of 5 kg. The apparatus was kept in hot air oven for four hours at $37 \pm 2^{\circ}\text{C}$. Then the test samples were removed from the oven and air dried with temperature not exceeding 60°C . The numerical grading for colour

change of test pieces and for staining of two adjacent pieces was done using a grey scale.

The acidic and alkaline perspiration samples were assessed against standard grey scales for colour change and colour staining. Different grades in the grey scale for change in colour and staining of colour were given as described in section 3.5.1.

RESULTS AND DISCUSSION

The present investigation was conducted to optimize the conditions for enzymatic pre-treatment and dyeing cotton with four selected natural dyes with four natural mordants. The effect of enzymatic pre-treatment and un-treated cotton samples dyed with four natural dyes and four mordants were compared on the basis of colour fastness properties. The results obtained for enzymatically pre-treated cotton and untreated cotton dyed with each dye are discussed under the following heads:

- 4.1 Optimization of conditions for enzymatic pre-treatment.
- 4.2 Optimization of dyeing conditions without mordants.
- 4.3 Optimization of conditions for mordanting.
- 4.4 Effect of enzymatic pre-treatment on CIE LAB values of dyed samples.
- 4.5 Fastness properties of the dyed samples.

4.1 OPTIMIZATION OF CONDITIONS FOR ENZYMATIC PRE-TREATMENT

Optimization of conditions for enzymatic pre-treatment was done to evaluate the optimum conditions for enzymatic pre-treatment. Effect of each of these parameters on weight loss, tensile strength, moisture absorption, fabric thickness and flexural rigidity of the samples was studied. Details of the optimum values of the three variables, namely pH of the enzyme solution, enzyme

concentration and treatment time, optimized on the basis of the physical properties have been discussed in this.

4.1.1 Optimization of the pH media

Table 4.1 Optimization of the pH media for enzymatic pre-treatment

pH media	Percentage weight loss	Percentage strength loss		Percentage moisture absorption	Percentage fabric thickness loss	Overall flexural rigidity
		Warp	Weft			
6.5	0.05	0.58	1.12	57.97	-	0.067
7.0	0.06	0.70	1.17	58.57	-	0.070
7.5	0.12	0.67	1.05	55.88	-	0.059

The results pertaining to effect of pH of the media on various properties of the test specimens have been furnished in the table 4.1. It is evident from the table 4.1 that there was no marked change in weight loss due to enzymatic pre-treatment.

Though a slight loss of percentage strength was evident in the samples, the percentage strength loss for the samples in the warp direction was all most negligible, i.e. 0.58, 0.70 and 0.67 percent for 6.5, 7 and 7.5 pH respectively. However, it was 1.12, 1.17 and 1.05 percent for 6.5, 7 and 7.5 pH respectively, in the weft direction.

The moisture absorption was maximum, i.e., 58.57 percent at 7 pH. The results showed that there was no percentage loss in the fabric thickness. This could be due to the fact that the change in pH of buffer solution was not active enough to remove the fuzz from the surface of the fabric samples.

Further, no significant effect of different pH levels could be observed on this bending stiffness as a results of the overall flexural rigidity are 0.067, 0.070 and 0.059 at 6.5, 7 and 7.5 pH respectively. It was evident from the results that the activity of cellulase had not adversely affected over the pH range of 6.5- 7.5. The results are in line with the findings of Ajgaonkar (1995) who reported that the activity of neutral cellulase is not adversely affected in the pH range of 6 to 8. Thus, pH 7 was taken optimum pH for the further study, as the moisture absorption was maximum at pH 7, but no other physical properties got affected.

4.1.2 Optimization of enzyme concentration

Table 4.2 Optimization of enzyme concentration for enzymatic pre-treatment

Enzyme Conc. (%)	Percentage weight loss	Percentage strength loss	Percentage moisture absorption	Percentage fabric thickness loss	Overall flexural rigidity	
Control		Warp	Weft			
1.0	0.12	0.70	1.17	58.57	-	0.058
2.0	0.30	1.55	2.95	67.78	-	0.065
3.0	0.53	1.95	4.88	71.15	-	0.087
4.0	0.84	4.51	6.06	74.54	0.82	0.054
5.0	1.77	5.02	6.64	78.29	1.65	0.057

Table 4.2 shows the results of effect of enzyme concentration on various physical properties of the samples. It is clear from the table that there was a slight but gradual increase in percentage weight loss with an increase in the enzyme concentration. The weight loss of 0.12 percent was observed at 1 percent concentration of the enzyme, which increased to 1.77 percent at 5 percent concentration. The gradual increase in weight loss was attributed to

degradation of fine yarns and freely accessible projecting fibres as reported by Buschle – Diller *et al.* (1994).

As the enzyme concentrations increased the percentage strength loss in both, the warp as well as weft direction of the fabric also increased. In the warp direction the percentage strength loss was 0.70 percent at 1 percent concentration of enzyme but it increased to 5.02 percent at 5 percent concentration. The percentage strength loss was 1.17 percent at 1 percent enzyme concentration but it increased to 6.64 percent at 5 percent enzyme concentration in the weft direction. Similar results were obtained with wool by Singh and Goel (2001) with more percentage strength loss in the weft direction.

The moisture absorption of cotton increased with the increase in enzyme concentration. At 1 percent enzyme concentration the moisture absorption was 58.57 percent but it was 78.29 percent at 5 percent concentration of the enzyme. Thus, an increase in enzyme concentration improved the wettability of the samples.

No percentage loss in fabric thickness was observed due to the change in the enzyme concentration, i.e. 1, 2 and 3 percent. A slight percentage loss in fabric thickness, i.e. 0.82 percent and 1.65 percent was evident when the samples were treated with 4 and 5 percent concentration of the enzyme respectively.

From the table 4.2 it is evident that no significant change in bending stiffness took place due to increase in concentration of enzyme.

Thus, 5 percent concentration of enzyme was taken optimum for the further study, as the loss in weight and fabric thickness was negligible here but

the tensile strength and moisture absorption was maximum at 5 percent % concentration.

4.1.3 Optimization of treatment time

Table 4.3 Optimization of treatment time for enzymatic pre-treatment

Treatment Time (min.)	Percentage weight loss	Percentage strength loss	Percentage moisture absorption	Percentage fabric thickness loss	Overall flexural rigidity
		<u>Warp</u> <u>Weft</u>			
45	1.73	5.02 6.64	78.29	0.82	0.062
60	2.13	6.79 7.84	81.81	1.65	0.075
75	2.37	7.32 9.96	84.45	1.65	0.066

Table 4.3 depicts that with an increase in treatment time, a slight increase in percentage weight loss could be envisaged. The weight loss was 1.73, 2.13 and 2.37 percent at 45, 60 and 75 minutes of the treatment time respectively. Raje *et al.* (2001) also observed a similar phenomena.

Similarly, the percentage strength loss increased from 5.02 to 7.32 percent in warp and 6.64 to 9.96 percent in weft direction when the treatment time was increased. The drastic increase in the strength loss of the fabric samples can be explained by the fact that the prolonged exposure to enzymes acts upon the weaker fibres from the surface of the fabric.

As the treatment time increased, the moisture absorption also increased. It was 78.29, 81.81 and 84.45 percent at 45, 60 and 75 minutes of treatment time respectively. Therefore, the samples showed considerable improvement in surface wetting property. Hartzell- Lawson *et al.* (2000) also observed the increase in moisture absorbency on cotton with increasing in reaction time. This

could possibly because the surface of the cellulosic fibres was partially hydrolyzed during enzymatic treatment, and the weakened fibres got removed during the experiment. According to Karmakar (1998) and Nishkam (2002) cotton fabric surface is hydrolyzed when treated with enzyme. As a result micro-fibrils protruding on the surface got weak and broke-off.

A negligible percentage loss in fabric thickness was observed as the treatment time progressed. It was 0.82 percent at 45 minutes of treatment time but increased to 1.65 percent at 60 and 90 minutes of treatment time. Thus, treatment time had no adverse effect on the thickness of the fabric.

In the same manner, no significant change in bending stiffness was observed with an increase in the treatment time. Therefore, 75 minutes of enzymatic treatment was considered optimum for the further study. Despite the slight loss in weight, tensile strength and fabric thickness. Comparatively more increase in percentage moisture absorption was observed at 75 minutes of treatment time.

4.1.4 Optimum enzymatic conditions

Based on the results described in the preceding tables, optimum conditions recommended for enzymatic pre-treatment of cotton with cellulase enzyme were -pH media 7, enzyme concentration 5 percent (o.w.f) and the treatment time of 75 minutes.

Therefore, cotton was pre-treated with cellulase at these conditions for the further research.

4.2. OPTIMIZATION OF DYEING CONDITIONS WITHOUT MORDANTS

Optimization of dyeing conditions without the use of mordants was done to evaluate the optimum conditions for the four natural dyes. Various parameters namely, dye extraction pH, dye extraction time, dyeing pH, dye concentration and dyeing time for each dye were studied.

4.2.1 Dyeing with *bansa* dye

Details of the optimum values of dyeing conditions namely, dye extraction pH, dye extraction time, dyeing pH, dye concentration and dyeing time have been discussed in the tables 4.4 to 4.8.

4.2.1.1 Optimization of dye extraction pH for *bansa* dye

Table 4.4 Optimization of dye extraction pH for *bansa* dye

Wave length (nm)	pH Media						
	4	5	6	7	8	9	10
400	.502	.510	.530	.529	.525	.520	.529
410	.509	.522	.536	.532	.536	.527	.533
420	.509	.528	.539	.534	.540	.539	.545
430	.500	.527	.539	.540	.549	.542	.550
440	.500	.530	.545	.548	.550	.547	.552
450	.514	.539	.552	.552	.554	.549	.554
460	.499	.520	.531	.552	.550	.550	.556
470	.475	.505	.525	.552	.549	.490	.553
480	.452	.400	.491	.541	.548	.450	.543
490	.390	.424	.475	.521	.530	.458	.520
500	.380	.437	.480	.496	.512	.466	.499
510	.352	.457	.475	.486	.498	.442	.480
520	.305	.477	.455	.465	.465	.435	.482
530	.288	.387	.425	.333	.342	.428	.414
540	.265	.305	.300	.345	.366	.300	.400
550	.255	.294	.332	.350	.370	.314	.366
560	.283	.285	.321	.345	.350	.302	.360
570	.220	.266	.291	.327	.301	.288	.340
580	.191	.243	.275	.298	.225	.265	.300
590	.173	.204	.260	.255	.245	.253	.231
600	.162	.186	.208	.238	.253	.200	.257

It can be seen from the table 4.4 that the optical density of the dye solution increased with an increase in the wavelength up to a certain level. Beyond that the optical density started decreasing. This trend was studied for the pH values ranging from 4 to 10. It was observed that the optical density was maximum at the pH 10 and wavelength 460 (nm). Therefore, it was adjudged as the optimum dye extraction pH for *bansa* dye.

4. 2.1.2 Optimization of dye extraction time for *bansa* dye

Table 4.5 Optimization of dye extraction time for *bansa* dye

Extraction time (min.)	Optical density
30	.539
45	.549
60	.554
75	.541
90	.523

Table 4.5 indicates that initially the optical density gradually increased with an increase in extraction time of dye. It showed the maximum optical density at 60 minutes of extraction, after which the optical density decreased.

4. 2.1.3 Optimization of dyeing pH for *bansa* dye

Table 4.6 Optimization of dyeing pH for *bansa* dye

pH	O D before dyeing	O D after dyeing	Percentage dye absorption
7	0.565	0.476	15.15
8	0.589	0.498	15.44
9	0.609	0.513	15.76
10*	0.609	0.508	16.58

From table 4.6 it is evident that the percentage dye absorption increased gradually with an increase in pH of the dye solution. Percentage dye absorption

was maximum at 10 pH. i.e. 16.58. Thus, pH 10 was considered as the optimum pH for dyeing fabric samples with *bansa* dye.

4. 2.1.4 Optimization of dye concentration for *bansa* dye

Data pertaining to the percentage dye absorption at different dye concentrations have been furnished in table 4.7. These reveal that with the increase in dye material concentration, the percentage dye absorption increased up to 4g/g of cotton. The colour of the dyed samples reduced on increasing the amount of dye further. Moreover, the percentage dye absorption decreased with

Table 4.7 Optimization of dye concentration for *bansa* dye

Dye conc.	O D before dyeing	O D after dyeing	Percentage dye absorption
1	0.565	0.466	17.52
2	0.609	0.502	17.56
3	0.607	0.500	17.62
4*	0.609	0.494	18.88
5	0.609	0.499	18.06

any further increase in dye concentration.

4. 2.1.5 Optimization of dyeing time for *bansa* dye

Table 4.8 Optimization of dyeing time for *bansa* dye

Dyeing time (min)	O D before dyeing	O D after dyeing	Percentage dye absorption
30	0.609	0.491	19.37
45	0.610	0.490	19.67
60	0.610	0.489	19.83
75*	0.612	0.487	20.42
90	0.610	0.501	17.86

Percentage dye absorption values for different dyeing times (Table 4.8)

reveals that the dye absorption increased up to 75 minutes of dyeing. Later, a

sharp decrease in the percentage dye absorption was observed. Hence, 75 minutes was considered as optimum dyeing time. Similar results were obtained by Pankaj (2002) in the case of ashoka dye on wool.

4.2.1.6 Optimum dyeing parameters used for *bansa* dye

From the results of the trials, it was evident that the maximum percentage of dye was absorbed at dye extraction pH of 10, dye extraction time of 60 minutes, dyeing pH 10, dye concentration 4 percent (o.w.f) and the dyeing time 75 minutes. Therefore, these conditions were considered to be optimum and were used for carrying out the further research.

4.2.2 Dyeing with bottle brush dye

Data pertaining to the optimum values of dyeing conditions i.e., dye extraction pH, dye extraction time, dyeing pH, dye concentration and dyeing time have been presented in the tables 4.9 to 4.13.

4. 2.2.1 Optimization of dye extraction pH for bottle brush dye

Table 4.9 Optimization of dye extraction pH for bottle brush dye

Wave length (nm)	pH Media						
	4	5	6	7	8	9	10
400	.444	.472	.488	.509	.546	.563	.560
410	.447	.476	.498	.516	.550	.563	.562
420	.410	.482	.499	.523	.553	.564	.562
430	.347	.450	.487	.521	.556	.565	.562
440	.297	.414	.459	.509	.556	.567	.565
450	.259	.376	.420	.489	.555	.567	.567
460	.232	.348	.399	.470	.551	.567	.569
470	.211	.321	.380	.453	.559	.568	.570
480	.200	.294	.353	.430	.541	.568	.570
490	.171	.265	.330	.421	.532	.567	.572
500	.156	.248	.310	.404	.535	.568	.572
510	.132	.200	.287	.376	.520	.568	.572
520	.119	.192	.257	.351	.525	.566	.574
530	.101	.154	.235	.330	.502	.564	.570

540	.087	.143	.197	.302	.450	.550	.570
550	.078	.124	.176	.221	.421	.548	.567
560	.060	.102	.145	.245	.404	.520	.560
570	.056	.097	.130	.234	.378	.501	.561
580	.049	.082	.120	.201	.341	.423	.555
590	.045	.072	.103	.198	.321	.440	.555
600	.041	.066	.099	.170	.290	.410	.550

It is clear from the table 4.9 that the optical density of the dye solution increased with an increase in the wavelength up to a certain level. Beyond that the optical density started decreasing. This trend was studied for the pH values ranging between 4 to 10. It was observed that the optical density was maximum at pH 10 and wavelength 520 (nm). Therefore, it was adjudged as the optimum dye extraction pH for bottle brush dye.

4. 2.2.2 Optimization of dye extraction time for bottle brush dye

Table 4.10 Optimization of dye extraction time for bottle brush dye

Time (min.)	Optical density
30	.535
45	.559
60	.573
75	.563
90	.542

From table 4.10 it is evident that the optical density gradually increased with an increase in the extraction time of dye. It showed the maximum optical density at 60 minutes of extraction, after which optical density decreased.

4. 2.2.3 Optimization of dyeing pH for bottle brush dye

Table 4.11 indicates that the percentage dye absorption increased gradually with an increase in pH of dye solution. The maximum percentage dye

absorption was at 9 pH, after which it decreased. Thus, pH 9 was considered as the optimum pH for dyeing fabric samples with bottle brush dye.

Table 4.11 Optimization of dyeing pH for bottle brush dye

pH	O D before dyeing	O D after dyeing	Percentage dye absorption
7	0.612	0.586	4.24
8	0.612	0.580	5.22
9*	0.612	0.573	6.37
10	0.611	0.578	5.40

4. 2.2.4 Optimization of dye concentration for bottle brush dye

Table 4.12 Optimization of dye concentration for bottle brush dye

Dye conc.(g/g)	O D before dyeing	O D after dyeing	Percentage dye absorption
1	0.611	0.586	4.09
2	0.613	0.581	5.22
3	0.613	0.574	6.36
4	0.613	0.572	6.68
5	0.613	0.576	6.03

Percentage dye absorption values for different dye concentrations (Table 4.12) indicated that the dye absorption increased gradually up to 4 g/g of cotton, after which a slight decrease in the percentage dye absorption was observed. Hence, 4 g/g of cotton was considered as optimum dye concentration.

4. 2.2.5 Optimization of dyeing time for bottle brush dye

Data pertaining to the percentage dye absorption at different dyeing times have been furnished in table 4.13. These reveal that the percentage dye absorption increased up to 75 minutes with the increase in dyeing time. Later, a

slow decrease in percentage dye absorption was observed. Therefore, 75 minutes was considered as optimum dyeing time.

Table 4.13 Optimization of dyeing time for bottle brush dye

Dyeing time (min)	O D before dyeing	O D after dyeing	Percentage dye absorption
30	0.612	0.567	7.35
45	0.612	0.565	7.67
60	0.612	0.562	8.17
75*	0.614	0.558	9.12
90	0.612	0.557	9.00

4.2.2.6 Optimum dyeing parameters used for bottle brush dye

The results of the trials elucidated that the maximum percentage of dye was absorbed at dye extraction pH10, extraction time 60 minutes, dyeing pH 9, dye concentration 4 percent (o.w.f) and dyeing time 75 minutes. Therefore, these conditions were considered to be optimum and were used for investigation.

4.2.3 Dyeing with duranta dye

Tables 4.14 to 4.18 furnish the details of the optimum values of dyeing conditions namely, dye extraction pH, dye extraction time, dyeing pH, dye concentration and dyeing time.

4. 2.3.1 Optimization of dye extraction time for duranta dye

It is evident from the table 4.14 that the optical density of the dye solution increased with an increase in the wavelength up to a certain level. After that the optical density started decreasing. This trend was studied for the pH values from 4 to 10. It was observed that the optical density was maximum at pH

10 and wavelength 480 (nm). Therefore, it was adjudged as the optimum dye extraction pH for duranta dye.

Table 4.14 Optimization of dye extraction pH for duranta dye

Wave length (nm)	pH Media						
	4	5	6	7	8	9	10
400	.478	.516	.508	.530	.551	.570	.573
410	.460	.520	.509	.530	.553	.570	.573
420	.447	.522	.511	.530	.553	.571	.573
430	.434	.530	.512	.530	.553	.572	.574
440	.423	.534	.478	.531	.557	.573	.575
450	.410	.562	.420	.531	.561	.574	.575
460	.400	.578	.399	.547	.554	.574	.576
470	.378	.581	.380	.553	.554	.574	.576
480	.320	.479	.353	.490	.545	.574	.580
490	.287	.439	.330	.454	.522	.572	.577
500	.252	.419	.310	.422	.532	.572	.572
510	.232	.378	.287	.376	.502	.568	.572
520	.219	.363	.257	.203	.475	.565	.574
530	.204	.355	.235	.233	.458	.562	.570
540	.187	.364	.197	.253	.445	.558	.570
550	.139	.388	.176	.262	.427	.545	.567
560	.135	.300	.237	.288	.407	.558	.567
570	.120	.330	.222	.263	.399	.540	.561
580	.099	.354	.102	.240	.369	.539	.564
590	.095	.398	.134	.218	.343	.526	.554
600	.084	.225	.153	.190	.326	.525	.556

4. 2.3.2 Optimization of dye extraction time for duranta dye

Table 4.15 Optimization of dye extraction time for duranta dye

Time (min.)	Optical density
30	.564
45	.566
60	.570
75	.577
90	.575

According to table 4.15 initially, there was a gradual increase in the optical density gradually increased with an increase in extraction time of the dye. It showed the maximum optical density at 75 minutes of extraction, after which the optical density decreased gradually.

4. 2.3.3 Optimization of dyeing pH for duranta dye

From table 4.16 it is evident that the percentage dye absorption initially increased, then decreased and later on it again increased to maximum with an increase in the pH of dye solution. The percentage dye absorption was maximum at 10 pH. i.e. 21.50. Thus pH 10 was considered as the optimum pH for dyeing fabric samples with duranta dye.

Table 4.16 Optimization of dyeing pH for duranta dye

pH	O D before dyeing	O D after dyeing	Percentage dye absorption
7	0.570	0.454	20.35
8	0.570	0.448	21.40
9	0.572	0.453	20.30
10	0.586	0.460	21.50

4. 2.3.4 Optimization dye concentration for duranta dye

Table 4.17 Optimization of dye concentration for duranta dye

Dye conc. (g/g)	O D before dyeing	O D after dyeing	Percentage dye absorption
1	0.582	0.462	20.61
2	0.593	0.470	20.74
3	0.595	0.456	23.36
4	0.595	0.463	22.18
5	0.601	0.472	21.46

Details of the percentage dye absorption at different dye concentrations have been furnished in table 4.17. It elicits that the percentage dye absorption

increased drastically up to 3g/g of cotton. A gradual decrease in percentage dye absorption was observed after this.

4.2.3.5 Optimization of dyeing time for duranta dye

Percentage dye absorption values for different dye concentrations (Table 4.18) revealed that there was an increase in dye absorption up to 60 minutes of dyeing. A gradual decrease in the percentage dye absorption was observed beyond that. Therefore, 60 minutes was considered as optimum dyeing time.

Table 4.18 Optimization of dyeing time for duranta dye

Dyeing time (min)	O D before dyeing	O D after dyeing	Percentage dye absorption
30	0.598	0.468	21.73
45	0.598	0.461	22.90
60	0.598	0.456	23.74
75	0.598	0.459	23.24
90	0.600	0.458	23.66

4.2.3.6 Optimum dyeing parameters used for duranta dye

The results of the trials, show that the maximum percentage of dye was absorbed at dye extraction pH10, dye extraction time 75 minutes, dyeing pH 10, dye concentration 3 percent (o.w.f) and dyeing time 60 minutes. Therefore, these were considered to be the optimum conditions and were used for further work.

4.2.4 Dyeing with mango dye

Details of the optimum values of dye extraction pH, dye extraction time, dyeing pH, dye concentration and dyeing time have been discussed in the tables 4.19 to 4.23.

4. 2.4.1 Optimization of dye extraction pH for mango dye

Table 4.19 Optimization of dye extraction pH for mango dye

Wave length (nm)	pH Media						
	4	5	6	7	8	9	10
400	.471	.509	.515	.548	.567	.571	.570
410	.485	.516	.526	.548	.567	.571	.570
420	.496	.525	.530	.550	.569	.571	.571
430	.455	.510	.532	.552	.570	.572	.571
440	.418	.502	.534	.555	.570	.572	.571
450	.371	.489	.529	.558	.571	.573	.572
460	.340	.451	.522	.559	.571	.573	.572
470	.325	.433	.500	.569	.571	.573	.572
480	.297	.412	.484	.561	.572	.573	.573
490	.267	.361	.462	.561	.572	.575	.573
500	.241	.337	.433	.560	.572	.580	.573
510	.235	.302	.399	.543	.570	.573	.571
520	.149	.282	.380	.521	.569	.572	.572
530	.165	.239	.273	.482	.567	.572	.572
540	.110	.193	.241	.466	.556	.570	.568
550	.099	.159	.194	.423	.544	.563	.562
560	.072	.148	.172	.392	.537	.555	.550
570	.060	.132	.155	.356	.501	.544	.548
580	.052	.125	.134	.308	.486	.533	.533
590	.045	.101	.128	.289	.452	.520	.512
600	.035	.070	.076	.241	.441	.500	.497

It is evident from the table 4.19 that the optical density of the dye solution increased with an increase in the wavelength up to the pH of 9 and wavelength 500 (nm). After that the optical density started decreasing. Therefore, it was adjudged as the optimum dye extraction pH for mango dye. Singh et al. (1996a) also found that an increase in the amount of alkali in the extraction bath led to a resultant increased in the extraction of *kamala* dye.

4. 2.4.2 Optimization of dye extraction time for mango dye

Table 4.20 Optimization of dye extraction time for mango dye

Time (min.)	Optical density
30	.558
45	.560
60	.569
75	.573
90	.570

Table 4.20 depicts that to begin with the optical density gradually increased with an increase in extraction time of the dye and was the maximum at 75 minutes of extraction. After this optical density decreased gradually.

4. 2.4.3 Optimization of dyeing pH for mango dye

Table 4.21 Optimization of dyeing pH for mango dye

pH	O D before dyeing	O D after dyeing	Percentage dye absorption
7	0.595	0.480	19.32
8	0.609	0.486	20.19
9	0.609	0.480	21.18
10	0.609	0.489	19.70

Table 4.21 indicates that the percentage dye absorption increased gradually with an increase in the pH of dye solution. The maximum percentage dye absorption was at 9 pH. Later on a sudden decrease in the percentage dye absorption was observed. Thus, pH 9 was considered as the optimum pH for dyeing fabric samples with mango dye.

4. 2.4.4 Optimization of dye concentration for mango dye

Percentage dye absorption values for different dye concentrations

(Table 4.22) revealed that the dye absorption increased up to 3 g/g of cotton after

Table 4.22 Optimization of dye concentration for mango dye

Dye conc.	OD Before dyeing	OD After dyeing	Percentage dye absorption
1	0.611	0.491	19.63
2	0.609	0.490	19.67
3	0.609	0.470	22.82
4	0.609	0.480	21.31
5	0.610	0.478	21.63

which a decrease in the percentage dye absorption was observed. Hence, 3 g/g of cotton was considered as optimum dye concentration.

4. 2.4.5 Optimization of dyeing time for mango dye

Table 4.23 Optimization of dyeing time for mango dye

Dye time.	OD before dyeing	OD after dyeing	Percentage dye absorption
30	0.609	0.484	20.52
45	0.609	0.479	21.34
60	0.610	0.471	22.78
75	0.610	0.485	20.49
90	0.611	0.487	20.29

The percentage dye absorption values for different dyeing times (Table 4.23) revealed that the dye absorption increased gradually up to 60 minutes dyeing time. A sudden decrease in the percentage dye absorption was observed after that. Hence, 60 minutes was considered as optimum dyeing time

4.2.4.6 Optimum dyeing parameters used for mango dye

The results of the trials, showed that the maximum percentage of dye was absorbed at dye extraction pH 9, dye extraction time 75 minutes, dyeing pH 9, dye concentration 3 percent (o.w.f) and dyeing time 60 minutes. Therefore, these

were considered to be the optimum conditions and the work was carried out using these.

4.3 OPTIMUM MORDANTING CONDITIONS

The mordant extraction pH, mordant extraction time were optimized on the basis of optical density, while the mordanting method and mordant concentration were selected on the basis of visual inspection using spectravide. The optimum and the selected values of the four mordantd have been presented below.

4.3.1 Optimization of mordant extraction pH

Table 4.24 Optimization of extraction pH for *arjun*, *babool*, eucalyptus and pomegranate mordants

pH media	Optical density			
	<i>Arjun</i>	<i>Babool</i>	Eucalyptus	Pomegranate
4	0.565	0.552	0.502	0.572
5	0.572	0.583	0.534	0.583
6	0.599	0.601	0.578	0.610
7	0.612	0.618	0.608	0.612
8	0.614	0.620	0.613	0.612
9	0.615	0.621	0.614	0.613
10	0.617	0.623	0.616	0.614

It can be observed from the table 4.24 that the optical density of all the four mordants namely, *arjun*, *babool*, eucalyptus and pomegranate in the acidic media was comparatively less but increased in the alkaline media. The colour of the dye extract also became darker. Therefore, the pH level of 10 was selected as the optimum pH for all the four mordants. Pankaj (2002) was of the view that alkaline media gave a darker colour due to some chromophoric rearrangement under alkaline condition.

4.3.2 Optimum mordant extraction time

According to table 4.25 the optical density of three mordants namely, *arjun*, eucalyptus and pomegranate increased up to 60 minutes of extraction time. After that there was a gradual decrease with an increase in the extraction time. Hence, 60 minutes of extraction time was adjudged as the optimum for mordants *arjun*, eucalyptus and pomegranate.

For the fourth mordant, namely *babool*, the optical density increased gradually up to 90 minutes of extraction time which was taken as the optical time.

Table 4.25 Optimization of extraction time for *arjun*, *babool*, eucalyptus and pomegranate mordants

Time (min.)	Optical density			
	<i>Arjun</i>	<i>Babool</i>	Eucalyptus	Pomegranate
30	0.614	0.622	0.613	0.610
45	0.615	0.623	0.612	0.612
60	0.618	0.625	0.616	0.614
75	0.617	0.625	0.612	0.612
90	0.617	0.628	0.608	0.611

4.3.3 Selection of mordanting methods for different dyes

For the selection of the mordanting methods the dyed samples were observed in the Spectra vide. The mordanting method was selected on the basis of the best colour. The selected mordanting methods of mordants have been presented in table 4.26

It is evident from the table 4.26 that for *bansa* dye, post mordanting method of mordant application was considered to be the most suitable in the case of *arjun*

Table 4.26 Selection of mordanting method for *arjun*, *babool*, *eucalyptus* and pomegranate mordants

Mordant	Dyes			
	<i>Bansa</i>	Bottle brush	Duranta	Mango
<i>Arjun</i>	Post	Simultaneous	Pre	Post
<i>Babool</i>	Simultaneous	Pre	Pre	Simultaneous
<i>Eucalyptus</i>	Pre	Simultaneous	Simultaneous	Simultaneous
Pomegranate	Post	Post	Simultaneous	Pre

and pomegranate mordants, while simultaneous mordanting and pre-mordanting methods gave the best results for *babool* and *eucalyptus* mordants, respectively.

The table 4.26 depicts that for bottle brush dye, simultaneous mordanting method of application was the best for both *arjun* and *eucalyptus* mordants. For *babool* and pomegranate mordants, pre-mordanting and post-mordanting methods of mordant application respectively, were considered to be the best.

Pre-mordanting method of application was considered to be the best for both *arjun* and *babool* mordants in the case of *duranta* dye, while the simultaneous mordanting method gave the best results for both *eucalyptus* and pomegranate mordants.

In the case of mango dye, post-mordanting method of mordant application was adjudged the most suitable for *arjun*. For both, *babool* and *eucalyptus*

mordants, it was simultaneous mordanting and for pomegranate, pre- mordanting method was considered to be the best.

4.3.4 Selection of mordant concentration for different dyes

Selection of the mordant concentration was done by observing the dyed samples in the Spectraaide, to select the best colour. The selected mordant concentrations (% o.w.f) for different mordants have been discussed below in table 4.27.

It is clear from table 4.27 that for both *arjun* and eucalyptus mordants the selected mordant concentration was 0.4 percent, while it was 0.5 percent for both *babool* and pomegranate mordants.

Table 4.27 Selection of concentration for *arjun*, *babool*, eucalyptus and pomegranate mordants (% o.w.f)

Mordant	Dyes			
	Bansa	Bottle brush	Duranta	Mango
<i>Arjun</i>	0.4	0.3	0.4	0.5
<i>Babool</i>	0.5	0.4	0.4	0.4
Eucalyptus	0.4	0.3	0.3	0.5
Pomegranate	0.5	0.5	0.5	0.5

The results showed that the mordant concentration of 0.3 percent was optimum for both *arjun* and eucalyptus mordants. *Babool* and pomegranate, gave the best results at 0.4 percent and 0.5 percent respectively.

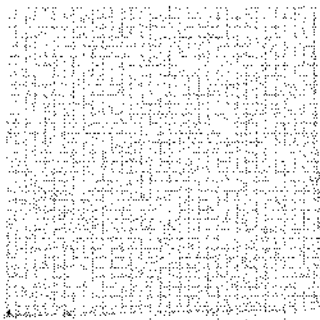
Data in table 4.27 also elicits that for both *arjun* and *babool* the selected mordant concentration was 0.4 percent, while it was 0.3 percent and 0.5 percent for eucalyptus and pomegranate mordants respectively.

The results further showed that the selected mordant concentration was 0.5 percent for all the mordants, except for *babool* mordant, where the selected mordant concentration was 0.4 percent (Table 4.27).

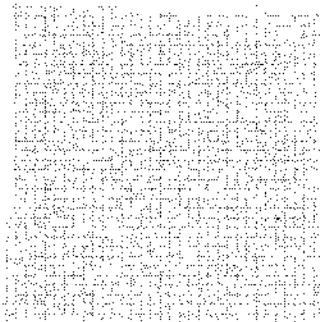
4.3.5 Optimized and selected mordanting conditions for all the dyes

The results of the trials showed that the maximum optical density was observed mordant extraction pH 10 for all the mordants, mordant extraction time was 60 minutes for *arjun*, eucalyptus and pomegranate mordants and 90 minutes for *babool* mordant. The selected mordanting method and mordant concentration has been summarized in table 4.28. All the optimized conditions were used for dyeing cotton with the four selected dyes with four natural mordants. The shades obtained on the control samples as well as each dye using each mordant have been put on sample sheets SS.1 to SS.4.

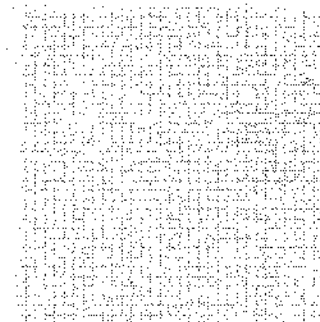
**Enzymatically untreated
control**



Unmordanted

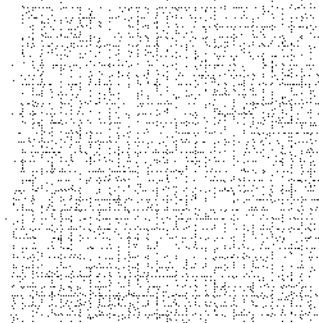


Mordanted with *arjun*

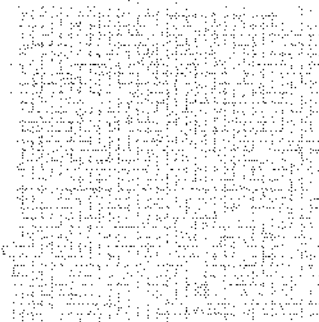


Mordanted with *babool*

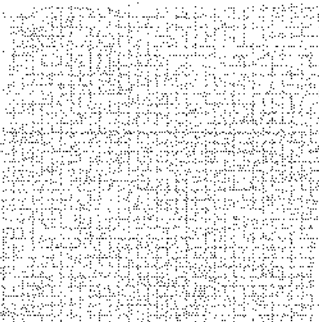
Enzymatically treated



Unmordanted



Mordanted with *arjun*



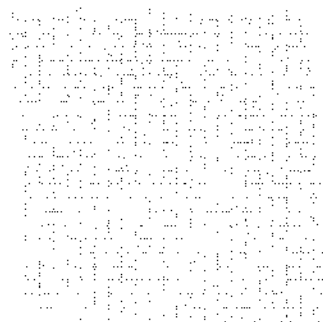
Mordanted with *babool*

**SS. 1 : Untreated and enzymatically pre-treated samples dyed
with *bansa* dye**

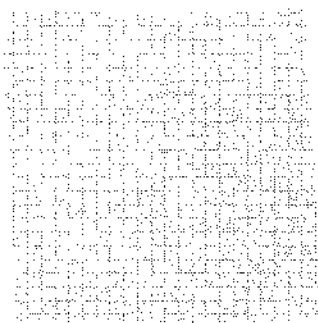
Cont.....

..... Cont.

**Enzymatically untreated
control**

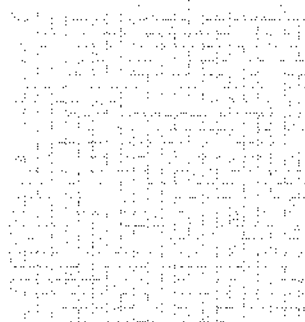


**Mordanted with
eucalyptus**

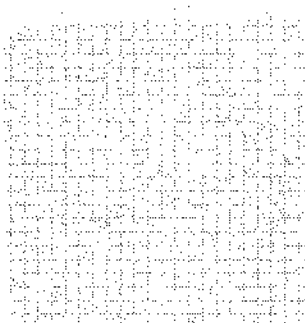


**Mordanted with
pomegrante**

Enzymatically treated

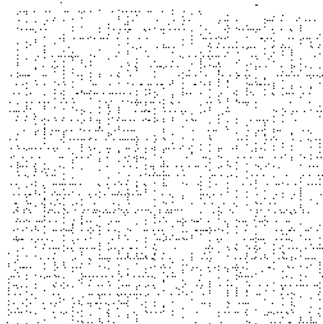


**Mordanted with
eucalyptus**

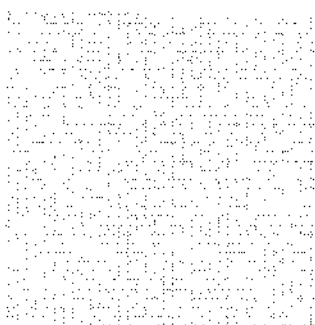


**Mordanted with
pomegrante**

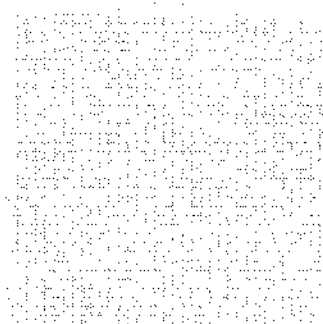
**Enzymatically untreated
control**



Unmordanted

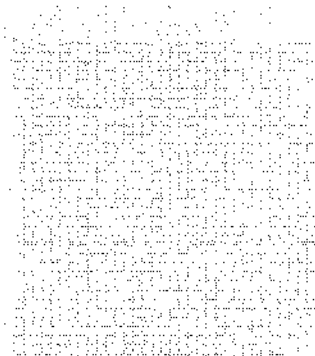


Mordanted with *arjun*

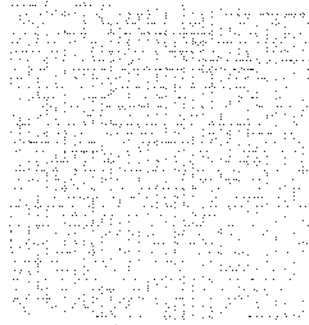


Mordanted with *babool*

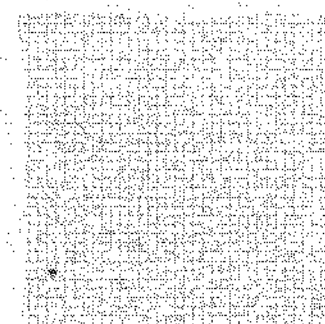
Enzymatically treated



Unmordanted



Mordanted with *arjun*



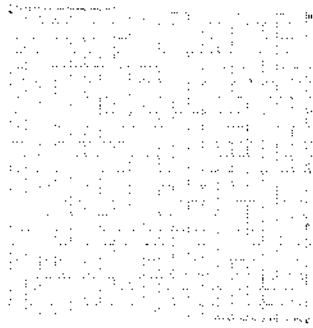
Mordanted with *babool*

**SS. 2 : Untreated and enzymatically pre-treated samples dyed
with bottle brush dye**

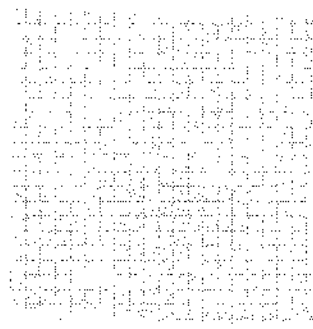
Cont.....

..... Cont.

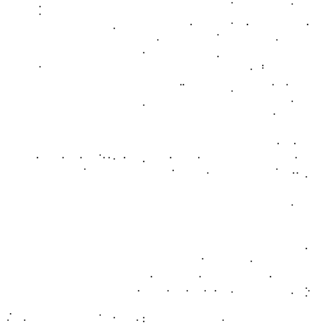
**Enzymatically untreated
control**



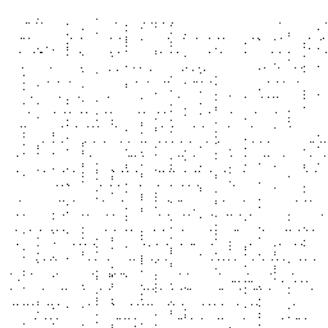
**Mordanted with
eucalyptus**



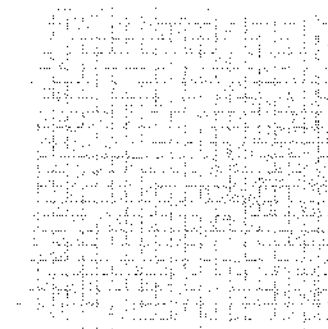
**Mordanted with
pomegrnate**



Enzymatically treated



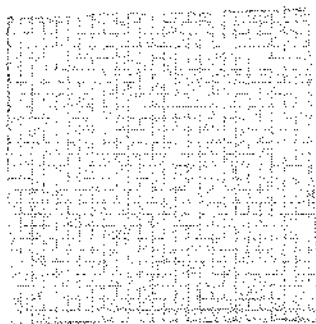
**Mordanted with
eucalyptus**



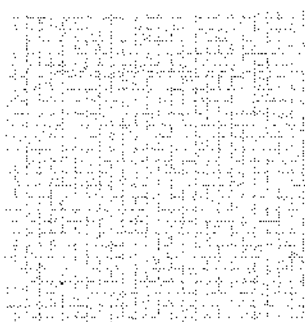
**Mordanted with
pomegrnate**



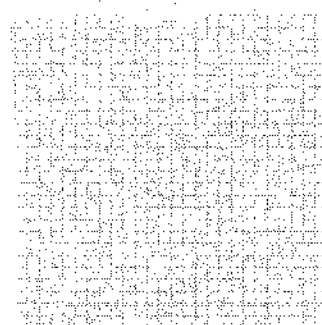
**Enzymatically untreated
control**



Unmordanted

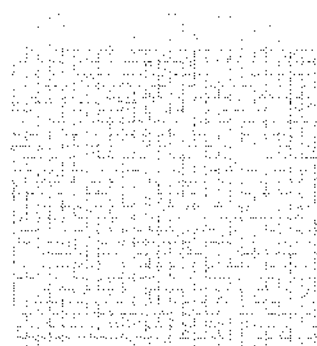


Mordanted with *arjun*

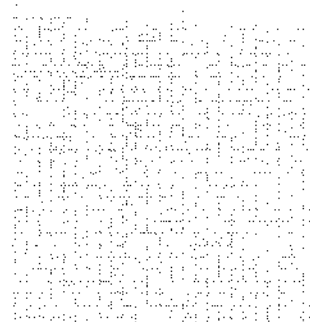


Mordanted with *babool*

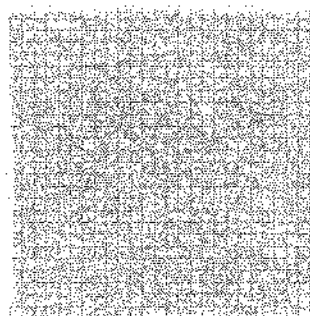
Enzymatically treated



Unmordanted



Mordanted with *arjun*



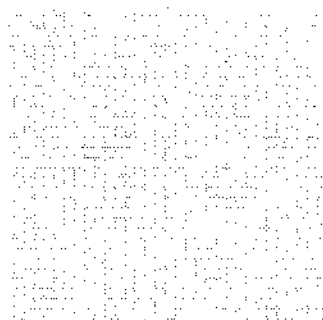
Mordanted with *babool*

**SS. 3 : Untreated and enzymatically pre-treated samples dyed
with duranta dye**

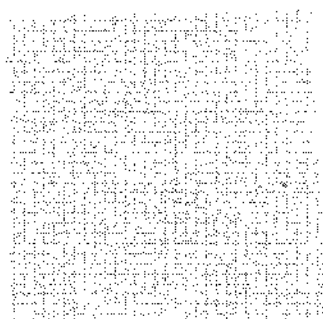
Cont.....

..... Cont.

**Enzymatically untreated
control**



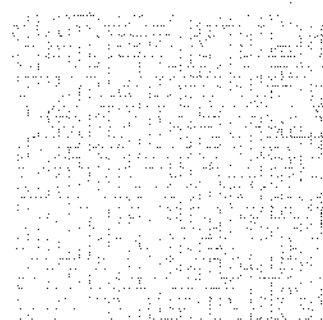
**Mordanted with
eucalyptus**



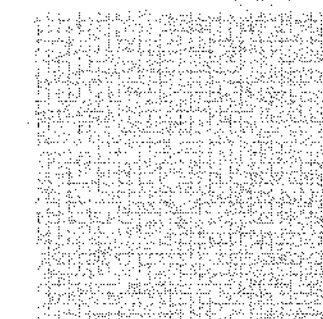
**Mordanted with
pomegranate**



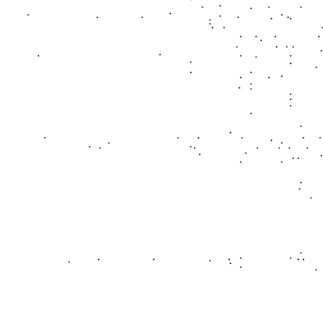
Enzymatically treated



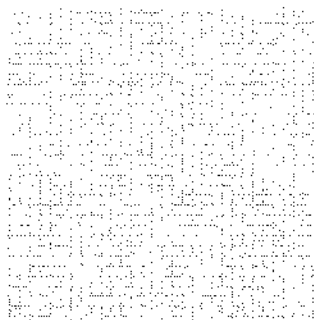
**Mordanted with
eucalyptus**



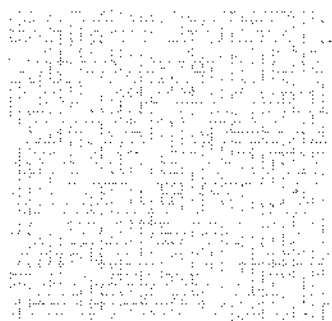
**Mordanted with
pomegranate**



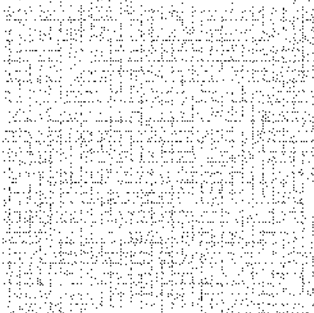
**Enzymatically untreated
control**



Unmordanted

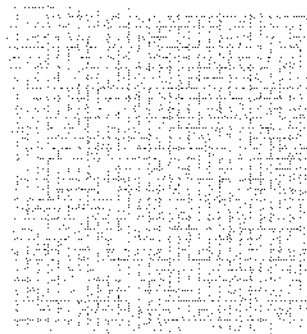


Mordanted with *arjun*

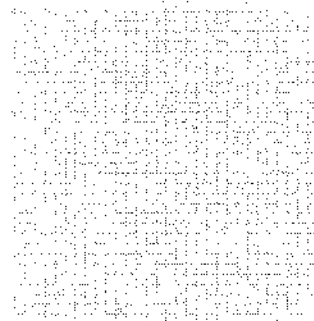


Mordanted with *babool*

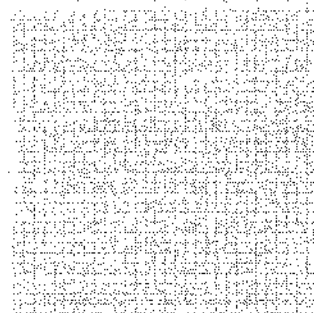
Enzymatically treated



Unmordanted



Mordanted with *arjun*



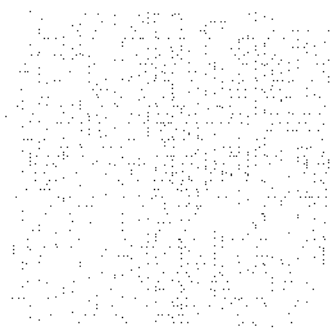
Mordanted with *babool*

**SS. 4 : Untreated and enzymatically pre-treated samples dyed
with mango dye**

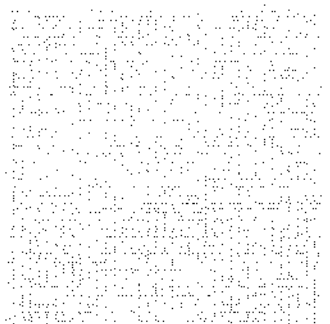
Cont.....

..... Cont.

**Enzymatically untreated
control**

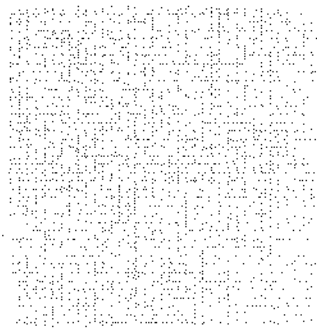


**Mordanted with
eucalyptus**

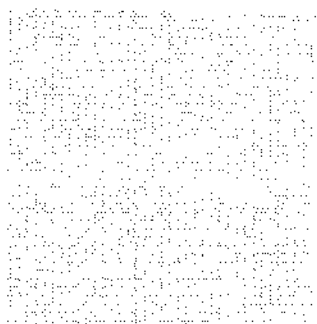


**Mordanted with
pomegranate**

Enzymatically treated



**Mordanted with
eucalyptus**



**Mordanted with
pomegranate**

Table 4.28 Optimized and selected mordanting conditions for arjun, babool, eucalyptus and pomegranate mordants with all the dyes

Mordant	Mordant Extraction pH	Mordant extraction time (min.)	Mordanting method				Mordant concentration	
			Bansa brush	Bottle	Duranta	Mango	Bansa brush	Mango
<i>Arjun</i>	10	60	Post	Sim	Pre	Post	0.4	0.5
<i>Babool</i>	10	90	Sim	Pre	Pre	Sim	0.5	0.4
<i>Eucalyptus</i>	10	60	Pre	Sim	Sim	Sim	0.4	0.5
<i>Pomegranate</i>	10	60	Post	Post	Sim	Pre	0.5	0.5

4.4 EFFECT OF ENZYMATIC PRE-TREATMENT ON CIE LAB VALUES OF DYED SAMPLES

The use of computer in measurement of colour increases the objectivity of the experimental results of dyeing (Giles 1974 and Valia 1987). Therefore, effect of enzymatic pre-treatment in dyeing cotton with natural dyes was seen by comparing the CIE LAB values.

4.4.1 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with *bansa* dye

The CIE LAB values of both, the control and treated samples with enzyme and dyed with *bansa* dye at optimum conditions have been presented in table 4.29.

Table 4.29 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with *bansa* dye

Mordants	L*		a*		b*		C*	
	EUC	ET	EUC	ET	EUC	ET	EUC	ET
Control	75.080	75.664	2.888	2.575	6.047	6.498	6.702	6.990
Arjun	76.191	76.375	4.883	4.887	3.227	1.561	5.852	5.130
Babool	76.412	74.567	4.469	5.175	2.421	3.304	5.083	6.139
Eucalyptus	78.016	76.164	5.075	5.628	0.250	2.482	5.081	6.151
Pome-granate	73.181	73.065	2.896	2.402	10.879	12.479	11.258	12.479

EUC = Enzymatically Un-treated control, ET = Enzymatically treated

4.4.1.1 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with *bansa* dye

The L* value of enzymatically treated sample was more than that of enzymatically untreated sample, which indicates that the enzymatically treated

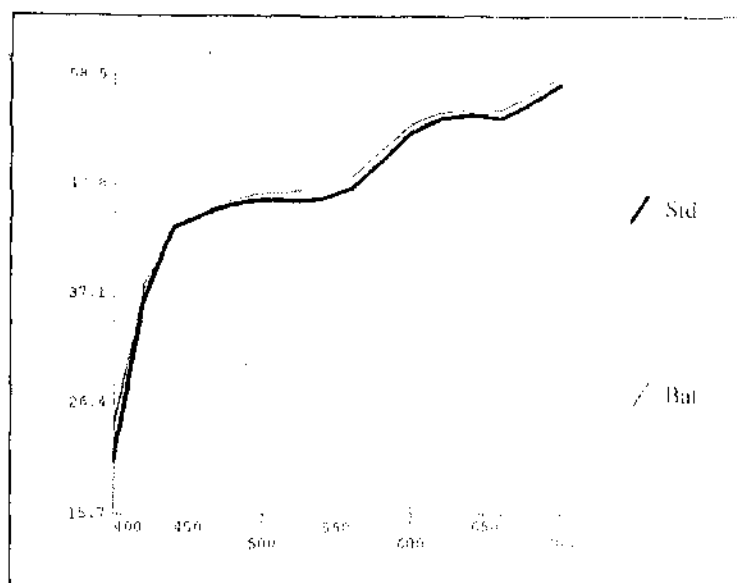
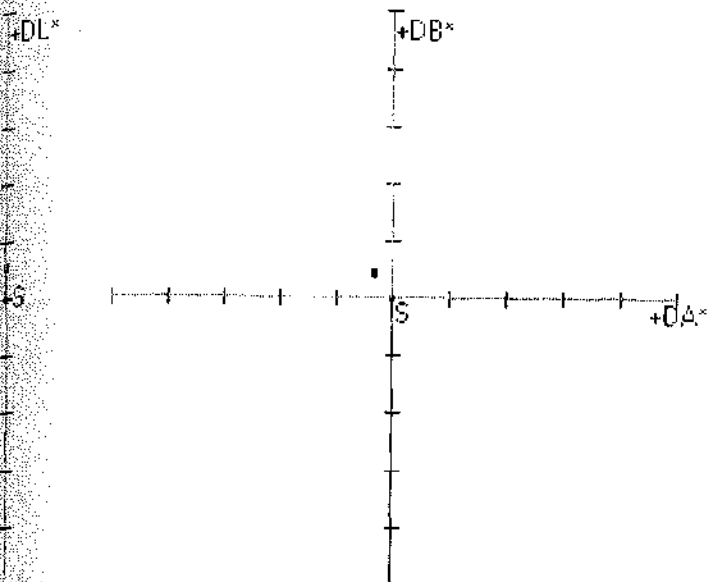
sample was lighter in colour than the enzymatically untreated sample (Fig. 4.1). The low a^* value and high b^* value of enzymatically treated sample indicate that these are less red and more yellow respectively. The higher C^* value of enzymatically treated sample than that of the control indicates that the enzymatic treatment led to increased saturation of colour.

4.4.1.2 Effect of enzymatic pre-treatment on CIE LAB values of bansa dye mordanted with *arjun*

The L^* value of enzymatically treated sample was more, which indicates that it was lighter in colour than the enzymatically untreated sample (Fig 4.2). The higher a^* value and lower b^* value of enzymatically treated sample indicate higher red content and lower yellow content respectively in the enzymatically treated sample. The lower C^* value of treated sample shows that the enzymatic treatment led to lesser saturation than the control when dyed with *bansa* dye when dyed with *arjun* mordant.

4.4.1.3 Effect of enzymatic pre-treatment on CIE LAB values of bansa dye mordanted with *babool*

In the case of *babool* mordant the L^* value of enzymatically treated sample was less than that of control eliciting that the enzymatically treated sample is darker in colour than the control (Fig. 4.3) The higher a^* and b^* value of enzymatically treated sample indicate high content of red and yellow colour respectively. The higher C^* value of enzymatically treated sample show that the enzymatically treated sample was more saturated and brighter.



	Standard	Batch
L *	75.080	75.664
a *	2.888	2.575
b *	6.047	6.498
C *	6.702	6.990
h *	64.471	68.385

Std: BC

Bat: BE

DL *	0.584	Lighter
DA *	-0.313	Less Red
DB *	0.451	More Yellow
DC *	0.288	More Saturated
DH *	0.467	
DE *	0.801	

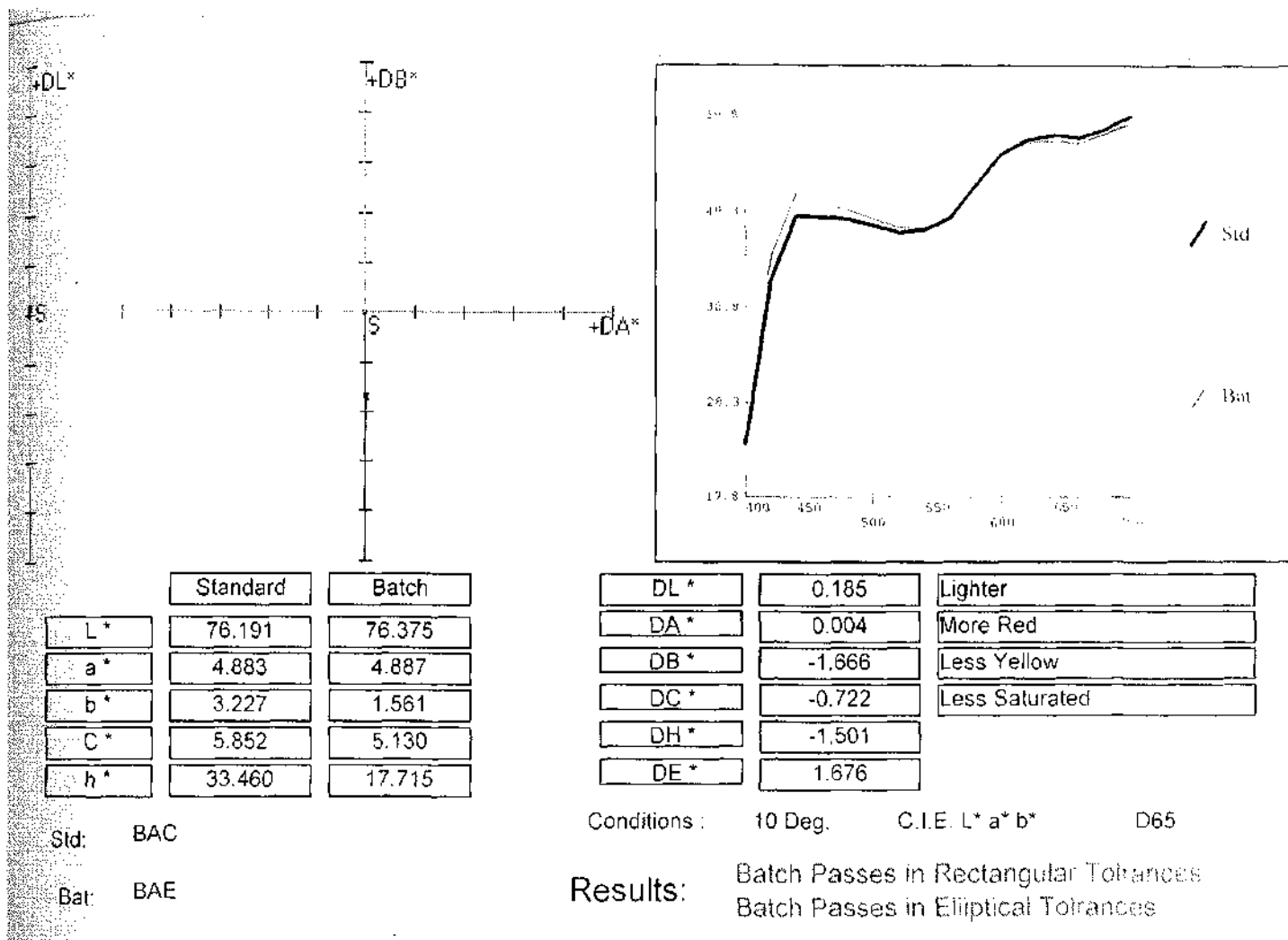
Conditions : 10 Deg C.I.E. L* a* b* D65

Results: Batch Passes in Rectangular Tolerances
Batch Passes in Elliptical Tolerances

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Fig. 4.1 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with bansa dye

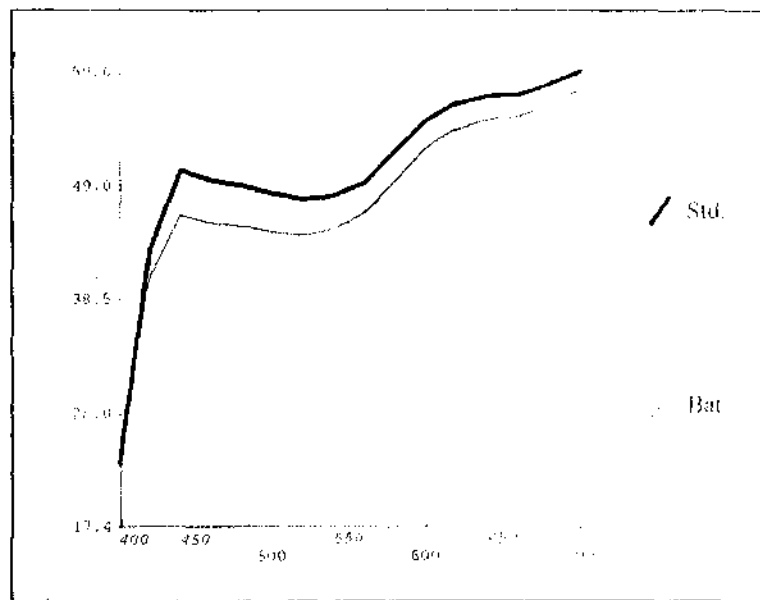
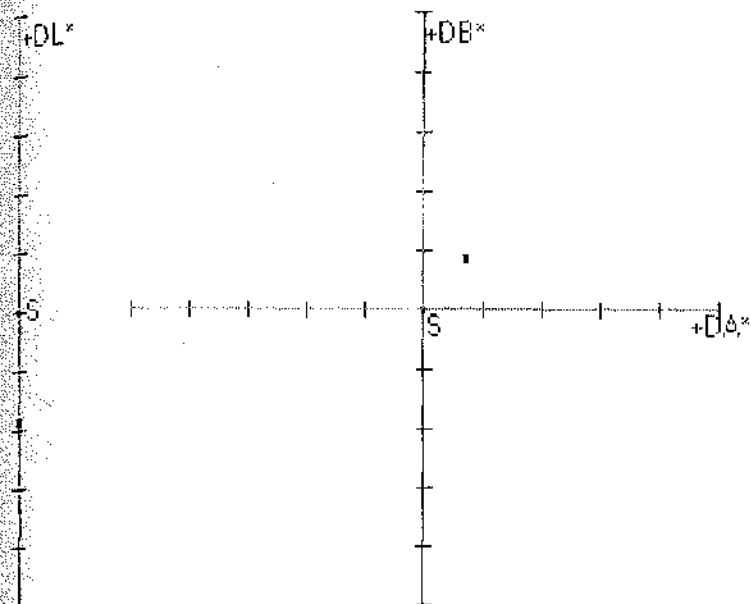
(BC= Samples dyed with bansa, unmordanted and enzymatically untreated control, BE= Samples dyed with bansa, unmordanted and enzymatically treated)



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Fig. 4.2 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *arjun* and dyed with *bansa* dye

(BAC= Samples dyed with *bansa*, mordanted with *arjun* and enzymatically untreated control, BAE= Samples dyed with *bansa*, mordanted with *arjun* and enzymatically treated)



	Standard	Batch
L *	76.412	74.567
a *	4.469	5.175
b *	2.421	3.304
C *	5.083	6.139
h *	28.450	32.554

DL *	-1.844	Darker
DA *	0.706	More Red
DB *	0.882	More Yellow
DC *	1.057	More Saturated
DH *	0.400	
DE *	2.163	

Std: BBC

Conditions : 10 Deg. C.I.E. L* a* b* D65

Bat: BBE

Results: Batch Passes in Rectangular Tolerances
Batch Passes in Elliptical Tolerances.

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Fig. 4.3 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *babool* and dyed with *bansa* dye

(BBC= Samples dyed with *bansa*, mordanted with *babool* and enzymatically untreated control, BBE= Samples dyed with *bansa*, mordanted with *babool* and enzymatically treated)

4.4.1.4 Effect of enzymatic pre-treatment on CIE LAB values of bansa dye mordanted with eucalyptus

The L^* value of enzymatically treated sample was less than that obtained on the control (Fig 4.4). This was an indication of the fact that the enzymatically treated sample was darker in colour than the control. The higher a^* , b^* and C^* value of enzymatically treated sample point out to relatively higher content of red, yellow colour and brightness than the enzymatically untreated sample.

4.4.1.5 Effect of enzymatic pre-treatment on CIE LAB values of bansa dye mordanted with pomegranate

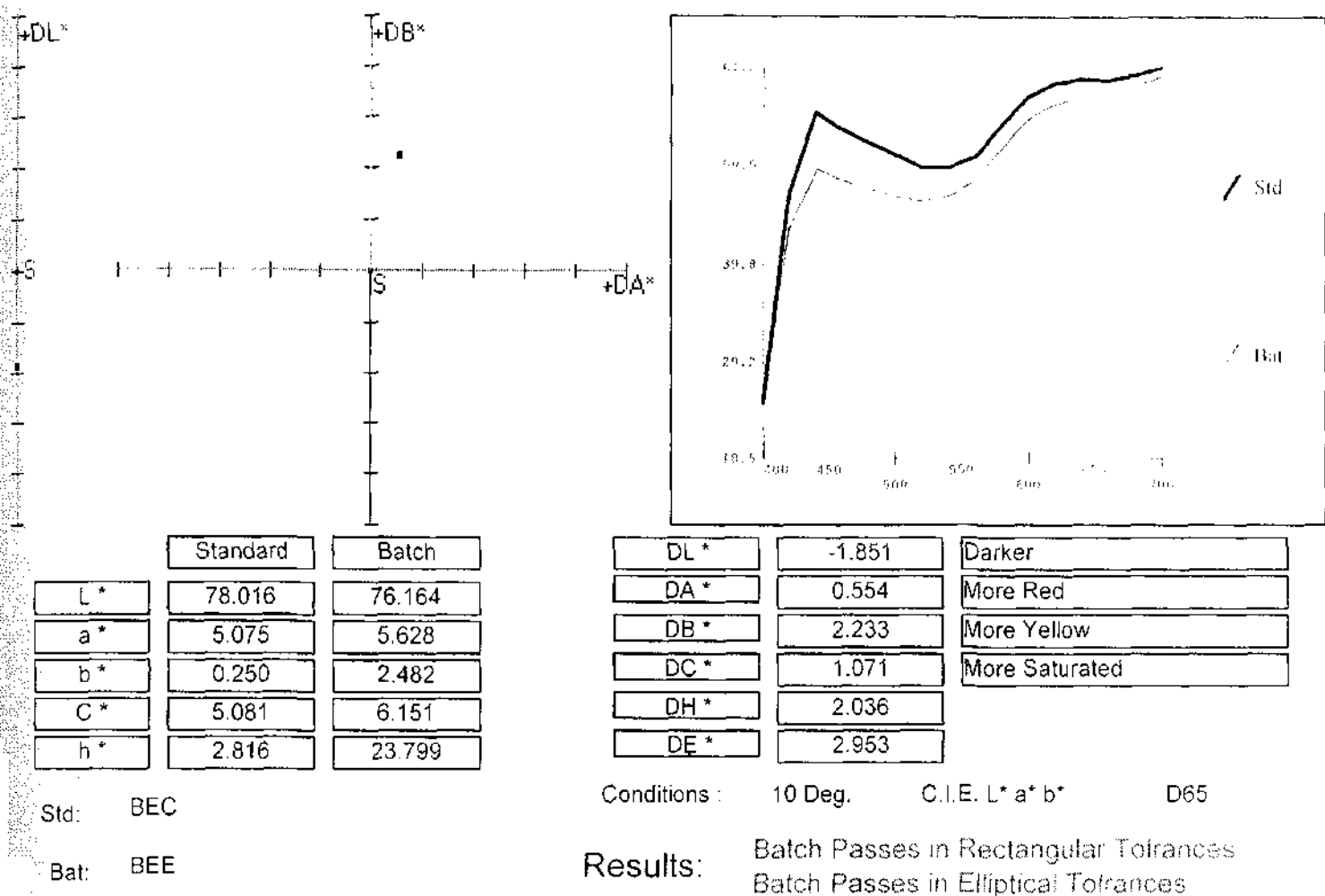
In this case also the L^* value of enzymatically treated sample was less than enzymatically untreated sample, eliciting that the enzymatically treated sample is darker in colour than the control (Fig 4.5). However, a^* value was lower but b^* was higher in the case of enzymatically treated sample indicating lesser content of red and more content of yellow colour respectively. The higher C^* value of enzymatically treated sample shows that the enzymatically treated sample was more saturated and thus brighter.

4.4.2 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with bottle brush dye

The CIE LAB values of both the treated and control samples with enzyme and dyed with bottle brush dye using different mordants under optimum conditions have been presented in table 4.30.

4.4.2.1 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with bottle brush dye

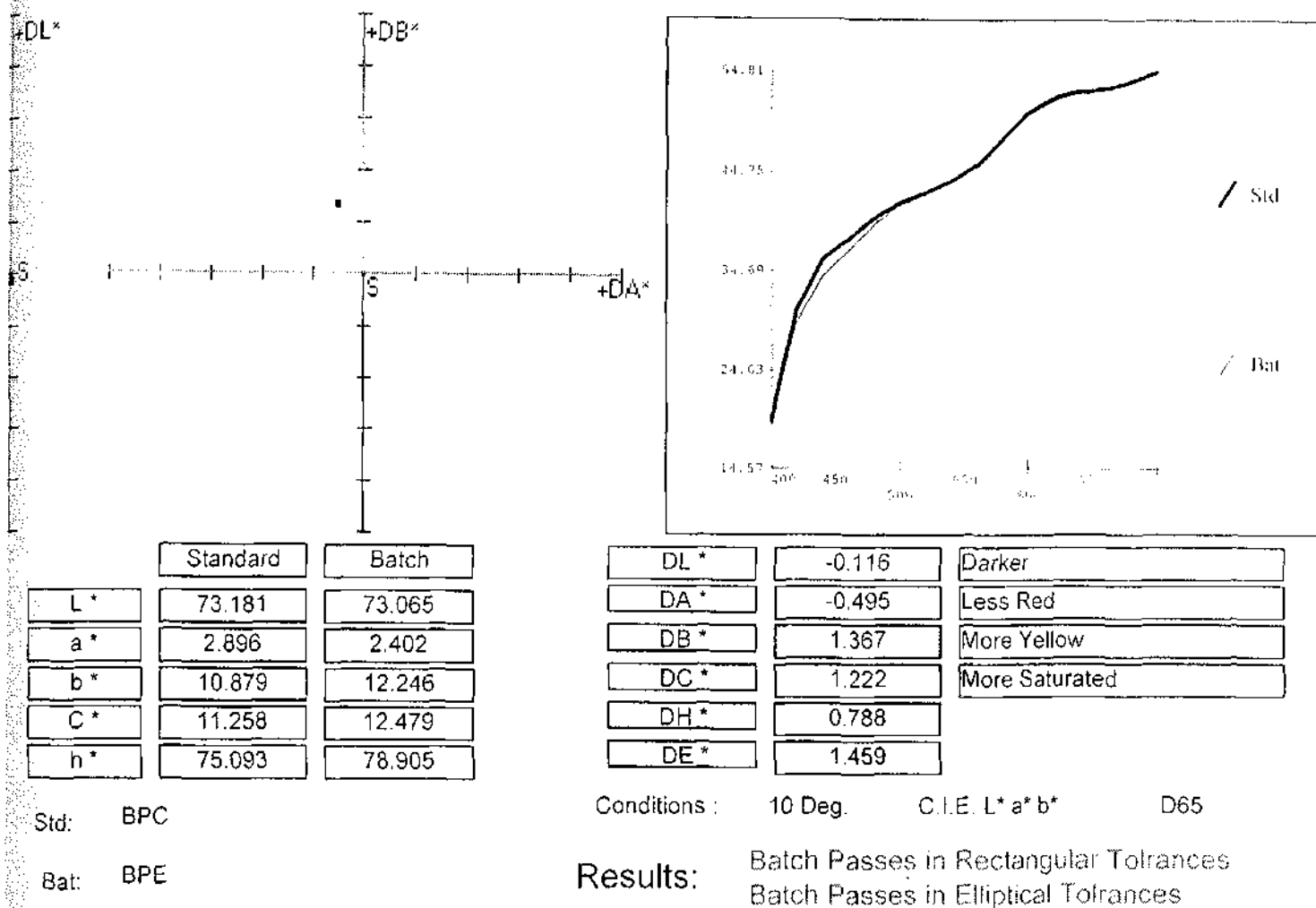
The table reveals that L^* value of enzymatically treated sample was more than that of the control, which indicates that the enzymatically treated sample was



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Fig. 4.4 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with eucalyptus and dyed with bansa dye

(BEC= Samples dyed with bansa, mordanted with eucalyptus and enzymatically untreated control, BEE= Samples dyed with bansa, mordanted with eucalyptus and enzymatically treated)



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Fig. 4.5 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with pomegranate and dyed with *bansa* dye

(BPC= Samples dyed with *bansa*, mordanted with pomegranate and enzymatically untreated control, BPE= Samples dyed with *bansa*, mordanted with pomegranate and enzymatically treated)

lighter in colour than the enzymatically untreated sample (Fig. 4.6). The lower a^* value and high b^* value of enzymatically treated sample indicate that the enzymatically treated sample has lesser content of red and yellow colour respectively. The lower C^* value of enzymatically treated sample as compared to control indicate that the enzymatically treated sample had less brightness.

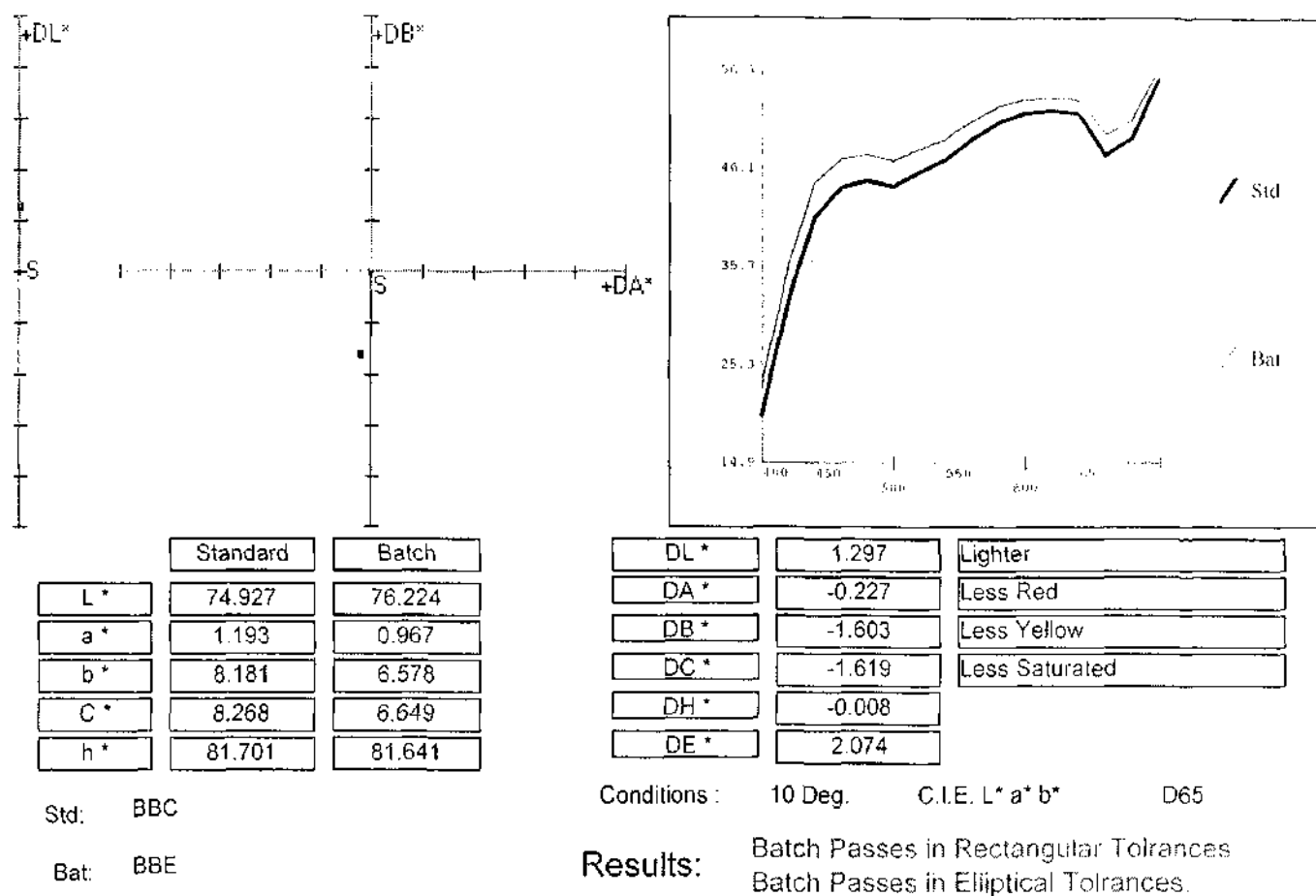
Table 4.30 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with bottle brush dye

Mordants	L*		a*		b*		C*	
	EUC	ET	EUC	ET	EUC	ET	EUC	ET
Control	74.927	76.224	1.193	0.967	8.181	6.578	8.268	6.649
Arjun	76.715	78.271	1.914	1.576	2.994	1.551	3.554	2.211
Babool	76.804	73.801	1.851	3.512	4.394	5.933	4.678	6.895
Eucalyptus	78.285	79.118	1.402	1.204	1.745	1.990	2.238	2.326
Pome-granate	73.732	74.564	1.370	0.934	11.300	11.372	11.383	11.410

EUC = Enzymatically Un-treated control, ET = Enzymatically treated

4.4.2.2 Effect of enzymatic pre-treatment on CIE LAB values of bottle brush dye mordanted with *arjun*

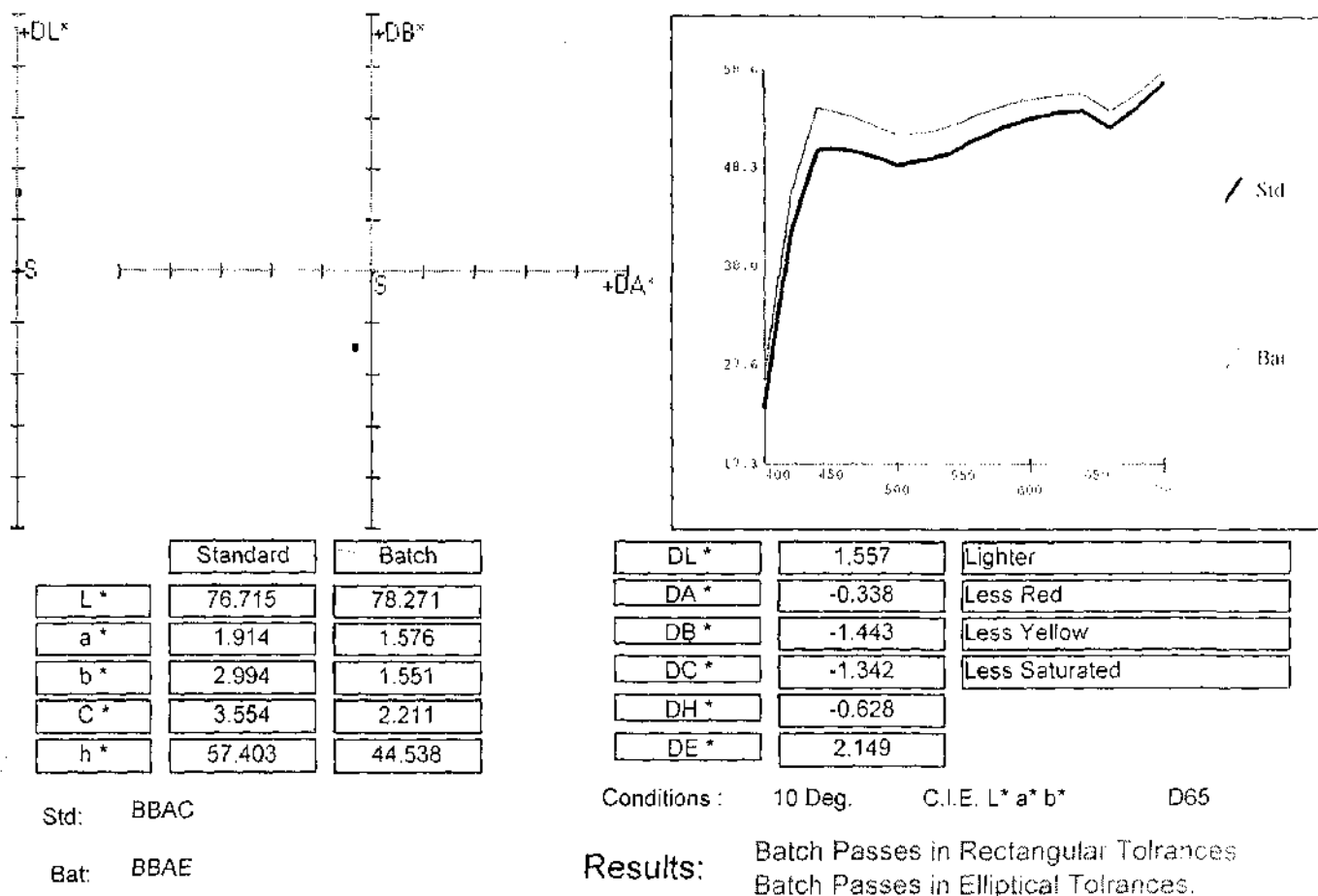
It is clear from the table that the L^* value of enzymatically treated sample was more than that of the control, which shows that the enzymatically treated sample was lighter in colour (Fig 4.7). The lower a^* , b^* and C^* values of enzymatically treated samples point out to relatively lower content of red, yellow colour and less brightness than enzymatically untreated samples.



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Fig. 4.6 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with bottle brush dye

(BBC= Samples dyed with bottle brush, unmordanted and enzymatically untreated control, BBE= Samples dyed with bottle brush, unmordanted and enzymatically treated)



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Fig. 4.7 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *arjun* and dyed with bottle brush dye

(BBAC= Samples dyed with bottle brush, mordanted with *arjun* and enzymatically untreated control, BBAE= Samples dyed with bottle brush, mordanted with *arjun* and enzymatically treated)

4.4.2.3 Effect of enzymatic pre-treatment on CIE LAB values of bottle brush dye mordanted with *babool*

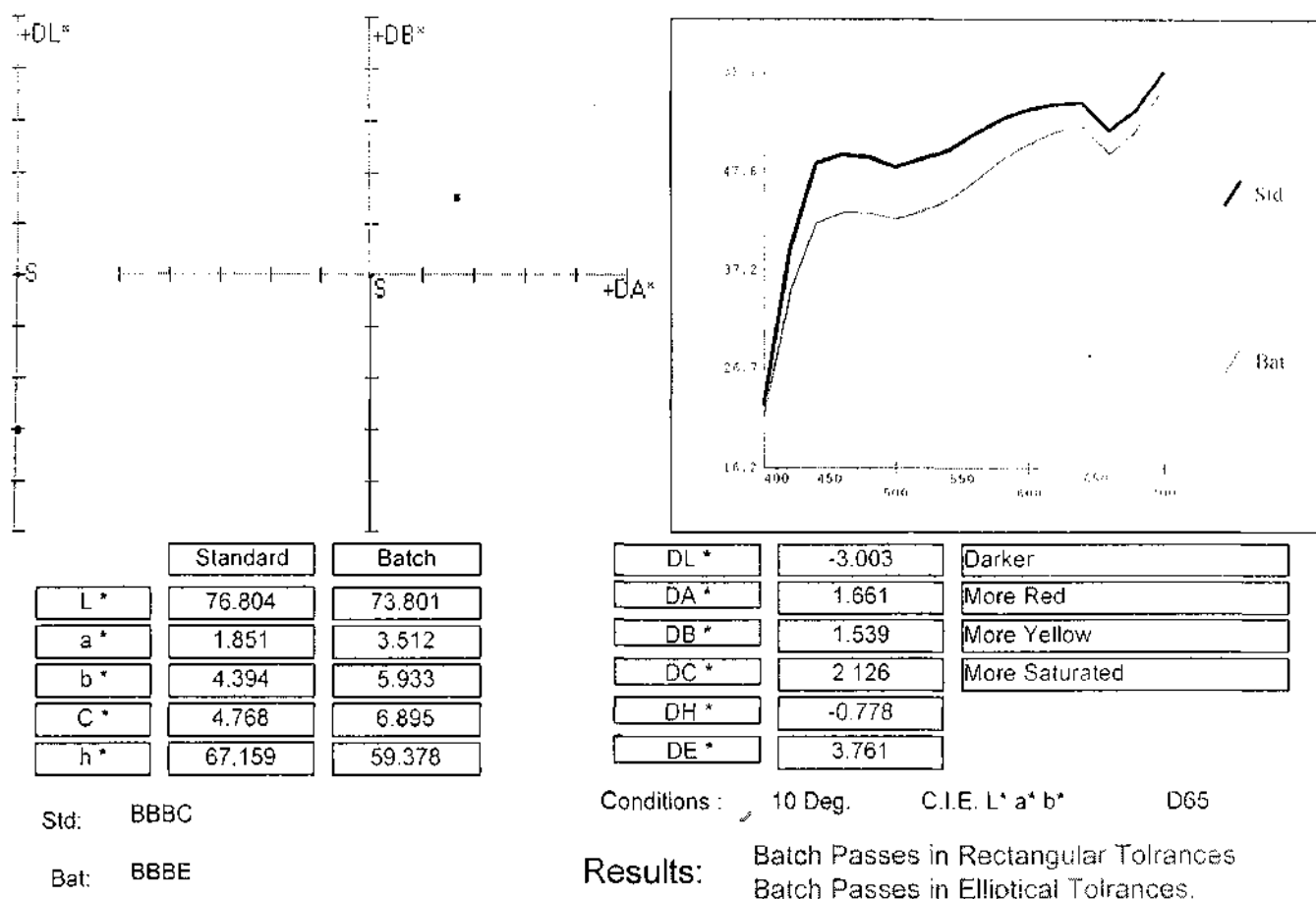
The L^* value of enzymatically treated sample was less than that of the control, which makes it clear that the enzymatically treated sample was darker in colour (Fig 4.8). The higher a^* , b^* and C^* values of enzymatically treated samples indicate high content of red, yellow colour and more saturated than enzymatically untreated samples.

4.4.2.4 Effect of enzymatic pre-treatment on CIE LAB values of bottle brush dye mordanted eucalyptus

The table makes it clear that the L^* value of enzymatically treated sample was more than that of the control, which further indicates that the enzymatically treated sample was lighter in colour (Fig. 4.9). The low a^* value and high b^* value of enzymatically treated samples indicate that the enzymatically treated samples have less content of red and high content of yellow colour respectively. The high C^* value of enzymatically treated sample indicate that the enzymatically treated sample was brighter.

4.4.2.5 Effect of enzymatic pre-treatment on CIE LAB values of bottle brush dye mordanted with pomegranate

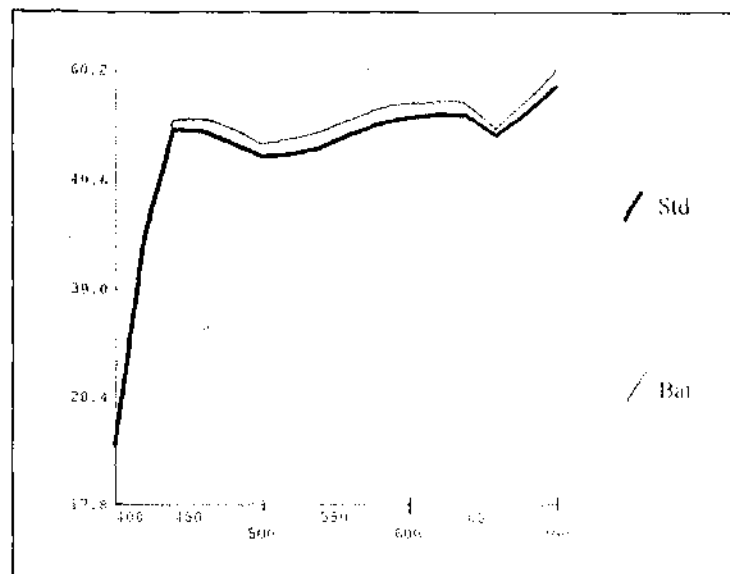
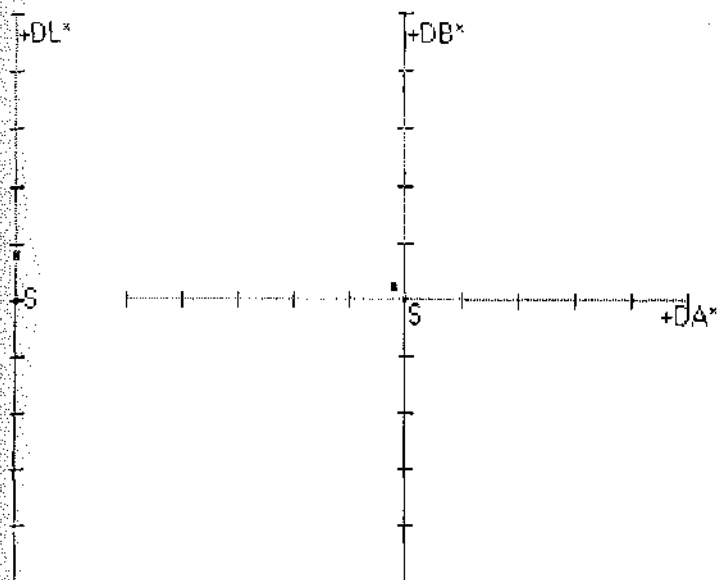
The L^* value of enzymatically treated sample was more than that of the control, which indicates that the enzymatically treated sample was darker in colour than the enzymatically untreated sample (Fig. 4.10). The low a^* and high b^* value of enzymatically treated samples indicate less content of red and more content of yellow colour respectively. The higher C^* value of enzymatically treated sample shows that the enzymatically treated sample was more saturated than control.



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Fig. 4.8 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *babool* and dyed with bottle brush dye

(BBBC= Samples dyed with bottle brush, mordanted with *babool* and enzymatically untreated control, BBBE= Samples dyed with bottle brush, mordanted with *babool* and enzymatically treated)



	Standard	Batch
L *	78.285	79.118
a *	1.402	1.204
b *	1.745	1.990
C *	2.238	2.326
h *	51.223	58.824

DL *	0.833	Lighter
DA *	-0.197	Less Red
DB *	0.246	More Yellow
DC *	0.088	More Saturated
DH *	0.302	
DE *	0.891	

Std: BBEC

Conditions : 10 Deg. C.I.E. L* a* b* D65

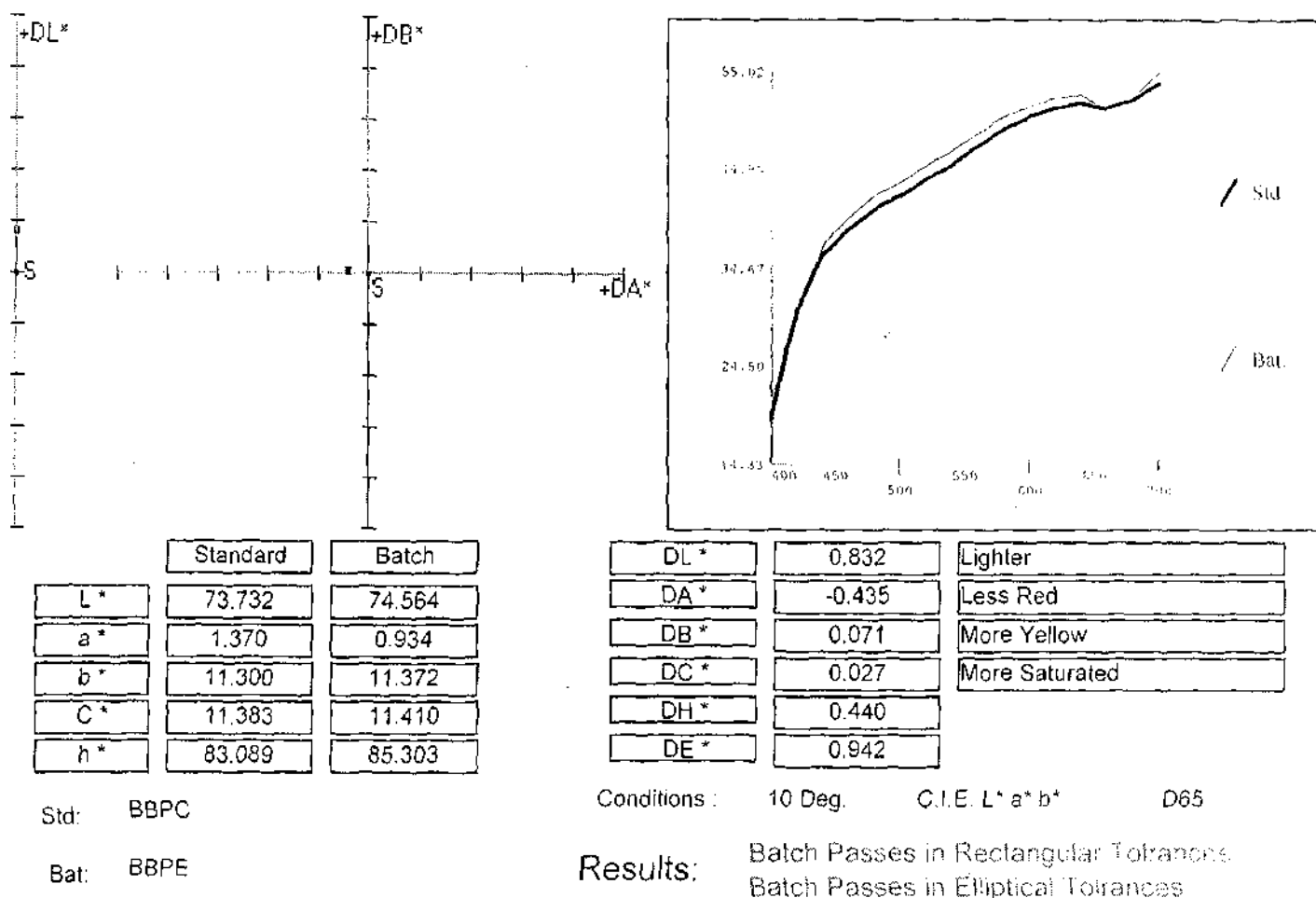
Bat: BBEE

Results: Batch Passes in Rectangular Tolrances
Batch Passes in Elliptical Tolrances

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Fig. 4.9 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with eucalyptus and dyed with bottle brush dye

(BBEC= Samples dyed with bottle brush, mordanted with eucalyptus and enzymatically untreated control, BBEE= Samples dyed with bottle brush, mordanted with eucalyptus and enzymatically treated)



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Fig. 4.10 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with pomegranate and dyed with bottle brush dye

(BBPC= Samples dyed with bottle brush, mordanted with pomegranate and enzymatically untreated control, BBPE= Samples dyed with bottle brush, mordanted with pomegranate and enzymatically treated)

4.4.3 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with duranta dye

The CIE LAB values of both the treated and control samples with enzyme and dyed with duranta dye using different mordants under optimum conditions have been presented in table 4.31.

Table 4.31 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with duranta dye

Mordants	L*		a*		b*		C*	
	EUC	ET	EUC	ET	EUC	ET	EUC	ET
Control	76.708	76.086	0.095	0.045	3.343	4.610	3.345	4.610
Arjun	76.764	77.537	2.484	2.573	1.156	1.455	2.740	2.956
Babool	75.743	69.301	2.899	6.762	4.107	6.409	5.027	9.317
Eucalyptus	78.979	77.874	1.383	1.713	0.445	1.903	1.453	2.561
Pome-granate	75.419	72.272	0.988	2.489	8.609	11.873	8.666	12.132

The CIE LAB values of the samples treated and untreated with enzyme and dyed with duranta dye using different mordants under optimum conditions have been presented in table 4.31.

4.4.3.1 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with duranta dye

The table reveals that L* value of enzymatically treated sample was less than that of control, which indicates that the enzymatically treated sample was darker in colour (Fig. 4.11). The low a* value but high b* value of enzymatically treated sample indicate that the enzymatically treated sample was less red and

yellow in colour respectively. The higher C^* value of enzymatically treated sample indicates that the sample was brighter than the control.

4.4.3.2 Effect of enzymatic pre-treatment on CIE LAB values of duranta dye mordanted with *arjun*

The higher L^* value of enzymatically treated sample, indicates that the sample was lighter in colour than the enzymatically untreated sample (Fig. 4.12). The higher a^* , b^* and C^* values of enzymatically treated sample show more content of red, yellow colour and brighter sample than the control.

4.4.3.3 Effect of enzymatic pre-treatment on CIE LAB values of duranta dye mordanted with *babool*

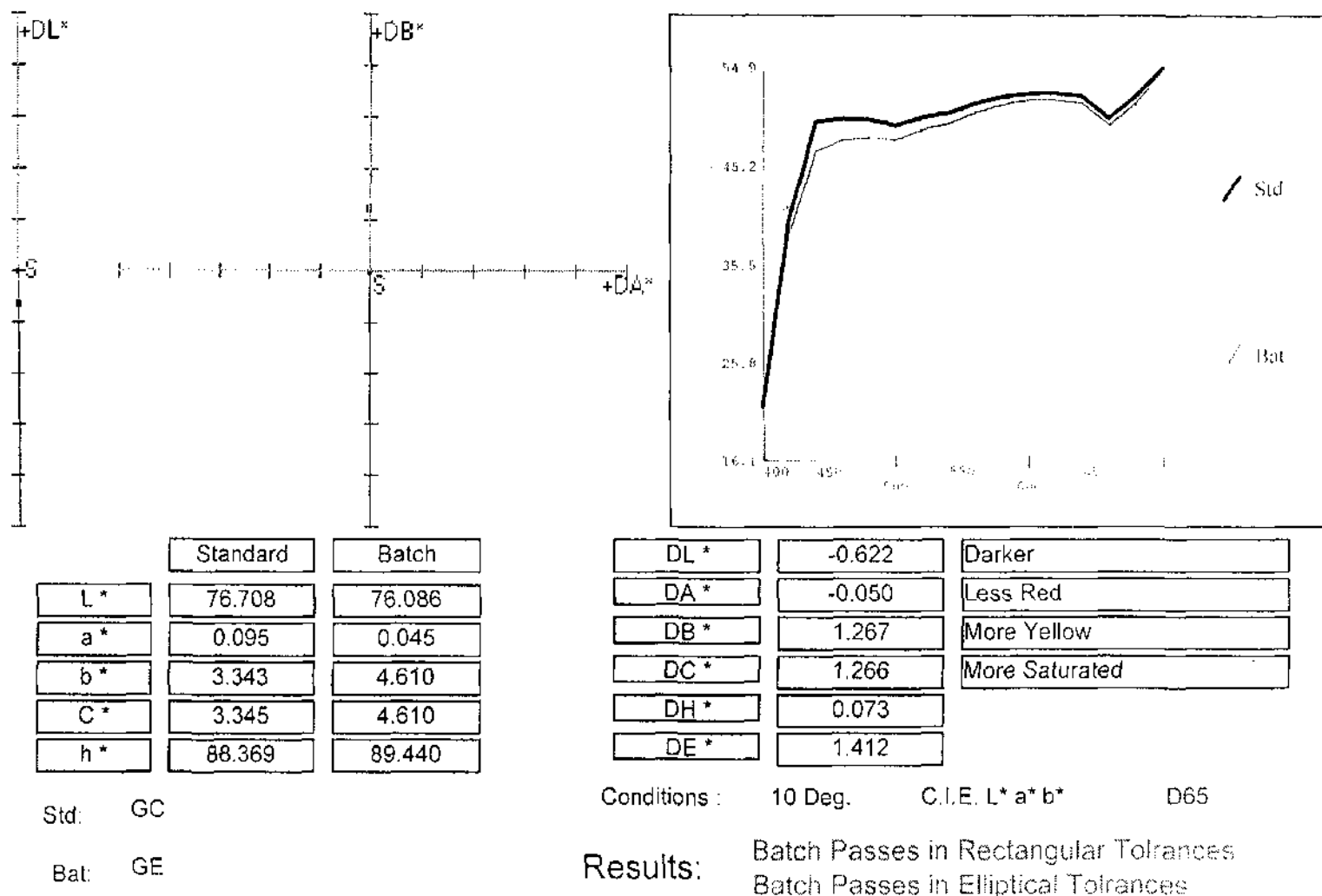
The table makes it clear that the L^* value of enzymatically treated sample was less than that of the control, which indicates that the enzymatically treated sample was darker in colour (Fig. 4.13). The higher a^* , b^* and C^* values of enzymatically treated samples show that the samples were more red, yellow in colour and more saturated than the control.

4.4.3.4 Effect of enzymatic pre-treatment on CIE LAB values of duranta dye mordanted with enzymatically untreated samples.

The low L^* value of enzymatically treated sample indicates that the sample was darker in colour than the enzymatically untreated sample (Fig 4.14). The higher a^* , b^* and C^* values of enzymatically treated samples indicate higher content of red, yellow colours and more saturated than enzymatically untreated sample.

4.4.3.5 Effect of enzymatic pre-treatment on CIE LAB values of duranta dye mordanted with pomegranate

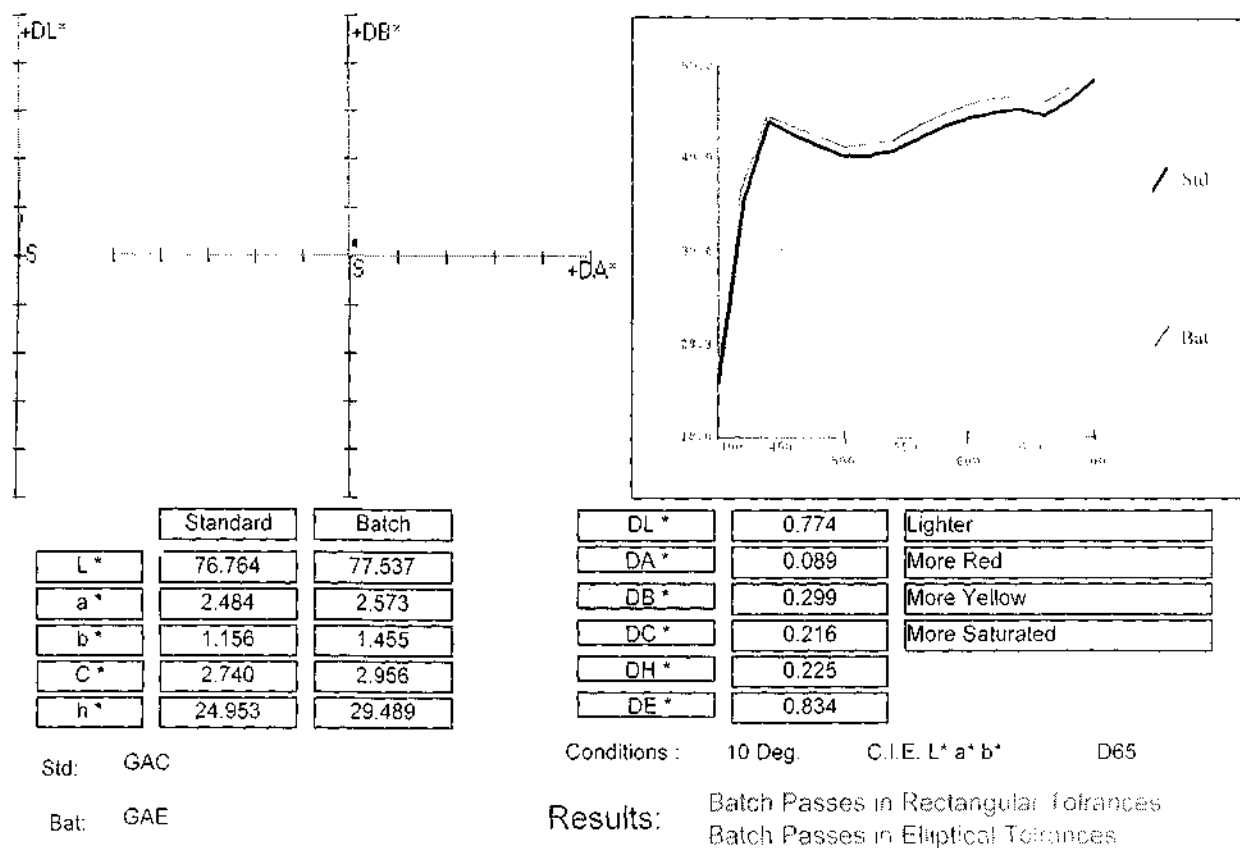
The table shows the lower L^* value of enzymatically treated sample, which indicates that the sample was darker in colour than the enzymatically untreated



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Fig. 4.11 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with duranta dye.

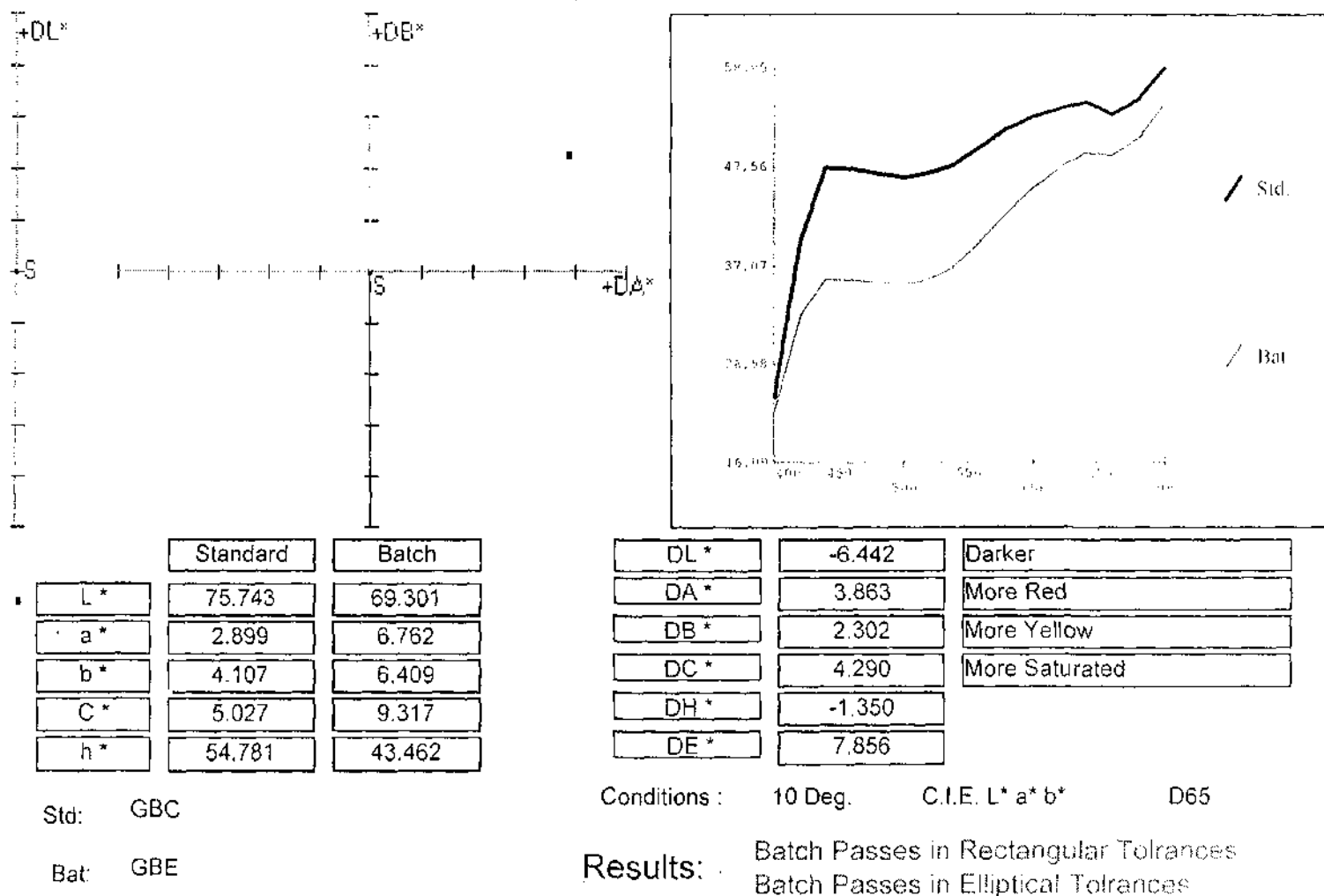
(GC= Samples dyed with duranta, unmordanted and enzymatically untreated control,
GE= Samples dyed with duranta, unmordanted and enzymatically treated)



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Fig. 4.12 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *arjun* and dyed with duranta dye

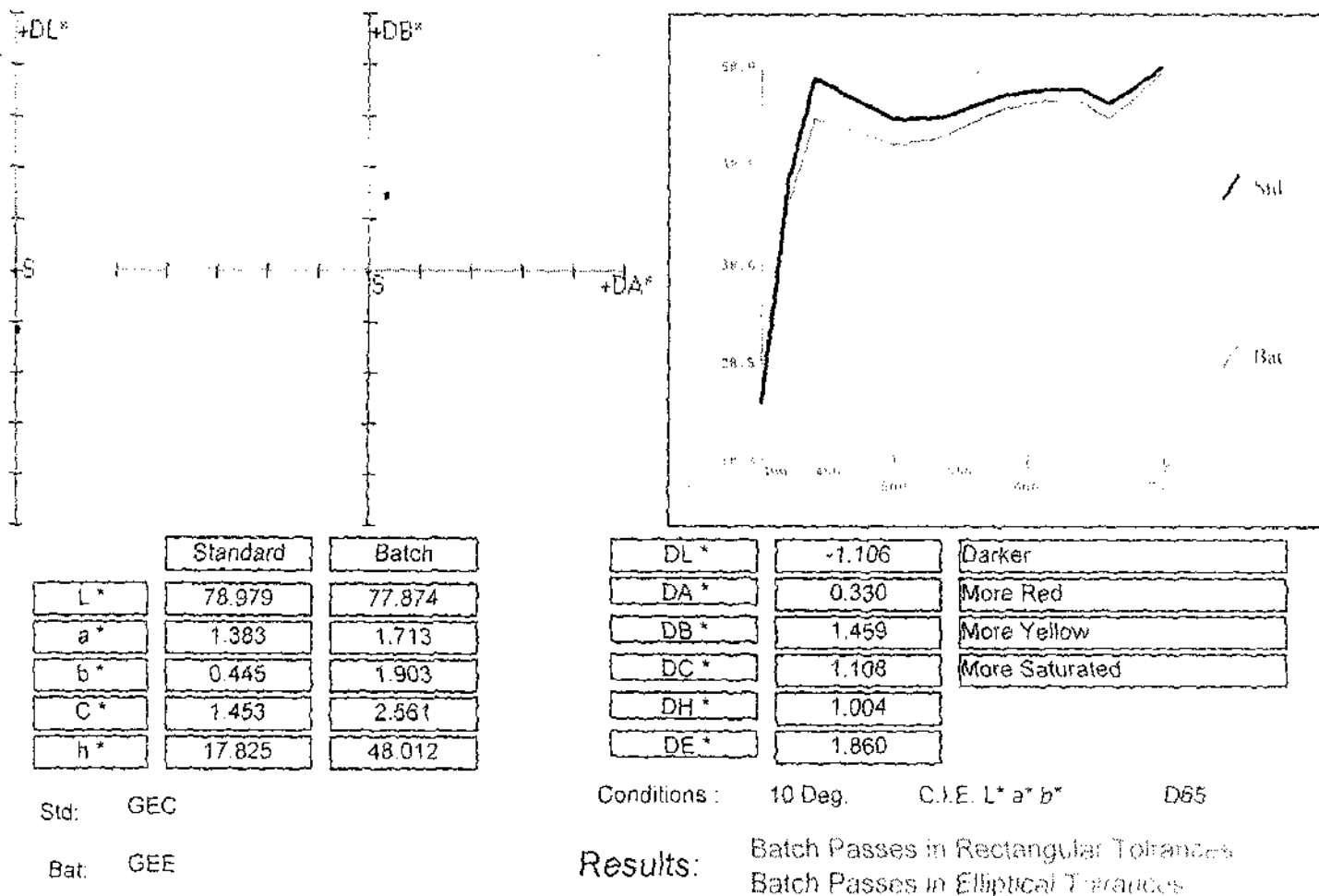
(GAC= Samples dyed with duranta, mordanted with *arjun* and enzymatically untreated control, GAE= Samples dyed with duranta, mordanted with *arjun* and enzymatically treated)



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Fig. 4.13 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *babool* and dyed with duranta dye

(GBC= Samples dyed with duranta, mordanted with *babool* and enzymatically untreated control, GBE= Samples dyed with duranta, mordanted with *babool* and enzymatically treated)



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Fig. 4.14 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with eucalyptus and dyed with duranta dye

(GEC= Samples dyed with duranta, mordanted with eucalyptus and enzymatically untreated control, GEE= Samples dyed with duranta, mordanted with eucalyptus and enzymatically treated)

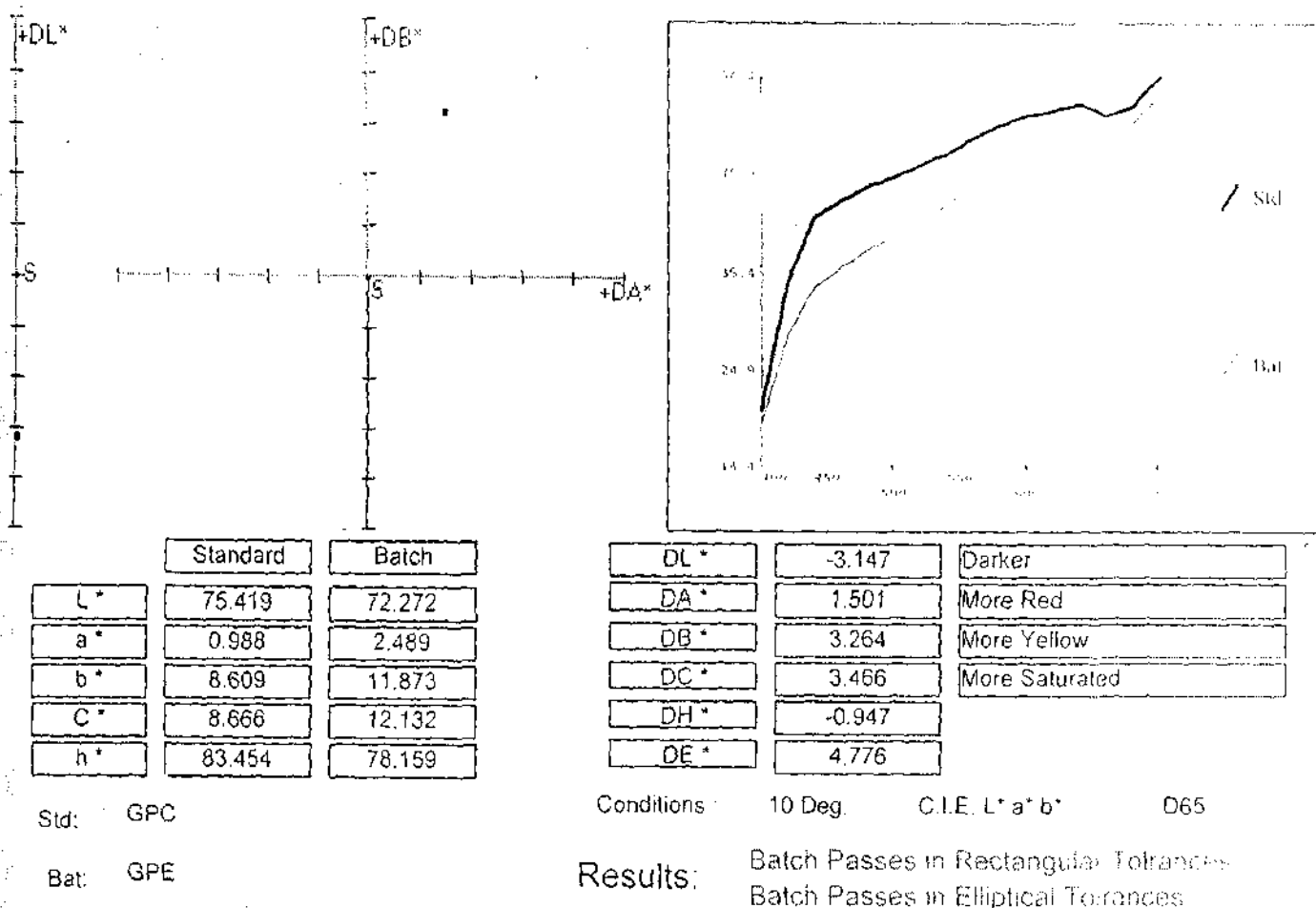


Fig. 4.15 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with pomegranate and dyed with duranta dye

(GPC= Samples dyed with duranta, mordanted with pomegranate and enzymatically untreated control, GPE= Samples dyed with duranta, mordanted with pomegranate and enzymatically treated)

sample (Fig 4.15). The higher a^* , b^* and C^* values of enzymatically treated samples indicate that the samples were more red, yellow and more saturated than the control.

4.4.4 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with mango dye

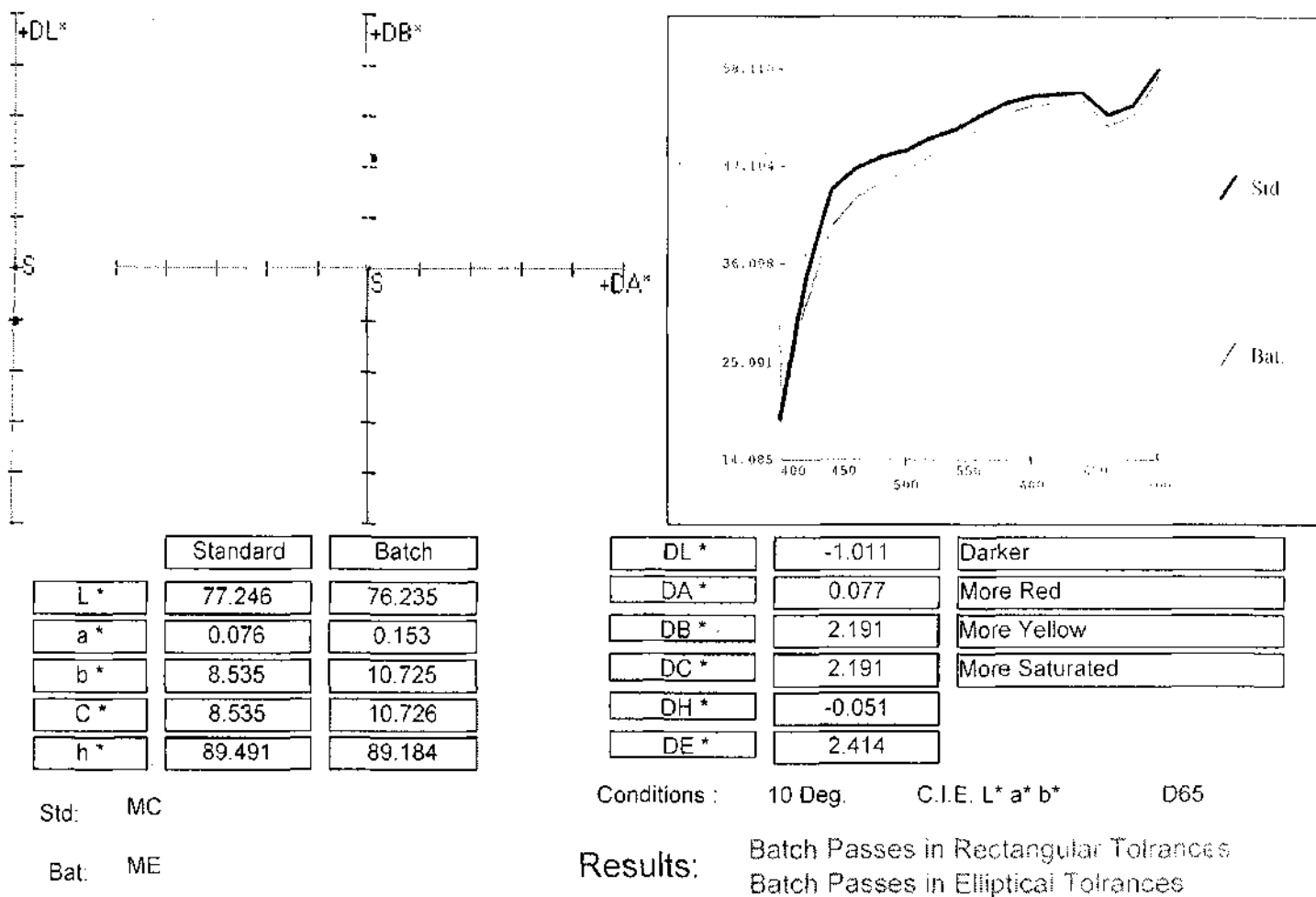
The CIE LAB values of both the treated and control samples with enzyme and dyed with mango dye using different mordants under optimum conditions have been presented in table 4.32.

Table 4.32 Effect of enzymatic pre-treatment on CIE LAB values of samples dyed with mango dye

Mordants	L^*		a^*		b^*		C^*	
	EUC	ET	EUC	ET	EUC	ET	EUC	ET
Control	77.246	76.235	0.076	0.153	8.535	10.725	8.535	10.726
Arjun	78.206	77.955	1.440	2.795	3.075	2.586	3.396	3.808
Babool	74.583	73.769	4.456	5.281	5.374	5.617	6.981	7.710
Eucalyptus	79.011	76.801	1.516	3.730	3.074	4.839	3.428	6.110
Pome-granate	77.406	76.505	0.686	0.876	8.345	9.793	8.373	9.832

4.4.4.1 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with mango dye

The L^* value of enzymatically treated sample was less than that of the control, which indicates that the enzymatically treated sample was darker in colour (Fig. 4.16). The higher a^* , b^* and C^* values of enzymatically treated samples indicate higher content of red, yellow colour and brighter than enzymatically untreated sample.



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Fig. 4.16 Effect of enzymatic pre-treatment on CIE LAB values of unmordanted samples dyed with mango dye

(MC= Samples dyed with mango, unmordanted and enzymatically untreated control, ME= Samples dyed with mango, unmordanted and enzymatically treated)

4.4.4.2 Effect of enzymatic pre-treatment on CIE LAB values of mango dye mordanted with *arjun*

The table reveals that the L^* value of enzymatically treated sample was low than enzymatically untreated sample, which indicates that the enzymatically treated sample is darker in colour than the control (Fig 4.17). The higher a^* value and lower b^* value of enzymatically treated samples indicate higher red content and lower yellow content respectively of the enzymatically treated sample. The higher C^* value of enzymatically treated sample shows that the enzymatically treated sample is more saturated than the control.

4.4.4.3 Effect of enzymatic pre-treatment on CIE LAB values of mango dye mordanted with *babool*

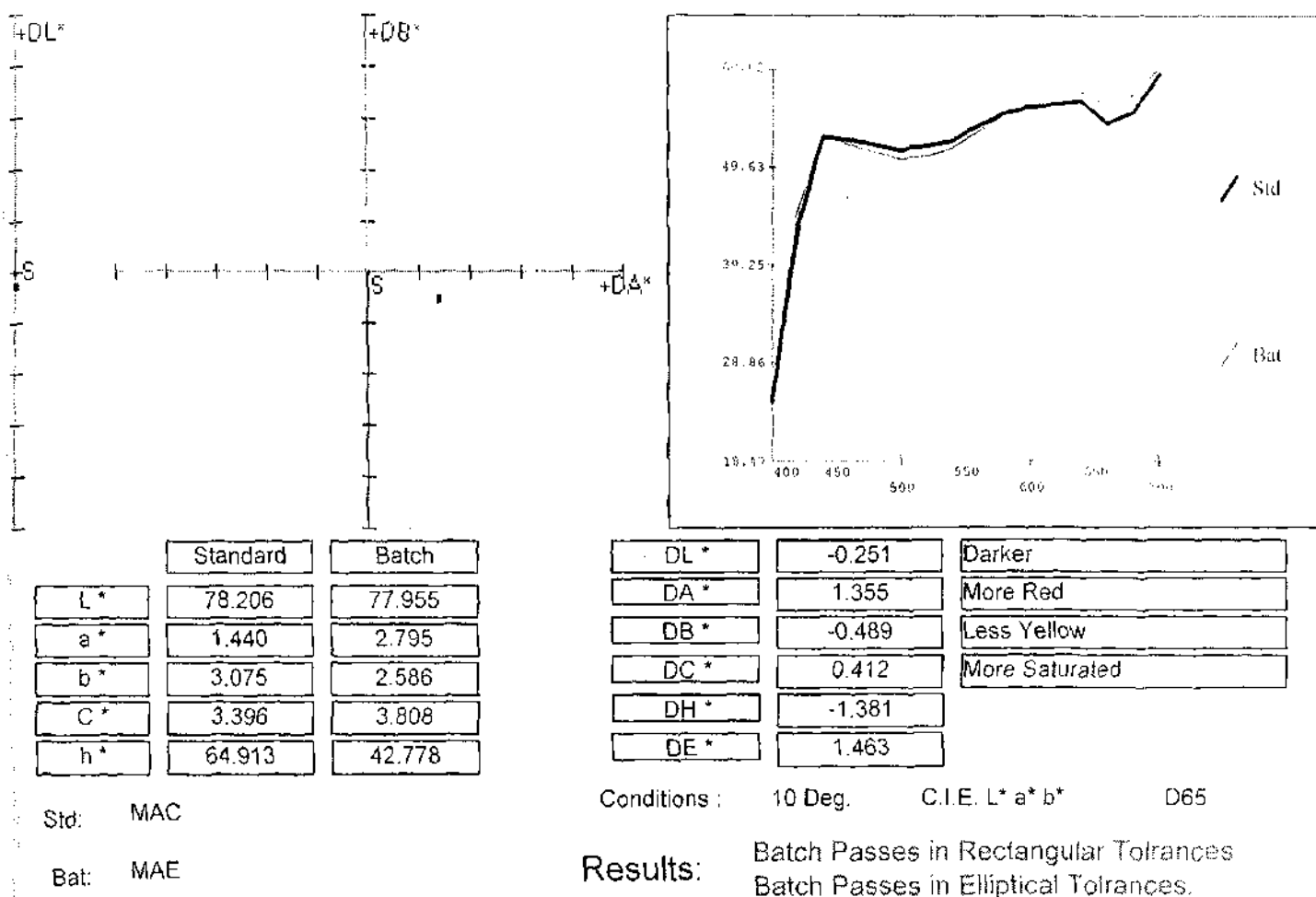
The lower L^* value of enzymatically treated sample indicates that the samples were darker than enzymatically untreated sample (Fig 4.18). The higher a^* , b^* and C^* value of enzymatically treated sample elicit the high content of red, yellow and more saturation than the control.

4.4.4.4 Effect of enzymatic pre-treatment on CIE LAB values of mango dye mordanted with *eucalyptus*

It is clear from the table that the L^* value of enzymatically treated sample was less than the control, eliciting that the enzymatically treated sample is darker in colour (Fig. 4.19). The higher a , b^* and C^* values of enzymatically treated samples indicate high content of red, yellow colour and more bright than the control.

4.4.4.5 Effect of enzymatic pre-treatment on CIE LAB values of mango dye mordanted with *pomegranate*

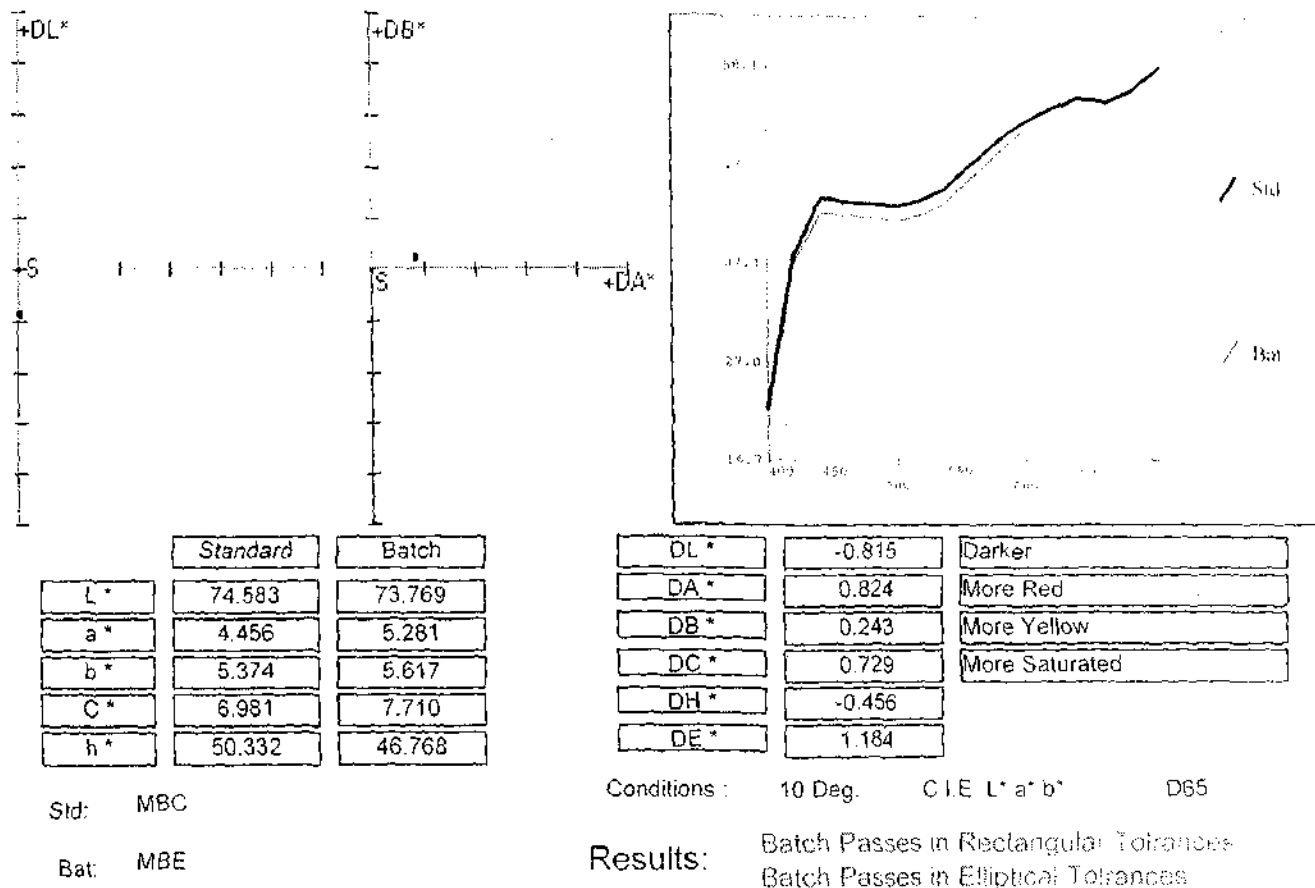
The L^* value of enzymatically treated sample was low than enzymatically untreated sample, which reveals that the enzymatically treated sample is darker in



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Fig. 4.17 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *arjun* and dyed with mango dye

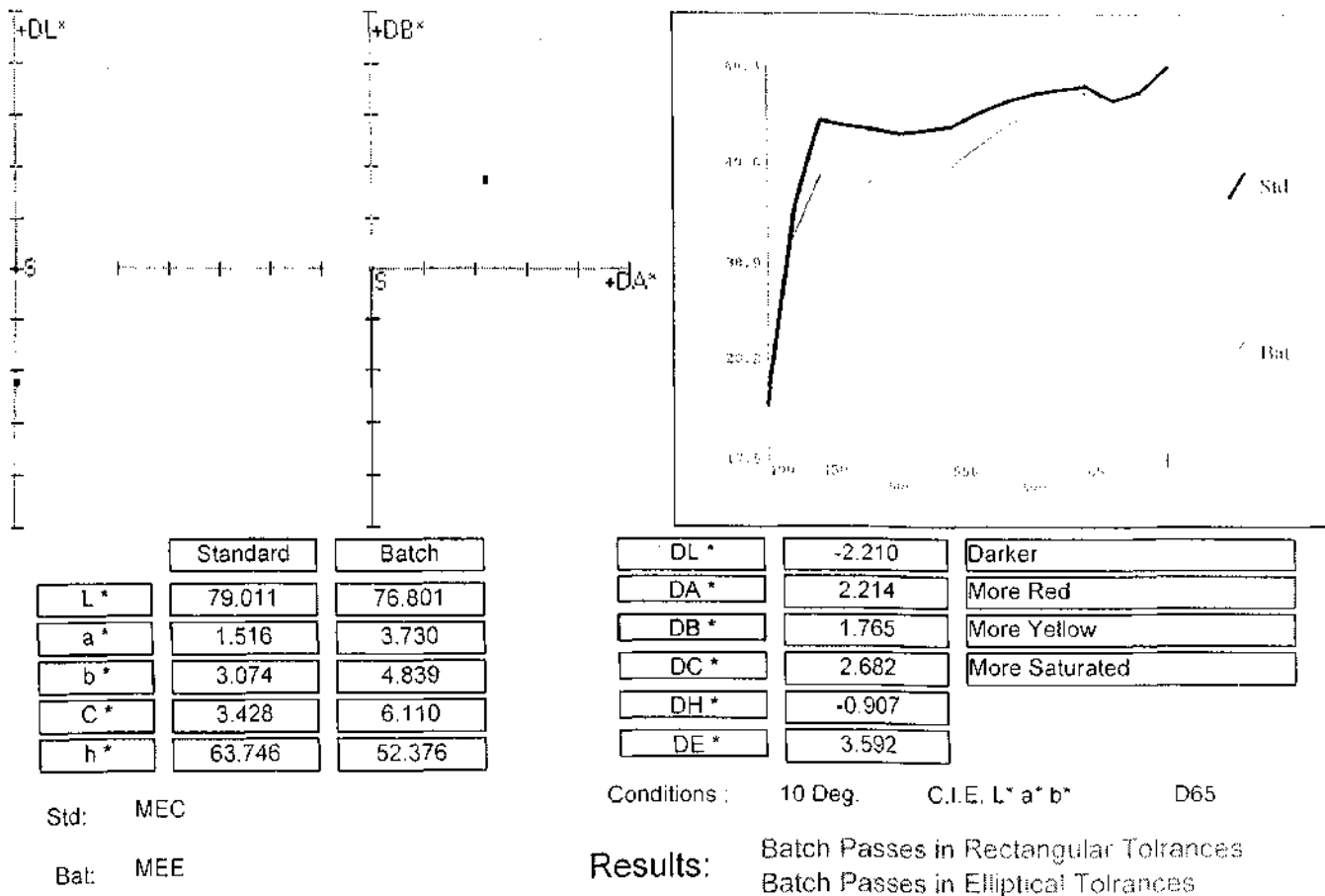
(MAC= Samples dyed with mango, mordanted with *arjun* and enzymatically untreated control, MAE= Samples dyed with mango, mordanted with *arjun* and enzymatically treated)



CHROMAFLASH

Fig. 4.18 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with *babool* and dyed with mango dye

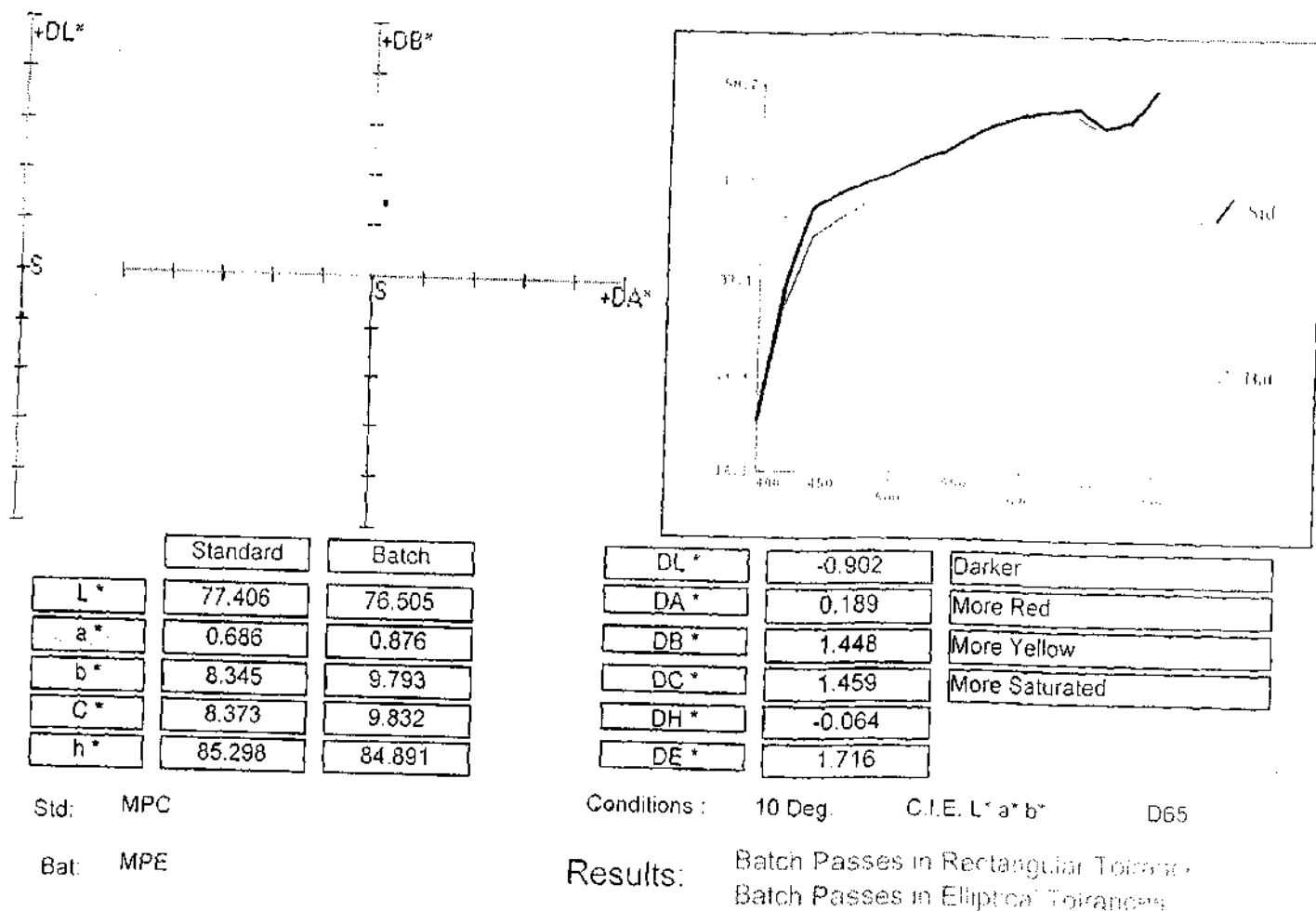
(MBC= Samples dyed with mango, mordanted with *babool* and enzymatically untreated control, MBE= Samples dyed with mango, mordanted with *babool* and enzymatically treated)



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Fig. 4.19 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with eucalyptus and dyed with mango dye

(MEC= Samples dyed with mango, mordanted with eucalyptus and enzymatically untreated control, MEE= Samples dyed with mango, mordanted with eucalyptus and enzymatically treated)



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Fig. 4.20 Effect of enzymatic pre-treatment on CIE LAB values of samples mordanted with pomegranate and dyed with mango dye

(MPC= Samples dyed with mango, mordanted with pomegranate and enzymatically untreated control, MPE= Samples dyed with mango, mordanted with pomegranate and enzymatically treated)

colour (Fig 4.20). The increased a^* , b^* and C^* values of enzymatically treated samples show that the samples were more red, more yellow and more saturated than the control.

4.5 FASTNESS PROPERTIES OF DYED SAMPLES

The colour fastness tests were conducted to study the effect of enzymatic pre-treatment on fastness properties of the dyed samples in both unmordanted and mordanted conditions. The results of the fastness properties have been discussed below:

4.5.1 Effect of enzymatic pre- treatment on colour fastness properties of samples dyed with *bansa* dye

The washing, light, rubbing and perspiration fastness grades of cotton samples dyed with *bansa* dye have been presented in table 4.33.

The washing fastness grade in terms of colour change was 3, for the control and unmordanted sample, which improved to 3/4 when the samples were enzymatically treated. In the case of samples mordanted with *arjun* and pomegranate mordants, the wash fastness increased from 4 (for control) to 4/5 due to the enzymatic treatment. The wash fastness grade for colour change for the control samples, mordanted with *babool* and eucalyptus was 4 but improved to 5 when the samples were enzymatically treated. None of the samples showed staining on wool and cotton fabric samples (Fig 4.21).

The light fastness grade for the control and the treated samples, both unmordanted and mordanted with *babool* mordant remained same, i.e. 3. The light fastness grade for the control was 2 and improved to 2/3 in the case of

Fig. 4.21: Effect of enzymatic pre- treatment on washing fastness grades (colour change) of samples dyed with bansa dye

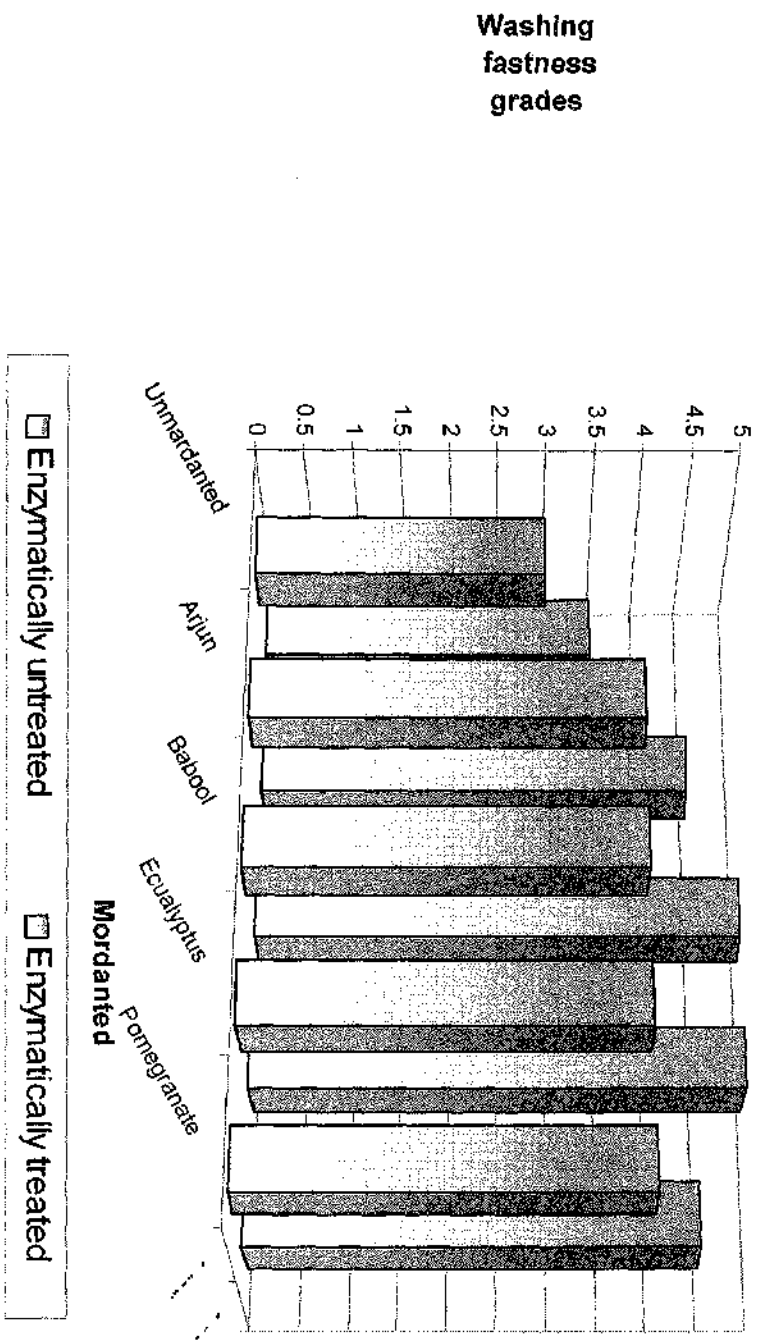


Fig. 4.22: Effect of enzymatic pre- treatment on light fastness grades of samples dyed with bansa dye

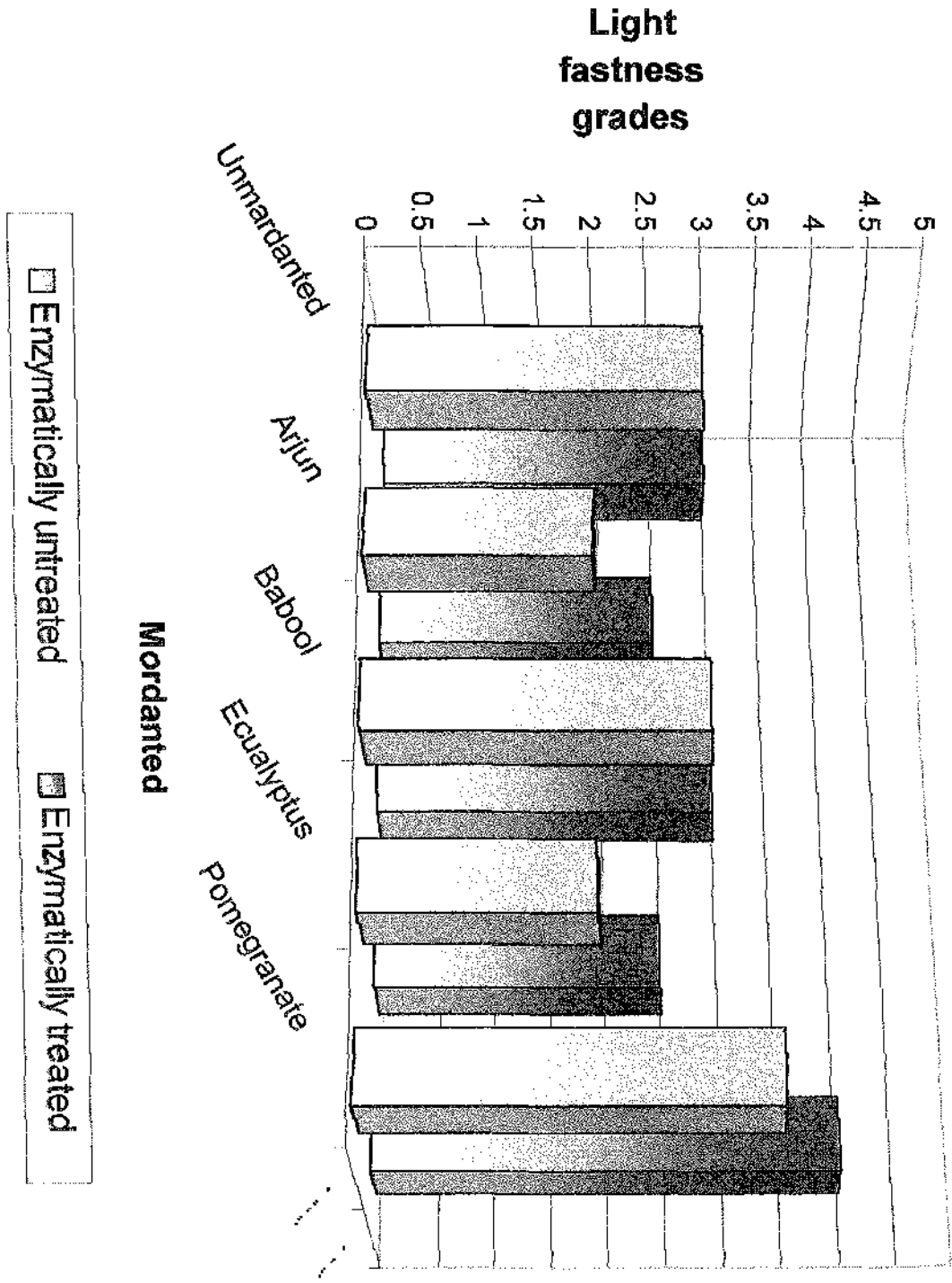


Table 4.33 Effect of enzymatic pre-treatment on colour fastness grades of *bansa* dye.

Mordant	Washing fastness			light fastness			Rubbing fastness						Perspiration fastness					
	CC	Grade		CC	grade		grade						grade					
		W	CS		CC	Dry		Wet		CC	CS	W	CS	CC	W	CS		
						C	C	CC	CS								CC	C
Control	3	5	5	3	5	5	5	5	5	5	5	4/5	5	5	4/5	5	5	
EUC	3/4	5	5	3	5	5	5	5	5	5	5	5	5	5	5	5	5	
ET																		
Arjun	4	5	5	2	5	5	5	5	5	5	5	4/5	5	5	5	5	5	
EUC	4/5	5	5	2/3	5	5	5	5	5	5	5	5	5	5	5	5	5	
ET																		
Babool	4	5	5	3	5	5	5	5	5	5	5	4	5	5	5	5	5	
EUC	5	5	5	3	5	5	5	5	5	5	5	5	5	5	5	5	5	
ET																		
Eucalyptus	4	5	5	2	5	5	5	5	5	5	5	4/5	5	5	5	5	5	
EUC	5	5	5	2/3	5	5	5	5	5	5	5	5	5	5	5	5	5	
ET																		
Pomegranate	4	5	5	3/4	5	5	5	5	5	5	5	4	5	5	5	5	5	
EUC	4/5	5	5	4	5	5	5	5	5	5	5	5	5	5	5	5	5	
ET																		

W = Wool. C= Cotton, CC = Colour change, CS = Colour staining, EUC = Enzymatically untreated control, ET = Enzymatically treated

enzymatically treated samples, mordanted with *arjun* and eucalyptus mordants. With the enzymatic treatment, the light fastness grades increased from 3/4 to 4 when these were mordanted with pomegranate (Fig 4.22).

The rubbing fastness grade was 5 for colour change in both dry and wet conditions for all the samples (Table 4.33). The colour staining also remained the same, i.e. 5 in both dry and wet conditions, except for the control samples as well as the samples that had been mordanted with pomegranate mordant, where the staining was 4.

The perspiration fastness grade was 4/5 for colour change in acidic medium for the unmordanted control and the control mordanted with *arjun*, eucalyptus and pomegranate. In the case of control it was 4 when mordanted with *babool* mordant. However, the perspiration fastness grade improved to 5 for both, the unmordanted and mordanted samples that had been enzymatically treated (Table 4.33). For the colour change in alkaline medium, the perspiration fastness grade was 4/5, for the unmordanted control samples, which improved to 5 when treated with enzyme. Similarly, in the case of all the samples, control as well as enzymatically treated both unmordanted and mordanted the perspiration fastness grade 5 was observed. No colour staining took place in any of the samples in either acidic or alkaline media.

4.5.2 Effect of enzymatic treatment on colour fastness properties of samples dyed with bottle brush dye

The washing, light, rubbing and perspiration fastness grades of cotton samples dyed with bottle brush dye have been presented in table 4.34.

The washing fastness grade for colour change for the control and enzymatically treated both unmordanted remained same, i.e. 4/5. In the case of both control and enzymatically treated mordanted with *arjun* and eucalyptus mordants also remained 5. However, the wash fastness increased for samples mordanted with *babool* and pomegranate mordants increased from 4/5 (for control) to 5 when samples were enzymatically treated. None of the samples showed staining on wool and cotton fabric samples (Fig 4.23).

The light fastness grade was 2/3 for the control and the unmordanted samples, which improved to 3 when samples were enzymatically treated (Fig 4.24). In the case of samples mordanted with *arjun*, *babool* and eucalyptus mordants the light fastness grade was 3, which increased to 3/4 when the samples were enzymatically treated. However, the light fastness grade for the control and enzymatically treated samples mordanted with pomegranate remained same, i.e. 4.

The rubbing fastness grade was 5 for colour change and colour staining in both dry and wet conditions for all the samples (Table 4.34).

The perspiration fastness grade for colour change in both the acidic and alkaline media for all the samples remained same, i.e. 5, except for the control sample mordanted with pomegranate where the perspiration fastness grade was 4/5. No colour staining took place in any of the samples in either acidic or alkaline media.

Fig. 4.23: Effect of enzymatic pre- treatment on washing fastness grades (colour change) of samples dyed with bottle brush dye

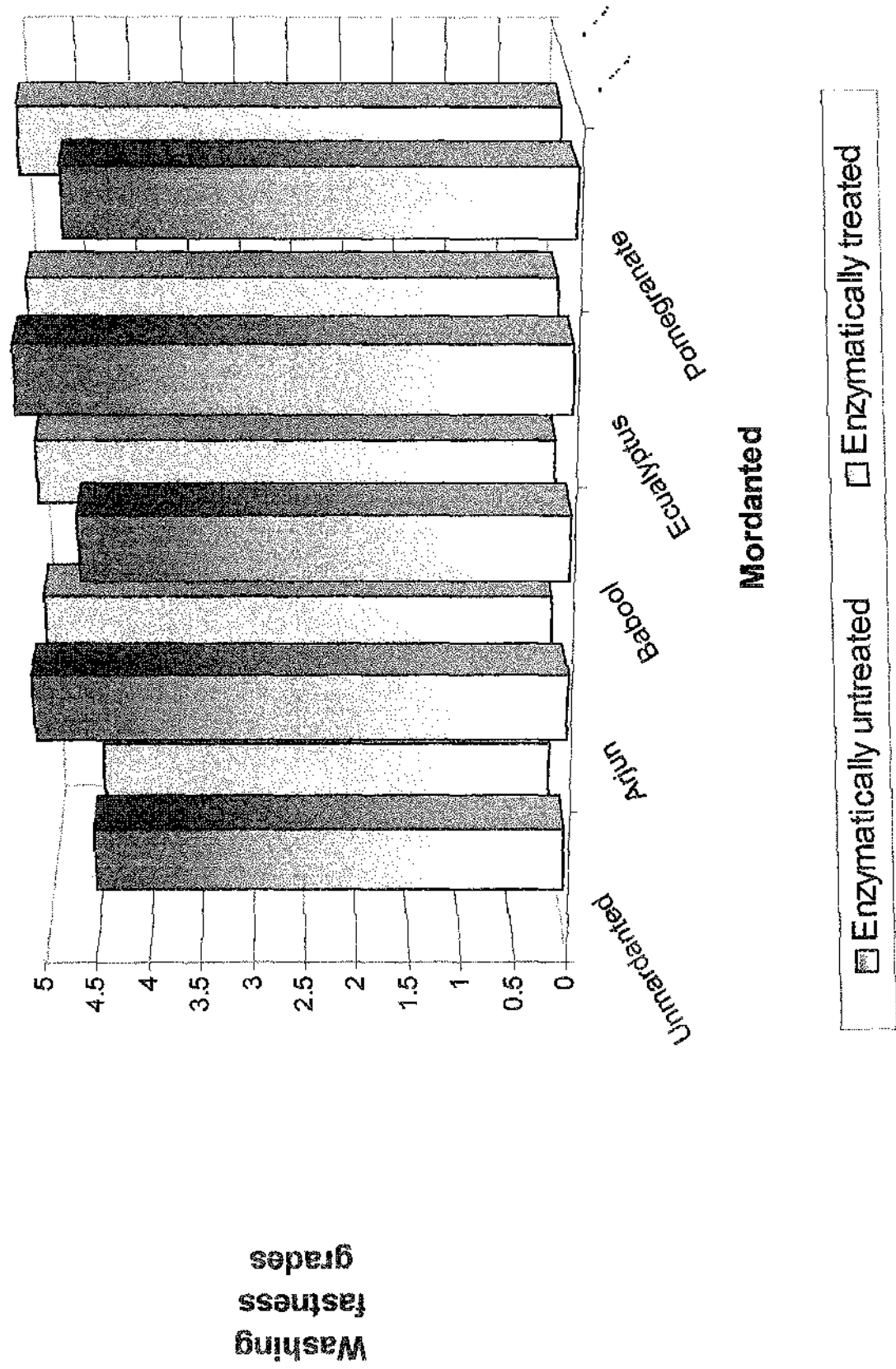
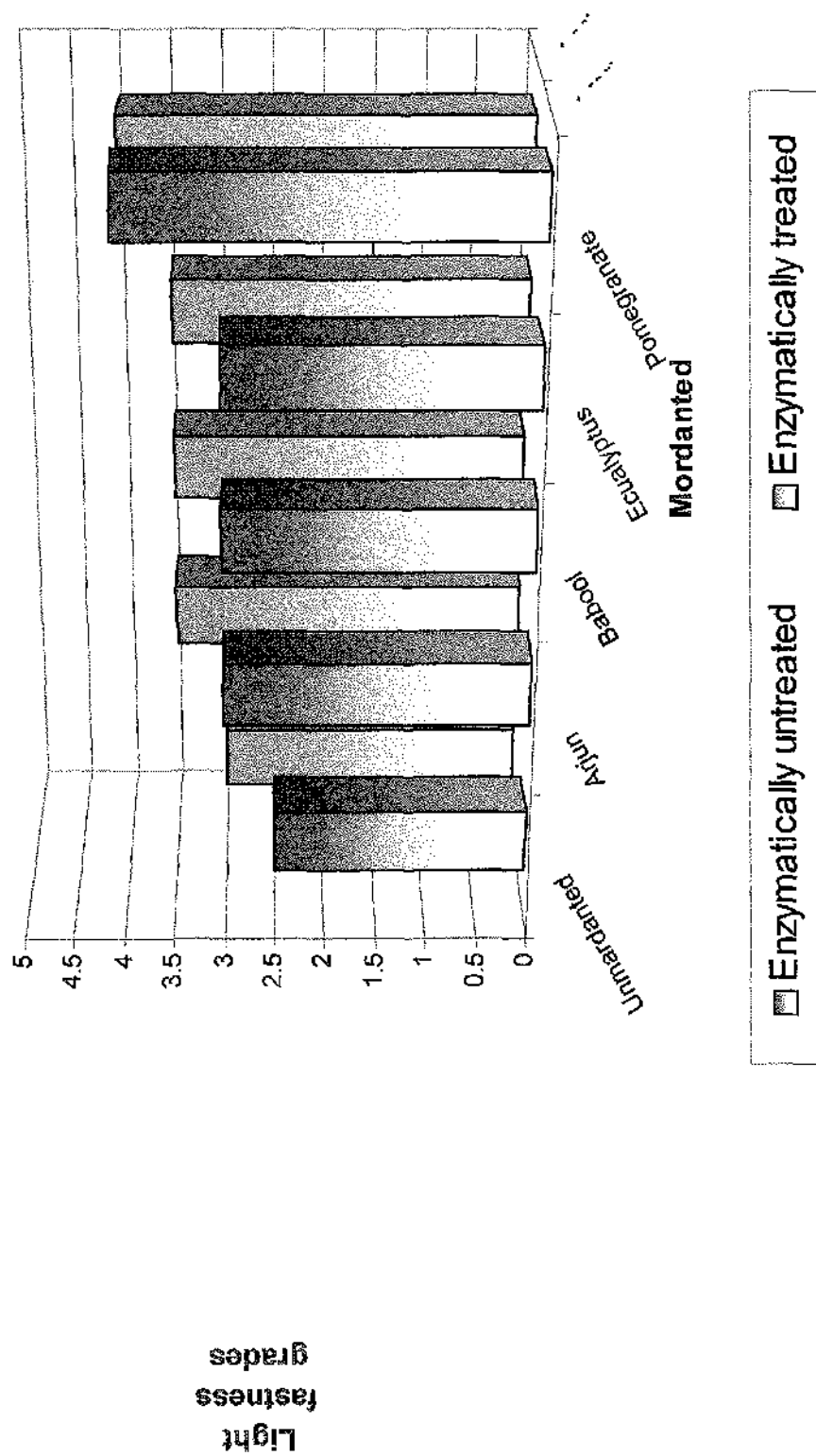


Fig. 4.24: Effect of enzymatic pre- treatment on light fastness grades of samples dyed with bottle brush dye



4.5.3 Effect of enzymatic treatment on colour fastness properties of samples dyed with duranta dye

The washing, light, rubbing and perspiration fastness grades of cotton samples dyed with duranta dye have been presented in table 4.35.

The colour change for washing fastness was 3, for the control and unmordanted sample, but rose to 3/4 when samples were enzymatically treated. The pre-treatment did not have any effect as the wash fastness grade remained unchanged for control and the enzymatically treated samples, mordanted with *arjun* mordant. For the control samples mordanted with *babool* and eucalyptus the fastness grade was 4. This improved to 5 with the enzymatic treatment and *babool* mordant and to 4/5 when mordanted with eucalyptus. The washing fastness grade for colour change for the control mordanted with pomegranate was 4/5, but improved to 5 when the samples were enzymatically treated. None of the samples showed staining on wool and cotton fabric samples (Fig. 4.25).

The light fastness grade for the control was 2 and improved to 2/3 when the samples were enzymatically treated. In the case of control and enzymatically treated samples, the mordanted with *arjun* and eucalyptus mordants, the light fastness grades remained the same, i.e. 3/4. The light fastness grade for the control was 2/3 and rose to 3 when the samples were enzymatically treated. Similarly, the grades of the control samples mordanted with pomegranate increased from 3/4 to 4 when the samples were enzymatically treated (Fig. 4.26).

The rubbing fastness grade was 5 for colour change and colour staining in both dry and wet conditions for all the samples (Table 4.35).

Fig. 4.25: Effect of enzymatic pre - treatment on washing fastness grades (colour change) of samples dyed with duranta dye

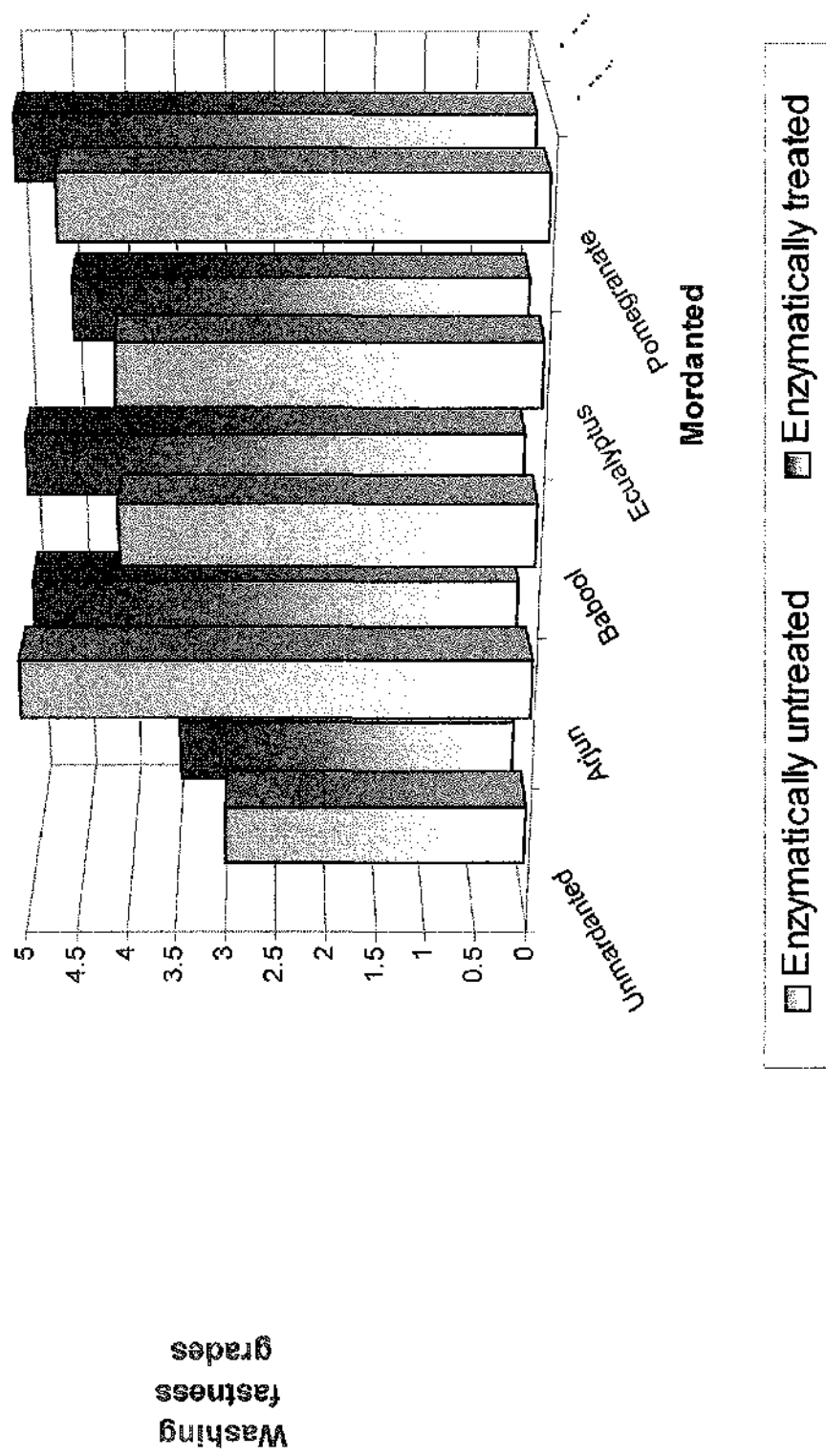


Fig. 4.26: Effect of enzymatic pre-treatment on light fastness grades of samples dyed with duranta dye

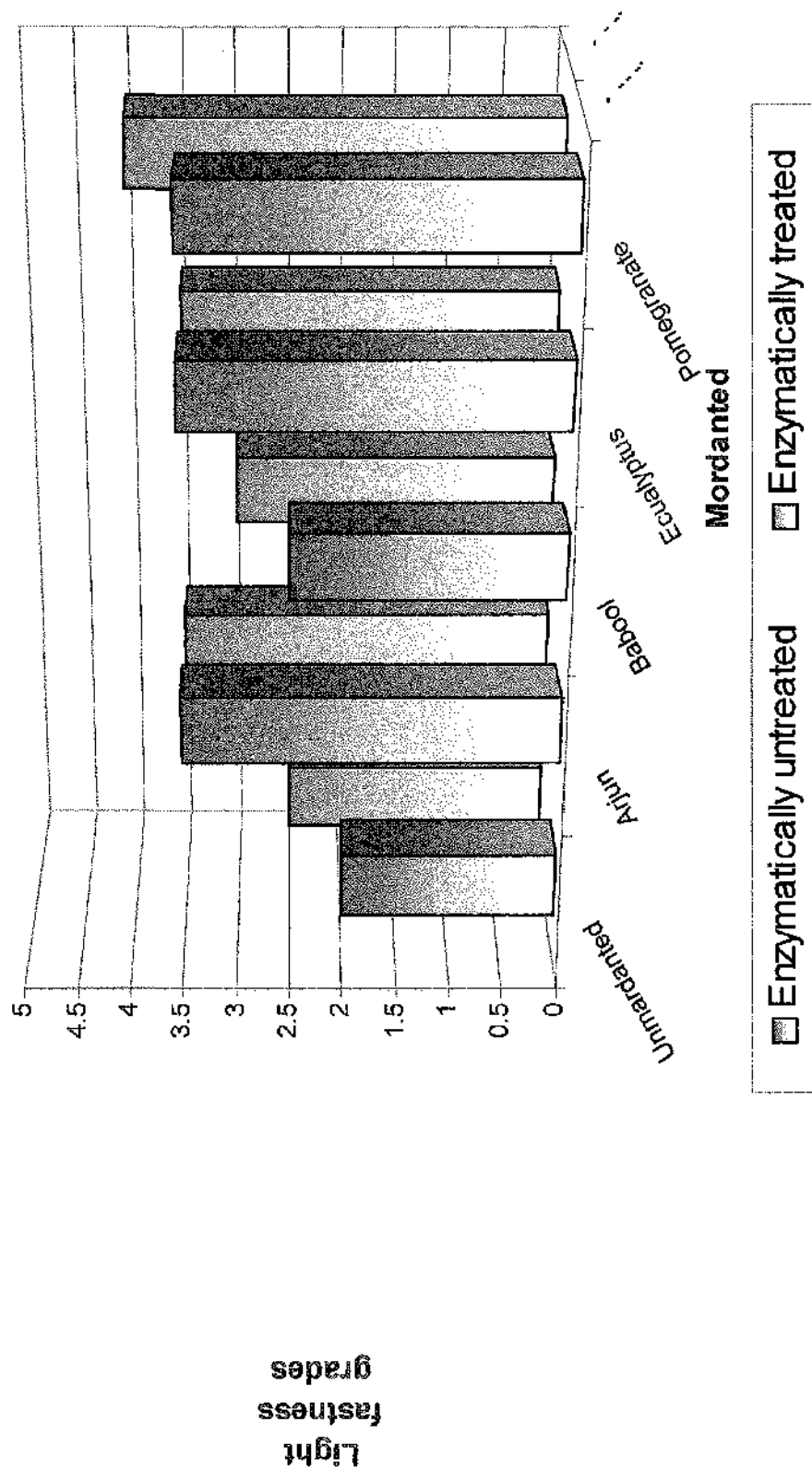


Table 4.35 Effect of enzymatic pre-treatment on colour fastness grades of duranta dye.

Mordant	Washing fastness			light fastness			Rubbing fastness				Perspiration fastness						
	CC	Grade		C	5	2	Dry		Wet		Acidic		Alkaline				
		W	CS				CC	CS	CC	CS	CC	W	CS				
														C	C	W	C
Control	3	5	5	5	5	2	5	5	5	5	4	5	5	4/5	5	5	5
	3/4	5	5	5	5	2/3	5	5	5	5	4/5	5	5	4/5	5	5	5
Arjun	5	5	5	5	5	3/4	5	5	5	5	4/5	5	5	5	5	5	5
	5	5	5	5	5	3/4	5	5	5	5	5	5	5	5	5	5	5
Babool	4	5	5	5	5	2/3	5	5	5	5	4	5	5	5	5	5	5
	5	5	5	5	5	3	5	5	5	5	5	5	5	5	5	5	5
Eucalyptus	4	5	5	5	5	3/4	5	5	5	5	4/5	5	5	4/5	5	5	5
	4/5	5	5	5	5	3/4	5	5	5	5	5	5	5	5	5	5	5
Pomegranate	4/5	5	5	5	5	3/4	5	5	5	5	4/5	5	5	5	5	5	5
	5	5	5	5	5	4	5	5	5	5	5	5	5	5	5	5	5

The perspiration fastness grade was 4 for colour change in acidic medium for the unmordanted control and the control mordanted with *babool*. It improved to 4/5 when unmordanted samples were enzymatically treated and 5 when the enzymatically treated samples were mordanted with *babool* mordant (Table 4.35). The perspiration fastness grade was 4/5 for colour change in acidic medium for the control samples mordanted with *arjun*, eucalyptus and pomegranate, which increased to 5 when the mordanted samples were enzymatically treated. For the colour change in alkaline medium the perspiration fastness grade for the control and the enzymatically treated, both unmordanted remained same, i.e. 4/5. Similarly the perspiration fastness grade 5 was observed in the case of all the samples, control as well as enzymatically treated and mordanted with *arjun*, *babool* and pomegranate mordants. However, the enzymatic treatment lead to an improvement in perspiration fastness grades from 4/5 to 5 when the control samples mordanted with eucalyptus were enzymatically treated. No colour staining took place in any of the samples in either acidic or alkaline media.

4.5.4 Effect of enzymatic treatment on colour fastness properties of samples dyed with mango dye

The washing, light, rubbing and perspiration fastness grades of cotton samples dyed with mango dye have been presented in table 4.36.

The washing fastness grade in terms of colour change was 3, for the control and unmordanted sample, which improved to 4 when the samples were enzymatically treated. The wash fastness grads for the control samples mordanted with *arjun* and pomegranate mordants was 4 and was 4/5 when

Fig. 4.27: Effect of enzymatic pre- treatment on washing fastness grades (colour change) of samples dyed with mango dye

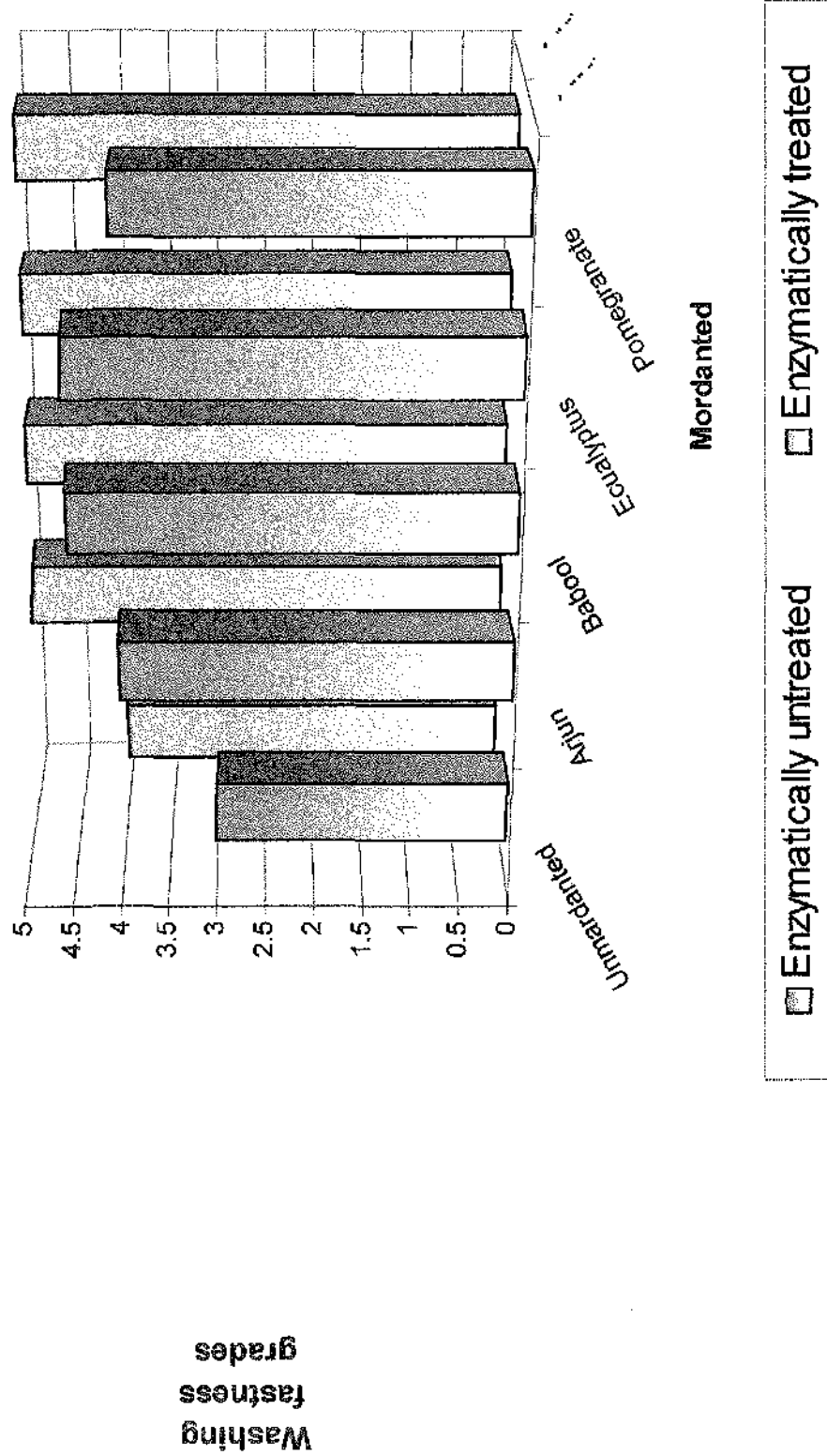


Fig. 4.28: Effect of enzymatic pre- treatment on light fastness grades of samples dyed with mango dye

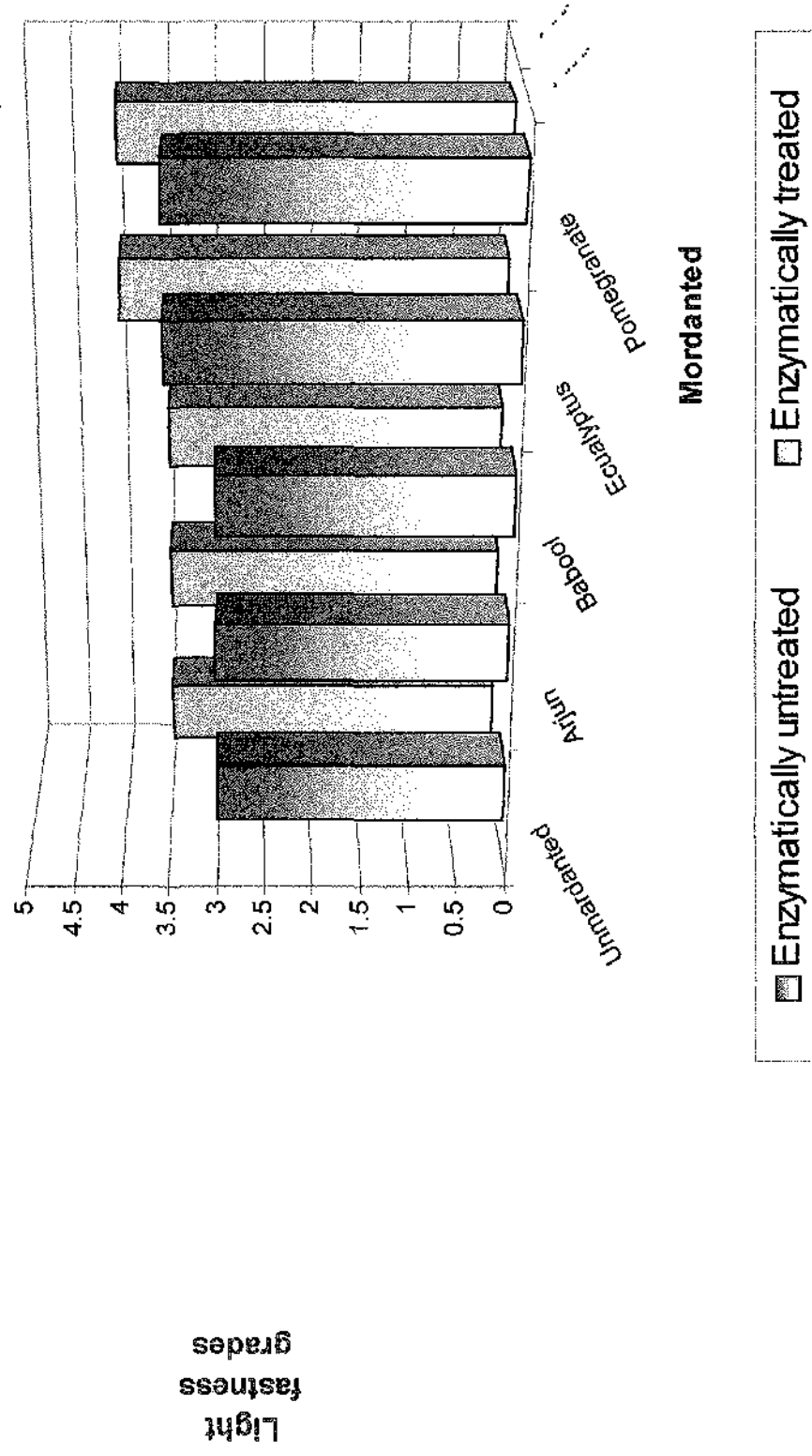


Table 4.36 Effect of enzymatic pre-treatment on colour fastness grades of mango dye.

Mordant	Washing fastness			light fastness			Rubbing fastness						Perspiration fastness					
	CC	Grade		C	grade		Dry		Wet		CC	CS	Acidic		Alkaline		CC	CS
		W	CS		W	C	CC	CS	CC	CS			W	C	W	C		
Control																		
EUC	3	5		5	3		5	5	4		5	5	5		5		4/5	5
ET	4	5		5	3/4		5	5	5		5	5	5		5		5	5
Arjun																		
EUC	4	5		5	3		5	5	5		5	5	5		5		5	5
ET	5	5		5	3/4		5	5	5		5	5	5		5		5	5
Babool																		
EUC	4/5	5		5	3		5	5	5		5	5	5		5		5	5
ET	5	5		5	3/4		5	5	5		5	5	5		5		5	5
Eucalyptus																		
EUC	4/4	5		5	3/4		5	5	5		5	5	5		5		5	5
ET	5	5		5	4		5	5	5		5	5	5		5		5	5
Pomegranate																		
EUC	4	5		5	3/4		5	5	5		5	5	5		5		5	5
ET	5	5		5	4		5	5	5		5	5	5		5		5	5

mordanted with *babool* and eucalyptus mordants. The enzymatic pre-treatment resulted in an increase in the wash fastness grades of all the samples. No colour staining took place in any of the wool or cotton samples (Fig. 4.27).

The light fastness grade for the control unmordanted, mordanted with *arjun babool* was 3, which improved to 3/4 when the samples were enzymatically treated. In the case of samples mordanted with eucalyptus and pomegranate mordants, the light fastness grade was 3/4, which rose to 4 when the sample were enzymatically treated (Fig. 4.28).

The rubbing fastness grade was 5 for colour change and colour change in both dry and wet conditions for all the samples (Table 4.36).

The perspiration fastness grade for colour change for unmordanted control samples in acidic medium and alkaline medium was 4 and 4/5 respectively. However, the perspiration fastness grades for colour change in both acidic and alkaline media improved to 5 for enzymatically treated samples (Table 4.36). The perspiration fastness grades for colour change in both acidic and alkaline media for the control and treated samples, mordanted with all the mordants remained unchanged. No colour staining took place in any of the samples in either acidic or alkaline media.

Therefore, it was evident from the results of the study that the enzymatic pre-treatment of cotton with cellulase enzyme results in an improvement in fastness when the fabric was dyed with natural dyes and mordanted. However, the extent of improvement was determined by the type of dye and the type of mordant used. Though no work has been done on cotton but the findings of Raval and Banerjee (2003) on enzymatically treated silk dyed with natural dyes support the present investigation.

SUMMARY AND CONCLUSION

Today the protection of environment has become a challenge for the chemical industry world wide and the water pollution caused by synthetic dyes, continues to be a problem. All over the world, environment regulations are becoming stricter and forcing a shift towards less polluting or non-polluting areas of technological development. Although attention has mostly been paid to modifying synthetic dyeing processes, the need to realize the importance and explore the technology of natural dyes is more urgent and sustaining. Any effort to reassess and promote the use of natural dyes deserves encouragement.

The use of natural dyes alone does not help the environment much because some of the mordants considered as an integral part of the natural dyes, are deadly poisonous by themselves. Keeping in view the environmental conditions, the anionic and cationic sites can also be created on cotton fibres by tannins, also called the 'natural mordants'. These enable to form effective cross links between proteins, cellulose and other macromolecules.

It is important to impart pre-treatment to cotton to attain whiteness, uniform good absorbency, without chemically damaging cotton. Traditionally, alkaline scouring using caustic soda at high temperature had been used for removal of impurities all over the world. This process consumes up to 8 per cent caustic soda, which after neutralization, exists as a salt load in the waste water

and also forms 75 percent of the total organic load (Achwal 1993). Efforts are being made in recent years to develop a mild and environment – friendly process. Thus, enzymatic pre-treatment has assumed more importance due to present concern of clean and eco-friendly environment (Alat 2001).

Enzymes have now become an integral part of the textile processing. This is because the enzymes are biodegradable, work under mild conditions, used in small quantities and save the precious energy (Raje 2001). These do not produce toxic effluents as these can be easily deactivated and disposed off. The use of enzymes in textile processing has revolutionized the textile industry and are being successfully used.

Thus, the present study was planned keeping in view the emerging trend of bio-processing and dyeing with natural dyes.

5.1 OBJECTIVES

1. To optimize the conditions for enzymatic pre-treatment of cotton.
2. To optimize the dyeing conditions of enzymatically pre-treated and untreated cotton with four natural dyes obtained from leaves using natural mordants.
3. To evaluate the colour fastness of the dyed samples.
4. To study the effect of enzymatic pre-treatment on dyeing and fastness properties of cotton.

5.2 MATERIALS AND METHODS

The present study was conducted to optimize the enzymatic conditions and dyeing conditions for cotton with four selected natural dyes using four natural mordants. The effect of enzymatic pre-treatment was studied by comparing the

control with the enzymatically treated samples, both of which were dyed, under unmordanted as well as mordanted conditions. The colour fastness properties of both the sets of samples were studied.

Commercial cellulase enzyme 'Neutrox BDN 100 Powder' was selected for enzymatic pre-treatment of cotton, using a phosphate buffer solution. Four natural dyes namely bansa (*Uricalum indacom*), bottle brush (*Callistemon lanceoiatus*), duranta (*Duranta vr. Goldeana*) and mango (*Mangifera indica*) were selected. The natural mordants used included *arjun* (*Terminalia arjuna*), *babool* (*Acacia nilotica*), eucalyptus (*Eucalyptus sp.*) bark and pomegranate rind (*Punica granatum*).

Using phosphate buffer solution, trials were conducted to determine optimum values of three variables for enzyme treatment, namely pH media, enzyme concentration and treatment time. Conditions for dyeing cotton with four dyes, using each of the four mordants were optimized. The dyeing parameters optimized were - dye extraction pH, dye extraction time, dye concentration, dyeing pH, dyeing time, mordant extraction pH and mordant extraction time. Mordanting method and mordant concentration were selected on the basis of visual inspection by Spectravide.

The colour fastness properties - wash, light, rubbing and perspiration fastness of both the control and the enzymatically treated and dyed samples were evaluated and compared, by employing tests prescribed by BIS, India. Effect of enzymes on hue, value and intensity of the colour of the dye and mordants were investigated by studying CIE LAB values.

5.3 MAJOR FINDINGS

5.3.1 Optimum enzymatic conditions

The percentage weight loss, percentage strength loss, percentage thickness loss and the overall flexural rigidity were not adversely affected over the pH range of 6.5-7.5. However, the percentage moisture absorption was maximum at pH 7. Therefore, 7 was considered to be the optimum pH.

The optimum enzyme concentration was 5 percent (o.w.f) as the percentage weight loss, strength loss and thickness loss was maximum but not significant at this concentration. The percentage moisture absorption was also maximum at 5 percent concentration. The overall flexural rigidity was not much affected by variation in enzyme concentration.

The optimum time for pre-treatment was 75 minutes, as percentage weight loss, strength loss and thickness loss was maximum at 75 minutes. The percentage moisture absorption was the maximum at 75 minutes, indicating a considerable improvement in surface wetting properties. The overall flexural rigidity was not much affected by variation in treatment time.

5.3.2 Optimum dyeing conditions

The best extraction pH for all the dyes was achieved in the media of pH 10, as the extracted dye was dark at alkaline pH. The optimum extraction time for all the dyes ranged between 60 - 75 minutes.

The optimum dyeing pH for all the dyes was 9 or 10 and the optimum dye concentration was 3 or 4. The optimum dyeing time for all the dyes ranged

between 60 - 75 minutes. The optimum dyeing conditions for all the dyes have been give in table 5.1

Table 5.1 Optimum dyeing conditions for dyeing cotton with *bansa*, bottle brush, duranta and mango dyes

Variables	Optimum values			
	<i>Bansa</i>	Bottle Brush	Duranta	Mango
Dye extraction pH	10	10	10	9
Dye extraction time (min.)	60	60	75	75
Dye concentration (g/g)	4	4	3	3
Dyeing pH	10	9	10	9
Dyeing time (min.)	75	75	60	60

5.3.3 Optimum mordanting conditions

It was found that the mordants were extracted best at pH 10 and between 60-90 minutes of extraction time. Simultaneous mordanting method was selected the best followed by pre-mordanting and post mordanting methods. The optimum mordant concentration was found to range between 0.3 - 0.5 percent (o.w.f).

5.3.4 Effect of enzymatic pre-treatment on CIE LAB values

The CIE LAB values for all the mordants and dyes of enzymatically treated samples have been give in table 5.2.

In majority of the cases, the enzymatic pre-treatment led to an increase in dye absorption. It was found that 60.5 percent each of the enzymatically treated samples were darker and more red, 80 percent of the enzymatically treated samples were more yellow and 80.5 percent were more saturated than the control samples.

Table 5.2 CIE LAB values of enzymatically pre-treated samples for all the mordants and dyes

	L*				a*				b*				C*			
	B	Bb	Du	M	B	Bb	Du	M	B	Bb	Du	M	B	Bb	Du	M
C	L	L	D	D	Lr	Lr	Lr	Mr	My	Ly	My	My	Ms	Ls	Ms	Ms
A	L	L	L	D	Mr	Lr	Mr	Mr	Ly	Ly	My	Ly	Ls	Ls	Ms	Ms
B	D	D	D	D	Mr	Mr	Mr	Mr	My	My	My	My	Ms	Ms	Ms	Ms
E	D	L	D	D	Mr	Lr	Mr	Mr	My	My	My	My	Ms	Ms	Ms	Ms
P	D	L	D	D	Lr	Lr	Mr	Mr	My	My	My	My	Ms	Ms	Ms	Ms

C = Unmordanted, A = Arjun, B = Babool, E = Eucalyptus, P = Pomegranate, B = Bansa, Bb = Bottle brush, Du = Duranta, M = Mango, L= Lighter, D = Darker , Lr = Less red, Mr = More red, Ly = Less yellow , My = More yellow , Ms = More saturated, Ls = Less saturated

5.3.5 Fastness properties of dyed samples

The wash fastness grades for bansa dye were fair and good for the control samples, which improved to good and excellent when the samples were enzymatically treated. The light fastness grades were poor to fair for the control samples, but improved to fair and fairly good due to enzymatic treatment. The rubbing and perspiration fastness grades were mostly excellent for both the control and enzymatically treated samples.

The wash fastness grades for bottle brush dye were excellent for both the control as well as enzymatically treated samples. The initial light fastness grades of fair for the control improved to fairly good when samples were enzymatically treated. The rubbing and perspiration fastness grades were excellent in both the cases.

The wash fastness grades for duranta dye were fair, good and excellent for the control samples. The enzymatic treatment improved to good and excellent. The light fastness grades were poor and fair for the control and improved to fair and fairly good when these were enzymatically treated. The

rubbing and perspiration fastness grades were excellent for both the control and the enzymatically treated samples.

For the mango dye, the wash fastness grades of fair, good and excellent for the control samples improved to good and excellent with the help of samples were enzymatically treated. The enzymatic treatment improved the light fastness grades from fair to fairly good. The rubbing and perspiration fastness grades were mostly excellent in both the cases.

5.4 CONCLUSIONS

The following conclusions were drawn from the results of the investigation:

- New dye sources were explored, which has increased the palette for colour selection.
- The majority of the enzymatically pre-treated samples were darker in colour than the enzymatically untreated samples.
- The natural mordants were helpful in improving the fastness grades of both enzymatically untreated and enzymatically treated samples.
- The mordants helped in modifying the colour of the dye, thus producing a variety of shades from single dye.
- The enzymatically treated samples showed improved fastness properties than enzymatically untreated sample.

5.5 LIMITATIONS

- The study was limited to the use of only cellulase enzyme for pre-treatment.
- The study was limited to the use of only four natural dyes *bansa*, bottle brush, *duranta* and mango.

- The study was limited to the use of only four natural mordants *arjun*, *babool*, eucalyptus and pomegranate.

5.6 RECOMMENDATIONS

- Cotton can be pre-treated before dyeing. The optimum enzymatic conditions include - 7 pH media, 5% enzyme concentration (o.w.f) and 75 minutes of treatment time.
- The optimum dyeing conditions for dyeing with *bansa* dye are – 10 dye extraction pH, dye extraction time 60 minutes, dye concentration 4 g/g, dyeing pH 10 and treatment time 75 minutes.
- Bottle brush can be used as a dye at the optimum dyeing conditions – dye extraction pH 10, dye extraction time 60 minutes, dye concentration 4 g/g, dyeing pH 9 and treatment time 75 minutes.
- For *duranta* dye, the optimum dyeing conditions are – dye extraction pH 10, dye extraction time 75 minutes, dye concentration 3 g/g, dyeing pH 10 and treatment time 60 minutes.
- The optimum dyeing conditions for *mango* are – dye extraction pH 9, dye extraction time 75 minutes, dye concentration 3 g/g, dyeing pH 9 and treatment time 60 minutes.
- Use of *arjun*, *babool*, eucalyptus and pomegranate mordants at optimized conditions - extraction pH 10, mordant extraction time for *arjun*, eucalyptus and pomegranate mordants was 60 minutes and for *babool* was 90 minutes, mordant concentration 0.3-0.5 percent (o.w.f) is recommended for better colour uptake and shade variation.

- Post – mordanting method of mordanting was best for arjun and pomegranate mordants and simultaneous mordanting method for *babool* and eucalyptus mordants.

5.7 IMPLICATIONS OF THE STUDY

- Enzymatic pre-treatment improves both the colour quality and fastness of natural dyes. Through this, the same shade depth can be obtained by using lesser amount of dye. Thereby, the cost of dyeing with natural dyes can be brought down by giving a comparatively inexpensive pre-treatment
- The knowledge generated by this study will be helpful to the traditional dyers in improving the shades and colour fastness quality of the traditional textiles. This may in turn enhance marketability specially the export market, there by improving the economic condition of the dyers. All this becomes an incentive for the craftpersons in continuing to preserve the textile heritage of India.
- Many Indian fashion designers are promoting eco-friendly dyeing. Studies such as this can further their cause and create a niche market for the natural dyed textiles in India.

5.8 SUGGESTIONS FOR FURTHER STUDIES

- New sources of dyes can be experimented on the enzymatically treated samples.
- Effectiveness of synthetic mordants can also be compared with that of the natural mordants.

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ABSTRACT

The present study was carried out to optimize the conditions of enzymatic pre-treatment using cellulase enzyme (Neutrox BDN 100 Powder) and dyeing of cotton with four natural leaf dyes - *bansa*, (*Uricalum indacom*), bottle brush (*Callistemon lanceolatus*), *duranta* (*Duranta* *vr. goldeana*) and mango (*Mangifera indica*). Four natural mordants selected on the basis of high tannin content namely, *arjun* bark (*Terminalia arjuna*), *babool* bark (*Acacia nilotica*), eucalyptus bark (*Eucalyptus* *sp.*) and pomegranate fruit rind (*Punica granatum*) were used for dyeing.

The optimized pre-treatment conditions were pH level 7, enzyme concentration 5 percent (o.w.f) and treatment time of 75 minutes. The optimum dye extraction pH for all the dyes was 9 or 10, dye extraction time was 60-75 minutes, dyeing pH 9 or 10, dye concentration was 3 or 4 g/g of cotton, dyeing time 60-75 minutes. All the mordants extracted best at 10 pH with mordant extraction time of 60-90 minutes and 0.3-0.5 percent (o.w.f) mordant concentration. The best mordanting method was found to be simultaneous-mordanting. The CIE LAB values revealed that enzymatic pre-treatment led to an increase in dye absorption. The colour fastness properties also showed an improvement when the samples were enzymatically pre-treated.

Therefore, it was recommended that the cotton may be pre-treated at the optimized conditions for quality dyeing with *bansa*, bottle brush, *duranta* and mango dyes using selected mordants.

Key words : Cellulase, Cotton, Natural dyes, Natural mordants, Optimized conditions, Pre-treatment, Dyeing.

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