EFFECT OF BIOPOLYMER TREATMENT ON DYEING EFFICIENCY OF COTTON FABRIC

By
MONA VERMA
[2013HS10D]

Thesis submitted to the Chaudhary Charan Singh Haryana Agricultural University in the partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

IN

TEXILE AND APPAREL DESIGNING

I.C.COLLEGE OF HOME SCIENCE
CCS HARYANA AGRICULTURAL UNIVERSITY
HISAR - 125004 (HARYANA)

2017

CERTIFICATE – I

This is to certify that this thesis entitled **"Effect of Biopolymer Treatment on Dyeing Efficiency of Cotton Fabric"** submitted for the degree of **Doctor of Philosophy**, in the subject of **"Textile and Apparel Designing"** to CCS Haryana Agricultural University, is a bonafide research work carried out by **Ms. Mona Verma (Admission No. 2013HS10D)** under my supervision and that no part of this dissertation has been submitted for any other degree.

The assistance and help received during the course of investigation have been fully acknowledged.

Dr. Saroj S. Jeet Singh
(Major Advisor)
Deptt. of Textile and Apparel Designing,
I.C. College of Home Science,
CCS Haryana Agricultural University,
Hisar-125004, India

CERTIFICATE – II

This is to certify that this thesis entitled, **"Effect of Biopolymer Treatment on Dyeing Efficiency of Cotton Fabric"** submitted by **Ms. Mona Verma (**Admission No. **2013HS10D)** to CCS Haryana Agricultural University in partial fulfillment of the requirements for the degree of **Doctor of Philosophy**, in the subject of **"Textile and Apparel Designing"** has been approved by the Student's Advisory Committee after an oral examination of the same.

MAJOR ADVISOR **EXTERNAL EXAMINER**

HEAD OF THE DEPARTMENT

DEAN, POST-GRADUATE STUDIES

CERTIFICATE –III

FORMAT FOR P. G. THESIS

It is certified that the thesis submitted by **Ms. Mona Verma**, Adm. No. **2013HS10D**, Ph.D. student of this department has been checked and found as per specification of the format circulated by the Dean, PGS vide his Memo No. PGS/A-1/09/6926-90 dated 26. 8. 09.

MAJOR ADVISOR

PROFESSOR AND HEAD

Acknowledgements

This thesis is dedicated to my parents for their love, endless support and encouragement.

To commence with, I pay my obeisance to GOD, the almighty to have bestowed upon me good health, courage, inspiration, zeal and the light. This thesis has been kept on track and been seen through to completion with the support and encouragement of numerous people including my well wishers, my friends and various institutions. On the completion of my thesis I would like to thank all those people who made this thesis possible and an unforgettable experience for me.

Firstly, I would like to express my sincere gratitude to my advisor Dr. Saroj S. Jeet Singh, Professor, (Deptt. of Textile and Apparel Designing) for the continuous support of my Ph.D study and related research, for her patience, motivation, and immense knowledge. Her guidance helped me in all the time of research and writing of this thesis.

I gratefully acknowledge Dr. Neelam M. Rose, Professor, Deptt. of Textile and Apparel Designing for her understanding, encouragement, personal attention and help in writing which have provided good and smooth basis for my Ph.D. degree programme. I can see the good shape of my thesis because of her help and suggestions in formatting the entire thesis.

I would like to express my indebtedness to the other members of my advisory committee Dr. Rajvir singh, Professor (Deptt. of Chemistry & Biochemistry), Dr. Seema Rani, Professor (Deptt. of Extension Education & Communication Management) and Dr. Pinky Boora (Deptt. of Foods and Nutrition) for their inspiration and critical suggestions for accomplishment of this manuscript successfully.

It's my pleasure to acknowledge Dr. Krishna Khambra, Professor, (Deptt. of Textile and Apparel Designing) for their constant moral support, parental care, suggestions and inspiration. My warm appreciation is due to Dr. Nirmal Yadav, Professor & Head (Deptt. of Textile and Apparel Designing) for expressing confidence in my abilities and providing all the necessary facilities in departmental lab. Sincere thanks are also due to the other faculty members and staff of the Department of Textile and Apparel Designing, for their cooperation and timely help.

I am thankful to Dr. Ajit Singh, Professor (Deptt. of Veterinary Microbiology) and Dr. Mahavir Singh, Scientist (College Central Laboratory) for their support and for providing me testing facilities in College Central Laboratory at College of Veterinary Sciences in Lala Lajpat Rai University of Veterinary and Animal Sciences, Hisar. I am thankful to Dr. Saleem Siddiqui (Professor) and Dr. Rekha (Assistant Professor) for their support during my experimentation and providing lab facilities in Centre of Food Science and Technology.

I would like to thank my parents Mr. Khem Karan Lal Verma and Mrs. Phoolwati Verma for allowing me to realize my own potential. The unconditional support they have provided me over the years was the greatest gift anyone has ever given me and teaching me the value of hard work and education. Their patience and sacrifice will remain my inspiration throughout my life.

I feel a deep sense of gratitude for my sisters Sarika Di, Laxmi Di, Bhawna Di, Uma Di and Nirmala Di. They formed part of my vision and taught me good things that really matter in life and thanks for providing me carefree childhood that has made me who I am now. Their infallible love and support has always been my strength.

It's my fortune to gratefully acknowledge the support of some special individuals. Words may fail to express my appreciation to my senior Ms. Arpana Rai for valuable advice and my best friend Neha Gahlot for her support, generous care and the homely feeling at Hisar. She was always beside me during the happy and hard moments to push me and motivate me.

I would also like to extend huge, warm thanks to my senior Dr. Geeta Gaba and my friends Pallavi Lakhichura, Aanchal, Rekha, Umang, Anu and Preeti for their support and creating a pleasant atmosphere for me in hostel. I thank my juniors especially Ritu and Sushma.

Last, but not the least, I take this opportunity to sincerely acknowledge the Deptt. of Science and Technology, Government of India, New Delhi, for providing INSPIRE FELLOWSHIP-JRF and CCS Hayana Agricultural University for shaping my personality and giving friendly environment to perform my work comfortably.

Place: Hisar ***(Mona Verma)***

Dated: September, 2017

CONTENTS

CHAPTER	TITLE	PAGE NO.
I	INTRODUCTION	1-4
II	REVIEW OF LITERATURE	5-14
III	MATERIALS AND METHODS	15-36
IV	RESULTS	37-99
V	DISCUSSION	100-120
VI	SUMMARY AND CONCLUSION	121-124
	BIBLIOGRAPHY	i-viii
	ANNEXURES	I-X

LIST OF TABLES

Table No.	Description	Page No.
1.	Preliminary properties of the cotton fabric	37
2.	Selection of biopolymer and natural dye on the basis of colour properties	39
3.	Selection of biopolymer and synthetic dye on the basis of colour properties	40
4.	Selection of cross linking agent for chitosan application	41
5.	Selection of catalyst for chitosan application	43
6.	Phytochemical analysis of onion skin dye	44
7.	Optimization of chitosan concentration on the basis of colour properties of onion skin dye	45
8.	Optimization of citric acid concentration on the basis of colour properties of onion skin dye	46
9	Optimization of sodium hypophosphite concentration on the basis of colour properties of onion skin dye	47
10.	Optimization of treatment pH on the basis of colour properties of onion skin dye	47
11.	Optimization of material to liquor ratio on the basis of colour properties of onion skin dye	48
12.	Optimization of treatment temperature on the basis of colour properties of onion skin dye	49
13.	Optimization of treatment time on the basis of colour properties of onion skin dye	49
14.	Optimization of drying temperature on the basis of colour properties of onion skin dye	50
15.	Optimization of drying time on the basis of colour properties of onion skin dye	51
16.	Optimization of curing temperature on the basis of colour properties of onion skin dye	52
17.	Optimization of curing time on the basis of colour properties of onion skin dye	53
18.	Optimum concentrations and conditions of biopolymer treatment for onion skin dye	53
19.	Optimization of dye concentration on the basis of colour properties of onion skin dye	54
20.	Optimization of dyeing pH on the basis of colour properties of onion skin dye	55
21.	Optimization of M: L Ratio for dyeing on the basis of colour properties of onion skin dye	56
22.	Optimization of dyeing temperature on the basis of colour properties of onion skin dye	56

23.	Optimization of dyeing time on the basis of colour properties of onion skin dye	57
24.	Optimized concentration/conditions for dyeing process of onion skin dye	58
25.	Optimization of chitosan concentration on the basis of colour properties of reactive red dye	59
26.	Optimization of concentration of citric acid on the basis of colour properties of reactive red dye	60
27.	Optimization of concentration of sodium hypophosphite on the basis of colour properties of reactive red dye	60
28.	Optimization of treatment pH on the basis of colour properties of reactive red dye	61
29.	Optimization of material to liquor ratio on the basis of colour properties of reactive red dye	62
30.	Optimization of treatment temperature on the basis of colour properties of reactive red dye	62
31.	Optimization of treatment time on the basis of colour properties of reactive red dye	63
32.	Optimization of drying temperature on the basis of colour properties of reactive red dye	64
33.	Optimization of drying time on the basis of colour properties of reactive red dye	64
34.	Optimization of curing temperature on the basis of colour properties of reactive red dye	65
35.	Optimization of curing time on the basis of colour properties of reactive red dye	66
36.	Optimized concentration and conditions for application of chitosan for reactive red dye	66
37.	Optimization of dye concentration on the basis of colour properties of reactive red dye	67
38	Optimization of dyeing pH on the basis of colour properties of reactive red dye	68
39.	Optimization of material to liquor ratio on the basis of colour properties of reactive red dye	68
40.	Optimization of dyeing temperature on the basis of colour properties of reactive red dye	69
41.	Optimization of dyeing time on the basis of colour properties of reactive red dye	69
42.	Optimized concentration and conditions for dyeing with reactive red dye	70
43.	Total dissolved solids present in dye bath after dyeing	70
44.	FTIR analysis of chitosan powder	71
45.	FTIR analysis of onion skin dye powder	72
46.	FTIR analysis of reactive red dye	73

47.	FTIR analysis of chitosan treated cotton fabric	74
48.	FTIR analysis of chitosan treated onion skin dyed cotton fabric	76
49.	FTIR analysis of chitosan treated reactive red dyed cotton fabric	77
50.	Measurement of dye absorption, colour coordinates and colour strength of dyed fabrics	78
51.	Colour fastness grades of dyed fabrics	79
52.	Effect of pretreatments and onion skin dye on preliminary properties of fabric	82
53.	Effect of pretreatments and onion skin dye on mechanical properties of fabric	83
54.	Effect of pretreatments and onion skin dye on performance properties of fabric	86
55.	Effect of pretreatments and onion skin dye on functional properties fabric	86
56.	Effect of pretreatments and reactive red dye on preliminary properties of fabrics	90
57.	Effect of pretreatments and reactive red dye on mechanical properties of fabric	91
58.	Effect of pretreatments and reactive red dye performance properties of fabric	92
59.	Effect of pretreatments and reactive red dye functional properties of fabric	93
60.	Retention of functional properties on onion skin dyed fabric after washing	95
61.	Retention of functional properties on reactive red dyed fabrics after washing	97

LIST OF FIGURES

Fig. No.	Description	Page No.
1.	Effect of enzymatic preparatory processes on the whiteness and brightness of cotton fabric	38
2.	FTIR analysis of chitosan powder	71
3.	FTIR analysis of onion skin dye powder	72
4.	FTIR analysis of reactive red dye powder	74
5.	FTIR analysis of chitosan treated cotton fabric	75
6.	FTIR analysis of chitosan treated onion skin dyed cotton fabric	76
7.	FTIR analysis of chitosan treated reactive red dyed cotton fabric	77
8.	Comparison between antibacterial property of natural and synthetic dyes	98
9.	Comparison between ultra-violet protection property of natural and synthetic dyes	99

LIST OF PLATES

Plate No.	Description
1.	Shades obtained with different natural dyes on alum and biopolymers treated fabrics
2.	Colours obtained with different natural dyes on chitosan treated cotton fabric
3.	Shades obtained with different synthetic dyes on alum and biopolymers treated fabrics
4.	Colours obtained with different synthetic dyes on chitosan treated cotton fabric
5.	Onion skin dye
6.	Shades of onion skin dye obtained during standardization of chitosan treatment
7.	Shades obtained during standardization of dyeing process of onion skin dye
8.	Shades of reactive red dye obtained during standardization of chitosan treatment
9.	Shades obtained during standardization of dyeing process of reactive red dye
10.	Shades obtained with natural and synthetic dye
11.	Bacterial growth on chitosan treated dyed fabrics
12.	Bacterial growth on alum and alkali treated dyed fabrics

CHAPTER -I

INTRODUCTION

Cotton is produced in over 50 countries worldwide with production averaging 20-24 million tons per year and most used textile fiber in the world. World textile fiber consumption in the end of 20th century was approximately 45 million tons and approximately 20 million tons was represented by cotton. India holds the largest area of 8 million hectare under cotton cultivation and ranked third in world's cotton production, next to China and USA. India is also one of the largest consumer of cotton, accounting for about 60 percent of the total consumption of cotton **(Furter *et al.*, 2007 and Moses and Radhika, 2012).** Today, cotton textiles represent more than half of the global textile market and the demand is expected to continue **(Borland, 2010).** This dominance of cotton fibre is mainly because of its natural comfort, appearance and excellent performance such as alkali resistance, hygroscopicity and moisture retention but cotton fiber has poor crease recovery, dye fixation, antibacterial properties, photo-yellowing and colour fastness which needs to be improved.

Currently, through scientific advancements, innovative textile products like functional textiles inclusive of fragrances, ultraviolet protection, dyes, insect repellants, chromic materials, phase-change materials, antimicrobial agents and fire retardants are developed but increasing awareness of consumers and concern for the safety of products led the textile industry to continuously make efforts for ecological productions as an alternative to conventional production **(Shahidi *et al.*, 2010).**

The textile dyeing industry growth is accelerating rapidly to fulfill the consumer's demands and colouration technology has dominated this industry. Colour of textile material play an important role in marketability of fabrics due to its psychological effect and catches the attention of the consumers. But the colouring of textile material is complex and specialized science in which colour is imparted by using the dyes and pigments through dyeing and printing processes.

The global consumption of textiles is estimated to grow at the rate of 3 percent per annum. The colouration of this huge quantity of textiles need about 7,00,000 tonnes of dyes and such a huge amount of required textiles substrate cannot be dyed and printed with natural dyes only. Therefore, the use of eco-safe synthetic dyes is the need of an hour. But a certain portion of coloured textiles can always be complemented and managed by eco-safe natural dyes **(Samanta and Agarwal, 2009).**

The synthetic dye classes mainly used for dyeing cellulosic fibres are direct, reactive, vat, sulphur and azoic dyes. The vat, sulphur and azoic dyes are nonionic and water-insoluble in their original form, direct and reactive dyes are water soluble anionic dyes as their anions

are the colour constituents. The wash fastness of direct dyes, even when given a conventional after treatment, do not meet the standards for most cellulosic apparel and furnishing materials. Consequently, direct dyes have been replaced by reactive dyes to a great extent due to better wash fastness of reactive dyed cotton. Reactive dyes have become very popular due to its brilliancy, variety of hue, high wet fastness, convenient usage and high applicability. In recent years, reactive dyes maintain the largest annual consumption in the world among the dyes used for cellulosic fibers which establishes its important status in the dye manufacturing industry. For dyeing of one kilogram of cotton textile with reactive dyes about 70 to 150 litre water, 600-800 gms sodium chloride and 30 to 60 gms dyestuffs is required. In application of reactive dyes use of large amount of electrolyte, unfixed dye and high volume of wastewater discharge create environmental problems. Reactive dyes are most unfavorable class of dye from the ecological point of view because effluent produced gives very high values of biological oxygen demand (BOD), chemical oxygen demand (COD) and increases salinity of river water which affect the delicate biochemistry of aquatic life. More than 80,000 tons of reactive dyes are produced and consumed every year, making it impossible to enumerate the total amount of pollution caused by their use. The best approach would obviously be to modify the textile processing technologies and chemistry to reduce the environmental discharge occuring during dyeing. So, most researchers focus on introducing salt-free/low-salt dyeing technology for reactive dyes.

Ancient art of dyeing of textiles substrate with natural dyes withstood the destructive effect of time but a swift decline in natural dyeing continued due to the ample availability of synthetic dyes at an economical price. However, even after a century, the uses of natural dyes never eroded completely and are still being used. Many practitioners of the craft of natural dyeing acknowledge that natural dyes have a far superior aesthetic quality which is much more pleasing to the eye. In many of the world's developing countries use of natural dyes, not only a rich and varied source of dyestuff but also the possibility of an income through sustainable harvest and trade of these dye plants. Natural dyes are obtained from plants renewable parts and wastes, shellfish, insects and minerals. India is still a major producer of most natural dyed textiles and the researches have been carried out to preserve the tradition of natural dyes.

Natural dyes can exhibit biodegradability, medicinal properties such as antibacterial property, antioxidant, ultraviolet protection property and generally have a higher compatibility with the environment. Thus, dyeing of various textiles with natural resources has persisted mainly in the decentralized sector for specialty goods. Conventional wisdom leads to the belief that natural dyes are safe to the environment than their synthetic counter parts. The application of eco-friendly natural dyes on textiles has become essential because of the increased environmental awareness and concern to avoid the use of carcinogenic and

hazardous synthetic dyes. However, worldwide the use of natural dyes for the colouration of textiles has mainly been limited to craftsman, small scale dyers and printers as well as small scale exporters and producers dealing with high valued environmental friendly textile production and trade.

Recently people have shown greater interest in the use of natural dyes in textile processing due to increasing awareness towards environment, health and water pollution and waste disposal. There are problems of toxicity and allergic reactions associated with synthetic dyes, while natural dyes exhibit fewer such type of problems and offer better biodegradability and more compatibility with the environment. However, natural dyes have some drawbacks such as poor fastness and intensity of colour which is overcome by use of mordants. Synthetic or metallic salts which are commonly used in dyeing of cotton fabric with natural dyes for better fixation of colour create problems because of its carcinogenic and harmful characteristics and take long time to degrade through environment cycles leading to water pollution. So, there is an urgent need to search natural, safe and biodegradable mordants to make natural dyeing process completely environmental friendly.

Cationization is one of the most important modifications for cotton to improve affinity toward anionic substances such as dyes in conventional textile processing and metal ions or unfixed dyes in effluent treatment. Cationic modification agents consist of two functional characteristics such as multiple functional groups that could react with cotton under alkaline conditions and cationic amino groups that could reduce the negatively charged barrier between fiber and dye. Modification is possible with the help of biopolymers, an environmentally benign route. It is well-known that biopolymers are capable of forming ionic interactions with cotton cellulose by rendering positive charge and provide other functional properties to fibre. Bioploymers can replace the salts such as alum, ferrous sulphate, sodium sulphate, sodium carbonate and sodium chloride which have been widely used for dyeing of cotton with natural and synthetic dyes to improve the fastness properties and absorption of dye. Biopolymers offer the complete elimination of electrolytes (salts) with low volume of water during wash off process and provides maximum dye absorption and colour strength which significantly contribute in saving of process cost.

Environmental pressure is pushing towards the ‘green’ options away from synthetic or petro-chemically derived products. Biopolymers are suitable replacement materials for different chemical processes. The surface modification of textile fibres through biopolymer is considered as the best route to obtain modern textile treatments to minimize the generation of wastewater containing salts, unfixed dye and other chemicals which may affect the environment and public health. To avoid these problems, the pretreatment of cotton with biopolymer is safe for eco-friendly dyeing.

Chitosan is a versatile polycationic biopolymer derived from alkaline deacetylation of chitin. Chitosan exhibits several valuable inherent properties such as antibacterial, antifungal, antiviral, non-toxic, biodegradability as well as film formation properties. Chitosan possesses hydroxyl and amino functional groups which can easily be fabricated with desired functional properties.

Recently, most of the commercial dyeing units and textile export houses have started re-looking to the maximum possibilities of using natural dyes and safe synthetic dyes for dyeing and printing of different textiles for targeting niche market. For successful commercial use of natural dyes for any particular fibres, newer shade with acceptable colour fastness behaviour and reproducible colour yield, appropriate standardized scientific dyeing techniques and procedures need to be adopted. Thus, relevant scientific studies and its output on standardization of dyeing methods, process variables, dyeing kinetics and analysis of compatibility of selective natural and synthetic dyes have become very significant, however the information on which is insufficient. Hence the present study was undertaken to utilize salt free dyeing on cotton using the natural and synthetic dyes which will contribute to minimize the pollution load on environment and to explore promising approach to provide multi-functionality to the cotton fabric. The present study has been taken with the following objectives:

- To optimize the process of biopolymer treatment for application on cotton fabric.
- To standardize the dyeing process for biopolymer treated fabrics and to assess the colour fastness properties.
- To analyze the effect of treatment on physical and functional properties of treated fabrics.

CHAPTER -II

REVIEW OF LITERATURE

Review of literature was explored in order to get the background knowledge, especially the comprehensive understanding about the biopolymers and their use in the textile industry so that the appropriate investigating route can be adopted. A brief resume of past literature and researches relevant to the present study have been incorporated in this chapter. The pertinent literature has been presented under the following subheads:

2.1 Enzymatic desizing and scouring of cotton fabric

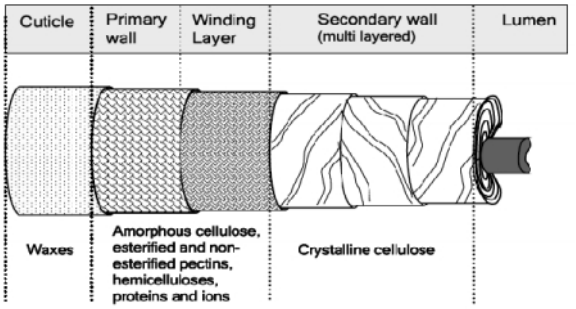
2.2 Application of dyes on cotton textiles

2.3 Uses of biopolymers in textiles and future perspective

2.4 Effect of biopolymer treatment on physical and functional properties

2.1 Enzymatic Desizing and Scouring of Cotton Fabric

Main constituents of cotton fibre are cellulose (90%-94%) beside this it contains waxes (0.6%-1.3%), pectic substances (0.9% -1.2%), protein (0.6%-1.3%), ash (1.2%), organic acids (0.8%) and others (1.2%). Chief purpose of scouring is the removal of waxes, pectin, hemi-celluloses and minerals from the raw cotton fibres during the preparatory processes to make the cotton fibres highly absorbent, which is necessary for the subsequent processes such as mercerization, bleaching, dyeing, printing and finishing.



Structure of Cotton Fibre

Etters *et al*. (1999) emphasized that nowadays amylases are commercialized and preferred for desizing due to their high efficiency and specificity, completely removing the size without any harmful effects on the fabric.

The disadvantages of scouring with sodium hydroxide has motivated the textile industry to introduce more enhanced biological agents which would be effective in removing non-cellulosic substances without any damaging effects on cotton and also less energy and water consuming. It was reviewed that the use of enzymes in the textile industry is an example of white industrial biotechnology, which allows the sustainable processing in fibre processing and strategies that are non-polluting, conserving energy and natural resources,

economically viable, safe and healthy for workers and communities. The various types of enzymes have been applied at different stages of the fabric manufacturing process to obtain less energy, fewer process stages and hydrolysis of proteins, starches, lipids, pectins, celluloses and hemicelluloses (**Menezes, 2011).**

Rajendran *et al*. (2011) found that the hydrolysis by enzymes such as pectinases promotes efficient interruption of the matrix to achieve good water absorbance without the negative side effect of cellulose destruction. This process is called bioscouring. It breaks down the pectin in the cotton and thus assists in removal of waxes, oils and other impurities. The optimum temperature is 50-65 ^{0}C and pH between 7.5 to 9.0. The bioscoured fabric possesses better wetting and penetration properties, making subsequent bleach process easy and resultantly giving much better dye uptake.

Bahrum (2012) reported that harsher chemicals used in conventionnal scouring cause strength loss of fabric than bioscouring. It is due to that bioscouring agent attacks on the primary cell wall of the fibres which is required for dye absorption but conventional scouring agent attacks both primary and secondary cell wall and causes higher strength damage. Bioscouring facilitates the higher revomal of pectin, causes higher space in the fibres for dyestuff penetration, reaction and fixation in comparison to conventional scoured fabrics. Chemicals used in conventional scouring are responsible to increase the amount of BOD, COD and TDS (total dissolved solids) in the effluent water and increase the unwanted pressure on environment. Caustic scouring is responsible for 10- 20% of the total pollution load generated during entire textile processing operation.

Mojsov (2012) highlighted the advantage of enzymes in textile finishing is that they are specific for starch, removing it without damaging to the support fabric and amylase enzyme can be used for desizing processes at low-temperature (30-60 ºC) at optimum pH i.e. 5.5 - 6.5. Several other enzymatic processes have also been developed for the different wet processing of textile goods in wide-ranging operations from cleaning preparations to finishing processes. Cellulases, hemicellulases and pectinases have become the target enzymes in bioprocessing of cotton and other cellulosic fibres and fabrics.

2.2 Application of Dyes on Cotton Textiles

Dyes as coloured unsaturated organic molecules must have affinity for fibers to be effectively applied. The dyes on fibers are physically bound to the fiber by one or more physical forces. Interest in eco-friendly textile wet processing techniques has been increasing in recent years due to the increased awareness of environmental issues throughout the world. The main challenge the textile industry faces is to modify production at a competitive price by using safe dyes and chemicals as well as by reducing treatment cost.

A high-quality coloured fabric possesses an acceptable level of colour fastness rating of at least 3 on a five-point grey scale. Depth of colour on a fabric depends on absorption

levels of dyes by the fibres and its distribution coefficient between the dye bath solution and the fibres **(Papita and Siddhartha, 2008).**

2.2.1 Application of natural dyes on cotton fabric

For many years, scientists have investigated the deodorizing/aroma (**Sricharussin *et al.*, 2004),** insect-repellent (**Specos *et al.*, 2010),** protection against to UV rays (**Grifoni *et al.*, 2011)** of plants dyeing and usability in the textile industry.

Parthiban and Thilagavathi (2012) reviewed that until the advent of the synthetic dyes in the second half of the nineteenth century, all dyes were derived directly from natural sources such as the leaves, flowers, berries, stems or roots of plants insects and shellfish, and even from a number of minerals and called 'natural dyes'. In the last 150 years, humans have produced artificial dyes to achieve a broader range of colours, and to render the dyes more stable to washing and general use. Different classes of dyes are used for different types of fibre and at different stages of the textile production process, from loose fibers through yarn and cloth to completed garments. Natural dyes are almost exclusively applied to natural fibers, with cotton being the most commonly tested fiber.

Natural dyes are environmental friendly, low toxic and less allergenic. Due to these advantages, over the last decade the use of natural dyes has gained momentum in food, pharmaceutical, cosmetic and textile dyeing industry. The dye-yielding plants, unlike synthetic dyes, may contain more than one chemical constituent, each exhibiting a different colour and properties, operating singly or in combination with different groups, depending on their chemical structure and composition**.** Natural dyes consist of catechins, rosmarinic acid, flavonoids, carotenoids, ascorbic acid and anthocyanin groups in the structure, which show natural anti-oxidant property**.** Natural dyes have antimicrobial properties and many of these are determined to be resistant to gram-negative bacteria **(Islam and Shahid, 2013).**

Bhuyan *et al.* (2016) stated that owing to the existence of large number of structurally diverse active compounds such as tannins, flavonoids, curcuminoids, alkaloids, and quinines in their extracts, the use of natural colourants offer promise in developing antimicrobial textiles for aesthetic, hygienic and medical applications. It was observed that the catechins from green tea extract induced leakage of 5,6-carboxyfluorescein from phosphatidylcholine liposome from bacteria and suggested that the death of cells resulted from the disruption of bacterial membrane. They found that gram-positive bacteria were more susceptible to catechins as compared to gram-negative bacteria.

i. Properties of selected natural dyes tried for selection

a. Banana leaves (*Musa balbisiana)***: Naikwade *et al. (*2014)** revealed that banana leaves exhibited antibacterial properties against *Escherichia coli* and *Staphylococcus aureus***.** Natural dye from banana leaves found to be suitable for natural dye extraction used from textile dyeing (**Saleh *et al.*, 2013).**

b. **Guava leaves (***Psidium guajava)***:** The active chemical saponins, flavonoids, tannins, eugenol and triterpenoids. Polyphenolic compounds dominate guava leaves are flavonoids and tannins **(Mailoa *et al.*, 2014).** It was reported by **Katewaraphorn and Kongdee, (2016)** that guava leaf extracts exhibited antibacterial activity against *S. aureus*, but it was not found effective against *E. coli*. It was found that guava leaf extract were effective for application as an antibacterial agent for finishing textiles.

c. **Mango leaves (***Mangifera indica)***:** Mango leaves are a rich source of phenolic compounds with strong antioxidant power, particularly mangiferin which is potent antimicrobial agent and responsible for providing colour. These also contain antioxidant capacity and other phenolic compounds like quercetin, widely studied due to its pharmacological properties **(Massibo and He 2008, Uddin, 2005).**

d. **Marigold petals (***Calendula officinalis)***:** Marigold flowers, which are yellow to orange red in colour, are a rich source of lutein, a carotenoid pigment. Nowadays, lutein is becoming an increasingly popular active ingredient because of its antioxidant property used in the food industry and textile colouration **(Jothi, 2008).**

e. **Onion skin (***Alleum cepa)***:** Red onion skin is a rich source of phenolic compounds, especially of quercetin. The amounts of isolated phenolic compounds and quercetin from onion skin were approximately 3 to 5 times higher as from the onion edible part. Onion skin extracts also exhibited high antioxidant, radical scavenging and antimicrobial activities. The skin of onions is inedible however it contains a dyestuff called Pelargonidin. **(Skerget *et al.*, 2009, Zubairu and Mshelia, 2015).**

f. **Peanut skin (***Arachis hypogeae)***:** The three classes of phenolics were found in peanut skins, including phenolic acids, flavonoids and stilbene. Natural phenolic compounds can be extracted from peanut skins as these are regarded as a low economic value by-product of the peanut industry; however, they contain high levels of bioactive compounds including catechins and procyanidins, which are known for their health-promoting properties. Due to their low cost, peanut skins have great potential to serve as an economical source of natural antioxidants **(Yu *et al.*, 2010).**

g. **Pomegranate rind (***Punica granatum)***:** The main colouring agent in pomegranate rind is granatonin which is present in alkaloid form. The phenolics and flavonoid compounds present in pomegranate have been found to be responsible for its antimicrobial activity. **Lee *et al.* (2009)** reported that fabrics dyed with the extract of pomegranate peel showed antimicrobial activity against *S. aureus and K. pneumonia*.

h. **Teak leaves (***Tictona grandis linn)***:** Teak has been found to be rich in reddish to brown colourants. Dye extracted from teak leaves with aqueous, methanol produced brick red shade on silk and wool in the presence of different mordants **(Samanta and Agarwal, 2009).** The leaves of the plant are widely used for the treatment of wounds, especially burn

wounds and are also useful to treat haemostatic and also useful in inflammation, leprosy and skin diseases etc.

2.2.2 Application of synthetic dyes on cotton fabric

Within each group, application and performance properties vary considerably so the choice of dyes to use is not easy.

Broadbent (2001) stated that cotton, and other cellulosic fibres, are dyed with direct, sulphur, vat, reactive or azoic dyes – more types than for any other fibre. Each of these classes of dye has its own application methods, dyeing characteristics, cost, fastness properties and colour range and therefore its own particular advantages and disadvantages. Direct dyes generally cannot meet today's more stringent washing fastness requirements for apparel and linens. In recent years, their share of the market has gradually declined in favour of reactive dyes. Reactive dyes have very good wash fastness on cellulosic materials and often have bright colours**.**

When cotton fibres are immersed in an aqueous dye bath, the fibre surface acquires an initial negative charge that is referred to as zeta potential. Anionic dyes are usually sulphonated to provide aqueous solubility and posess a negative charge in the aqueous dyebath. Therefore, there is an electrostatic repellency for the dyes to diffuse through the fibre-water interface. The only widely used method of overcoming this barrier is the addition of large quantities of inorganic electrolyte, such as sodium chloride or sodium sulphate **(Khatri, 2015).**

i. Properties of synthetic dyes tried for selection

a. Direct dyes: Direct or substantive dyes are a special class of dyes which penetrate cellulosic fibers readily and have good affinity for these fibers due to their size and shape. Direct dyes are long, narrow and flat in molecular structure, which allows them to readily enter the cellulose structure and interact with the cellulose in such a way as to provide good fiber affinity. Direct dyes often contain one or more azo groups connecting aromatic chromophores, thereby providing a straight chain dye molecule. Direct dyes are usually applied from basic solutions in which cellulosics are more stable and more likely to swell **(Needles, 1986).**

b. Reactive Dyes: Reactive dyes are dyes which usually have the basic structure of acid, direct or mordant dyes but which in addition have a reactive group capable of covalent bond formation with the fiber. Since the fiber must have reasonable reactivity toward the dye reactive group, application of these dyes has been limited to protein and nylon fibers **(Needles, 1986)**

c. Acid dyes: The acid dyes are large dyes containing one or more sulfonic or carboxylic acid salt functional groups. These dyes are dyed onto fibers from acid solution, since positive charge development within the fiber in acid solutions that acts as a driving force for dye

diffusion and migration into the fiber. Only fibers which develop a positive charge in the presence of acid, such as wool, silk and other protein fibers like nylon, and certain modified synthetics, are readily dyed by acid dyes. Acid dyes on fibers are reasonably colourfast to light and laundering, but mordanting (more complete insolubilization of the dye through reaction with a metal salt) can improve the overall fastness properties of the dye (**Needles, 1986).**

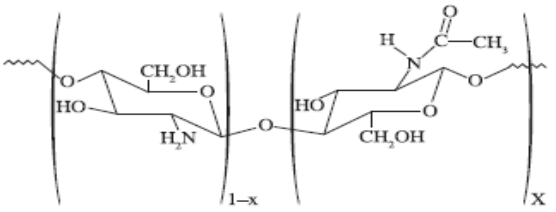
2.3 Uses of Biopolymers in Textiles and Future Perspective

Increased environmental consciousness and consumer demands have taken attention to natural textile surfaces with functional properties and to polymers that can be used to give these properties.

2.3.1 Uses of biopolymers in textiles

Cireli and Yurdakul (2006) revealed that the beta-cyclodextrins can act as retardant with dyes with which it can form complexes. Beta-cyclodextrins can replace the role of surfactants used in dyeing without the loss of dyeing quality, and also improve wash fastness of nylon and cotton with reactive-disperse dyes. Dyeing and easy care finish can be achieved by using a formulation containing a reactive dye, monochlorotriazynil (MCT)- beta-cyclodextrins and a resin.

Gupta and Haile (2007) reported that chitosan can be used in production of man-made fibers and textile wet processing. Its potential can be utilized in dyeing to improve the dye-ability, in finishing as antimicrobial agent and in printing as natural thickener in printing paste.



Structure of chitosan

Ibrahim *et al.* (2007) reported the improvement of UV protective properties of cotton/wool and viscose/wool blends by incorporating reactive beta-cyclodextrin-monochlorotriazynil (MCT) in the easy care finishing formulations, followed by subsequent treatment with copper-acetate or post-dyeing with different classes of dyestuffs i.e. acid, basic, direct and reactive. It was found that post-dyeing of the prefinished textile blends resulted in significant increase in the UPF (UV-protection factor) values as direct consequence of a remarkable reduction in UV radiation transmission through the plain weave fabric.

Kondgee and Chintrawan (2007) investigated the modification of cotton fibre with silk sericin in a pad- dry-cure method using gluteraldehyde and dimethylol- dihydroxy- ethylene

urea as crosslinking agents. It was found that the sample treated with sericin exhibited increase in colour strength and drecease in L* values indicating darkness of shade.

Voncina *et al.* (2007) investigated beta-cyclodextrin as a retarding agent in dyeing of Polyacrylonitrile (PAN) fibres with cationic dyes. The retarding effect of beta-cyclodextrin was comparable to that of a commercial product based on a quaternary ammonium compound and significant improvement of colour levelness and some improvement in colour depth were reported. It was found when PAN fibres were dyed in the presence of beta-cyclodextrin were comparable to dyeing in the presence of commercial retarding reagent.

Davarpanah *et al.* (2009) claimed that the usage of chitosan could decrease the amount of salt required in the dyeing with direct and reactive dyes by about 50%, resulting in the production of comparable shade compared with conventional methods.

Raslan *et al.* (2009) found that the disperse dyeing of cellulose acetate treated with beta-cyclodextrin showed improved colour intensity as well as the possibility of dyeing at lower temperatures than conventionally dyed.

Giri *et al*. (2009) envisaged that th**e** chitosan which has a similar structure to cellulose and is a natural polymer has been widely used in textile industry for improving the properties like colour yield, antibacterial and antifelting of the textile surfaces.

Rashmi *et al.* (2011) stated that beta-cyclodextrins play an important role in innovative textile processing and the functionalisation of textiles, both of which currently hold the increased interest of textile researchers. The uses of beta-cyclodextrins provide immediate opportunities for developing new innovative products and eco friendly textile processes which are of specific interest to the textile industry. From the wide spread of industrial applications as auxiliaries, beta-cyclodextrins also have a great potential in newer applications in the area of medical and technical textiles.

Sundrarajan *et al.* (2012) reported that the dyeing of cotton with natural dyes using biocompatible and biodegradable modification agents such as chitosan and cyclodextrin will be the cost effective environmental friendly approach in the field of dyeing industry and emphasized that the modification of the fabric is one of the best routes to improve the affinity between dye and fabric. The chemical modification of organic cotton fabric was done in the greener way with the use of beta-cyclodextrin and chitosan and the modification level were measured by dyeing with natural dye parijataka (*Nyctanthes arbor-tristis*). Results of dyeing showed better dye uptake after modification on organic cotton fabrics, especially with chitosan treatment.

Zhou *et al.* (2012) reported the adsorption behavior of annatto dye on cotton fabric pre-treated with sericin. It was inferred that the sericin largely developed the positive charge on the cotton fibres following a decrease in the pH. The modified cotton showed that sericin enhanced the adsorption capacity of the annatto dye on cotton.

Nasir *et al.* (2015) investigated that the dyeing of knit cotton fabric with rengas dye was successfully done in presence of chitosan and sodium nitrite. The colour fastness to light, wash and perspiration improved with the treatments and acidic mordants. In contrast, the basic mordanted fabric gave moderate fastness properties.

Waly *et al.* (2016) treated cotton fabrics with cationic agent at 10 percent conc. (owf) with suitable conditions followed with a second treatment with chitosan polyacrylic acid which was prepared in nano particles. The dye uptake was greatly increased with both cationization and chitosan treatments due to creation of positive sites on fabric surface capable of attracting the negatively charged dye anions. A better dyeing property for cotton fabrics with cochineal dye was obtained with treatment in a bath containing 10 percent cationic agent at 50º C and pH 8 for 40 minutes and dyeing at 90ºC with pH 4 for 60 minutes. The colour fastness properties of treated cotton dyed with cochineal were also found to be good.

2.3.2 Future perspective of biopolymer

Wu *et al.* (2007) reported that Indian production of 1600 tons of silk can be source of about 250-300 tons of sericin every year. If this sericin protein is recovered and recycled, it would be a significant economic and social benefit. Sericin, has a combination of many unique properties such as biodegradability, nontoxicity, oxidation resistance, antimicrobial activity, UV resistance and absorbent.

Agrawal *et al.* (2008) stated that the use of beta-cyclodextrin in the textile industry is of great significance due to its wide range of applications. In the last few years, the new direction in textile researches is the functionalisation of textile system and it is believed that beta-cyclodextrin will play a very important role in these new developments and can act as a host for various guest molecules. This enables the development of fabrics that release chemical compounds such as fragrances and antimicrobial agents and it can be incorporated onto textiles by means of spraying, printing, padding, grafting, surface coating, impregnation, ink jet printing or via sol gel, etc.

Sundar *et al.* (2010) reported that chitosan is a very useful and interesting bioactive polymer because of its availability, biocompatibility, bioactivity, cost-effectiveness, non-toxicity and biodegradability. It has many amino side groups, which offer possibilities of chemical modifications, formation of a large variety of useful derivatives that are commercially available or can made available via graft reactions and ionic interactions. The unique characteristics of chitosan providing bio-adhesion, sorption and antimicrobial properties are the major reasons for its multiple applications.

2.4 Effect of Biopolymer Treatment on Physical and Functional Properties

2.4.1 Effect of Biopolymer Treatment on Physical Properties

Neorati (2008) studied that cotton samples were padded with aqueous chitosan succinate solutions containing a sodium di-hydrogen phosphate as catalyst at 80 percent wet

pick-up by using a padding mangle. The padded samples were dried at 100^{o}C for 2 min and cured in an oven for 2 min at 170^{o}C. It was found that the crease resistant and antibacterial properties were durable till ten washing cycles.

Allam *et al.* (2009) reported that sericin is an efficient agent in felt proofing of wool fibers, especially in the presence of a crosslinker such as Dimethylol Dihydroxy Ethylene Urea (DMDHEU), Dimethyl Dihydroxy Ethylene Urea (DMeDHEU) or Epichlorohydrin (ECH). The felting resistance of wool fibres treated with the system Hydrogen peroxide (H_2O_2) / Sodium sulphite (Na_2SO_3) /sericin is the same as the felting resistance obtained using commercially available synthetic polymers. Being a relatively cheap natural biodegradable polymer produced from renewable resources, sericin is an acceptable base for felt proofing treatments of wool tops.

Hebeish and El-hilw (2001) and Sricharussin *et al.* (2009) reported that easy care characteristics can be achieved with a specific combination of Monochlorotriazinyl derivative of β -CD (MCT- β -CD), resin and catalyst concentrations. Novel scouring agents containing β-CDs can be used for sizing and bioscouring of textiles. Monochlorotriazinyl derivative of β–CD finished polyester or polyester-cotton blend fabrics also improved anti-static properties. It was also found that β-CD-MCT can be fixed to cotton fabrics with pad-dry-cure method at high temperatures, no loss of tensile strength of the treated fabrics was reported.

2.4.2 Effect of Biopolymer Treatment on Functional Properties

El-Tahlawy *et al.* (2006) carried out a novel technique for preparation of cyclodextrin-grafted chitosan. β- CD citrate was synthetized by esterifying of β-CD with citric acid (CA) in presence or absence of sodium hypophosphite as a catalyst in a semi dry process. It was found that the chitosan and β-CD/grafted chitosan, exhibited antimicrobial activity against different microorganisms.

Kim (2006) found that chitosan mordanted green tea dyed cotton showed better dyeing characteristic and higher UV protection property as compared to the unmordanted green tea dyed cotton. As the chitosan concentration in mordanting increased, dyeing efficiency and the UV protection property also increased.

Giri *et al.* (2009) reported that chitosan was found to inhibit the growth of microbes. It is a naturally available biopolymer which is now increasingly being used as a functional finish on textile substrates to impart antimicrobial properties. Henna a natural dye with proven bactericidal properties was applied on wool fabrics along with chitosan to impart antimicrobial characteristics.

It was found that beta-cyclodextrin cavities on the textile can also trap bad odours and these cavities can be emptied during the washing process. Empty cavities can be reloaded with padding, dipping or spraying or by keeping the moist beta-cyclodextrin fabric in an atmosphere of the guest molecules at 50-60ºC for a few hours (vapour method). The odour

molecules being hydrophobic become trapped in the cavities of the cyclodextrins and are removed during laundering. Beta-cyclodextrins are also known to stabilise the perfumes in washing powders for several days. The fragrance release rates were greatly decreased and the results of sensorial evaluations demonstrated that the performance of the fabric lasted for over 30 days (**Sricharussin *et al.*, 2009).**

Kurioka and Shiozaki (2011) treated cotton fabrics with sericin (1.2%) soloution containing citric acid (9%) as a crosslinking agent to improve their hydrophilic and thermal properties. The treated fabrics absorbed more water than the non treated fabrics and the water diffusion time decreased in sericin treated fabrics. Moreover, q-max, thermal conductivity and air permeability resistance values were higher in sericin treated fabric.

Angela *et al.* (2015) revealed that the application of chitosan and cyclodextrin with essential oils on textile supports allows a controlled release of the active substance in time, as well as a prolonged antimicrobial effect. Most frequently the textile supports are made of natural cellulose fibres, the resulting products being used as wound dressings, bandages, absorbent items, suturing products, hygiene products. These materials present good liquid sorption, softness, good permeability and they are commonly known as biomaterials with improved comfort indexes.

CHAPTER -III

MATERIALS AND METHODS

This chapter deals with the materials and methods used for the present investigation. The present study was undertaken to study the effect of biopolymer treatment on dyeing efficiency of cotton fabric. The different methodological procedures adopted for the study have been described under the following headings and subheadings:

3.1 Selection and procurement of raw material
3.2 Preliminary properties of cotton fabric
3.3 Preparation of the cotton fabric
3.4 Standardization of biopolymer treatment
3.5 Standardization of dyeing process for natural dye
3.6 Standardization of dyeing process for synthetic dye
3.7 Measurement of total dissolved solids (TDS)
3.8 Fourier transform infrared spectroscopy (FTIR) analysis
3.9 Assessment of colour properties of the dyed fabrics
3.10 Testing of physical and functional properties
3.11 Retention of physical and functional properties of dyed fabrics after washing
3.12 Statistical analysis

3.1 Selection and Procurement of Raw Material

3.1.1 Procurement of fabric

A survey was conducted in local market of Hisar city of Haryana and the pure cotton fabric which is commonly used by consumers for apparel purpose was purchased. To confirm the purity of cotton fabric, burning, microscopic and chemical tests were conducted.

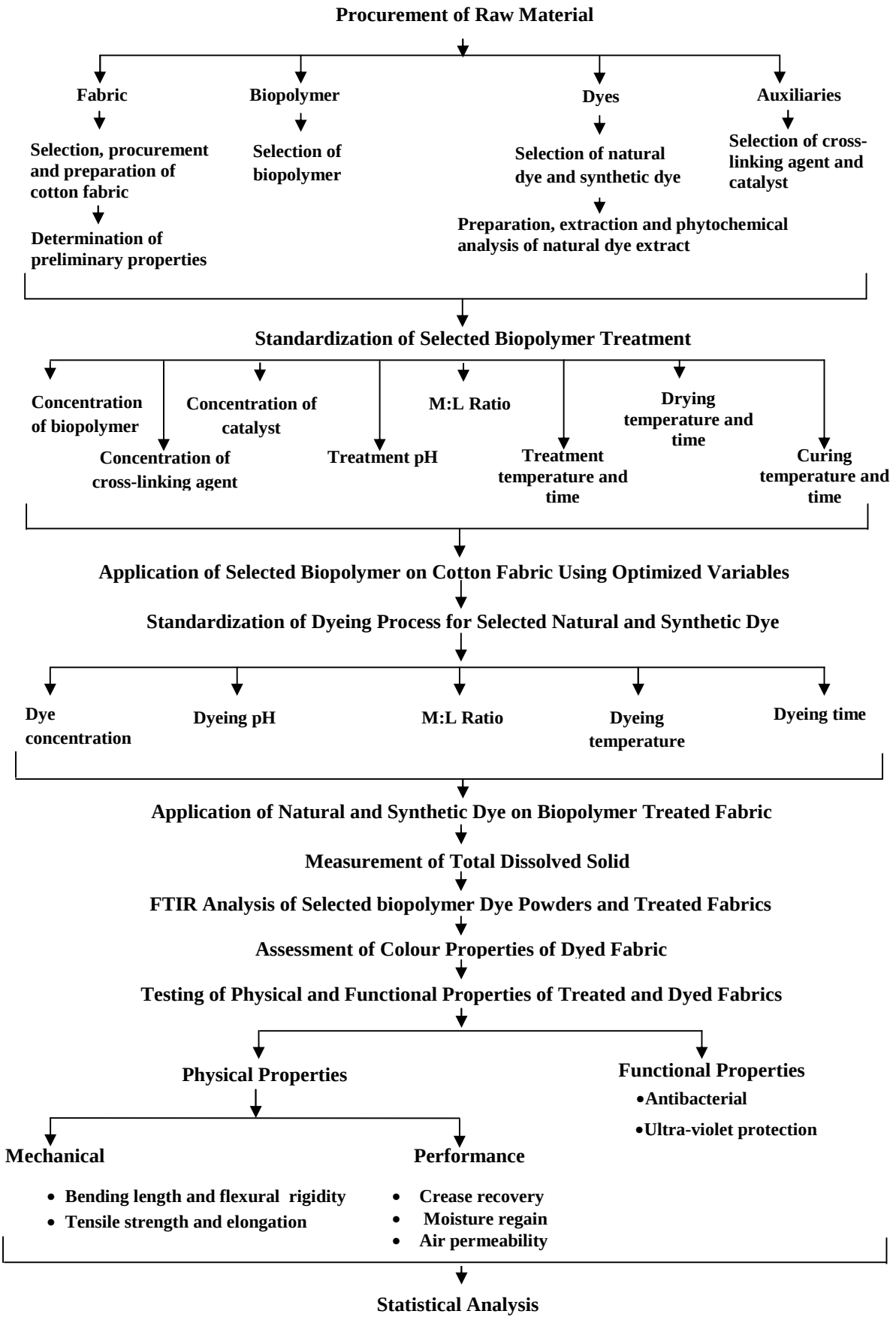
3.1.2 Procurement of enzymes*:* For increasing the absorbency of the cotton fabric, enzymatic desizing treatment was given using Americos Amylase 543 and enzymatic scouring was done with Palkoscour APCL on review basis. Americos Amylase 543 was purchased from Alps Industries Ltd, Ghaziabad (Uttar Pradesh) and Palkoscour APCL was procured from Maps Enzyme Ltd, Ahmadabad.

3.1.3 Procurement and selection of biopolymer

On the review basis three biopolymers viz. beta-cyclodextrin, chitosan and sericin were used as mordant for enhancing the dyeability of cotton with natural and synthetic dye without using metals based salts as mordant.

i. **Procurement of biopolymers:** Chitosan was procured from Indian Sea Food Company Cochin, Kerala**,** sericin from Swapnroop Drugs and Pharmaceuticals, Maharashtra and beta-cyclodextrin from Jay Chemical, Ahemdabad.

RESEARCH DESIGN



ii. **Selection of biopolymer:** Three biopolymers i.e. beta- cyclodextrins chitosan and sericin were taken and one biopolymer each was selected for the natural and synthetic dye on the basis of percent dye absorption, colour strength (k/s) value and wash fastness in terms of colour change (CC) of dyes. Biopolymers were applied using the following methods:

a) **Beta-cyclodextrin:** The surface modification of cotton fabric was carried out with beta cyclodextrin (0.75 g/l) and cross-linking agent (citric acid 0.25 g/l) at 80^0C for 60 minutes using 1:30 M:L Ratio. The treated samples were washed and dried **(Sundrarajan *et al.*, 2012).**

b) **Chitosan application:** Scoured cotton fabric was soaked in 1 % chitosan solution (dissolved in 1% acetic acid (v/v) containing 6% citric acid and 6% sodium hypophosphite and squeezed in padding mangle for uniform fixing and dried at 80^0C for 10 minutes followed by fixing at 100^0C for 5 minutes **(Sundrarajan *et al.*, 2012).**

c) **Sericin application:** Cotton sample was dipped in 0.50 percent sericin solution (owf) with 4% concentration of citric acid and 1% sodium hypophosphite using 1:30 material to liquor ratio at pH 8.0. The fabric was treated for 45 minute at 50^0C temperature. The fabric was passed between padding rollers, dried at 70^0C for 4 minutes and cured at 150^0C for 2 minutes **(Bhandari, 2014).**

3.1.4 Procurement and selection of cross-linking agent and catalyst: Different laboratory grade chemicals were selected for study on the basis of available literature, easy availability and eco-friendly nature. Toxic and banned chemicals were excluded from experimental work.

i. **Procurement of cross-linking agent and catalyst:** Three cross-linking agents [Butan-tetra carboxylic acid (BTCA), Citric acid and Glyoxal] and three catalysts [Magnesium chloride ($Mgcl_2$), Phosphoric acid and Sodium hypophosphite] were procured from HIMEDIA Company.

ii. **Selection of cross-linking agent and catalyst**: All the three cross-linking agents and catalysts were applied with selected biopolymer. On the basis of percent dye absorption, colour strength (k/s) value and wash fastness (colour change) basis one cross-linking agent and one catalyst was selected.

3.1.5 Assortment and selection of natural dye

i. **Assortment of natural dye material:** On the basis of available review, eight dye yielding plants having bacterial efficacy were taken. Only renewable parts of the plant and waste parts were used. The fresh leaves, flowers, fruits and vegetables waste parts were collected, washed to remove debris and shade dried. After being completely dried, the material was crushed into small pieces, pulverized into coarse powder and stored in a air tight containers free from environmental climatic changes, till usage.

ii. **Selection of natural dye:** All the eight natural dyes were applied on cotton samples after treatment with different biopolymers. On the basis of percent dye absorption, colour

strength (k/s) value and wash fastness (CC), one natural dye was selected. The list of plants used as dyes for dyeing of cotton fabric for selection of one dye are given in the Table 3.1.

Table 3.1: Plants material used for dyeing of cotton fabric for selection of dye

S. No.	Local name of the plant	Botanical name of plant	Family	Part used as dye
1.	Banana	*Musa balbisiana*	Musaceae	Leaves
2.	Guava	*Psidium guajava*	Myrtaceae	Leaves
3.	Mango	*Mangifera indica*	Anacardiaceae	Leaves
4.	Marigold	*Calendula officinalis*	Calendulaeae	Petals
5.	Onion	*Alleum cepa*	Amaryllaidaceae	Bulb outer skin
6.	Peanut	*Arachis hypogeae*	Fabaceae	Skin
7.	Pomegranate	*Punica granatum*	Punicaceae	Rind
8.	Teak	*Tictona grandis linn*	Lamiaceae	Leaves

The dyeing of cotton fabric was done with different natural dyes using following method.

Dyeing with natural dyes: The pre-mordanting of scoured cotton fabric was done with 15 % mordant (alum) owf, treated at 60°C temperature for 45 minute using of 1:20 M:L Ratio. Dyeing of mordanted cotton samples was done with 5% dye owf using 1:30 M:L Ratio at 70 ^{0}C for one hour. The samples were washed with hot water followed by cold water and dried in shade **(Annapoorani and Sundarraj, 2014 and Saravanan *et al.*, 2013).**

3.1.6 Selection of extraction method for natural dye: Extraction refers to separating the desired colour components by physical and chemical means with aid of solvent. On the review basis three different mediums of extraction were used and one medium of extraction was chosen on the basis of presence of phytochemicals in dye extract, simplicity of process and cost. The extraction of selected dye was done using following methods:

i. **Aqueous extraction:** Aqueous extraction was traditionally used to extract dyes from plants and other materials. The dye containing material was first broken into small pieces, powdered and sieved to improve extraction efficiency. Aqueous extract was prepared by soaking 10 g of dye powder in 100 ml distilled water, in a stainless steel vessel overnight to loosen the cell structure. The mixture was boiled at 80-85°C for 1 hour to get the dye solution, allowed to stand till it reached to room temperature and filtered to remove non dye plant remnants **(Lokesh and Kumara-Swamy, 2013).**

ii. **Ethanolic extraction:** Dye powder was soaked in 100% ethanol and heated in a beaker, in water bath at 45-50°C for 1 hour to get the dye solution, allowed to cool at room temperature and then filtered to remove non dye plant remnants **(Lokesh and Kumara-Swamy, 2013).**

iii. **Methanolic extraction:** 5 g of dye powder was soaked in 100 ml methanol at 45-50°C for 1 hour to get the dye solution and allowed to cool till it reached to room temperature. The solution was filtered to remove non dye plant remnants and sieved through fine mesh nylon cloth **(Lokesh and Kumara-Swamy, 2013).**

The extracts were sieved through fine nylon mesh and filtrate was collected for phytochemical analysis.

3.1.6.1 Phytochemical analysis of the dye extract: The phytochemiocal analysis of the dye extract was done using standard procedure given by **Edeogal *et al.* (2005) and Selvi *et al*. (2011).** The following analysis was done:

a) **Alkaloids:** Plant extracts were boiled with 1% aqueous HCl in water bath and filtered. The filterate was treated with 2g iodine in 6g of KI (Potassium Iodide) in 100 ml distilled water. Formation of brown or reddish brown precipitate indicated presence of alkaloids.

b) **Phenol:** Phenols were tested by adding 2 ml of ferric chloride solution to 2 ml of plant extract. Appearance of bluish green colour solution indicated the presence of phenols.

c) **Tannins:** Few drops of 1% lead acetate were added to 5 ml of plant extract and appearance of yellow precipitate indicated the presence of tannins.

d) **Saponins:** 5 ml of extract was boiled in 10 ml distilled water in a test tube and was shaken vigorously for about 30 seconds. The test tube was allowed to settle for half an hour, formation of froth indicated the presence of saponins.

e) **Steroids:** 1 ml dye extract was dissolved in 10 ml chloroform and equal volume of concentrated sulphuric acid was added from the walls of the test tube. Appearance of red colour in the upper layer with yellow with green fluorescence indicated the presence of steroids.

f) **Cardiac glycosides:** 1 ml of dye extract was added in glacial acetic acid with few drops of ferric chloride followed by adding concentrated sulphuric acid from the walls of the test tube. Appearance of the reddish brown colour at the junction of two layers and the bluish green colour in the upper layer indicated the presence of cardiac glycosides.

g) **Anthraquinones:** 5 ml of dye extract was boiled with 10 ml of sulphuric acid and filtered while hot. The filtrate was shaken with 5 ml of chloroform. The chloroform layer was pipette out into another test tube and 1 ml of dilute ammonia was added. The resulting solution was observed for colour changes. The change in colour indicated the presence of anthraquinones.

h) **Flavonoids:** A few drops of dilute sodium hydroxide were added to 1 ml of extract. An intense yellow colour was observed which became colourless on addition of few drops of dilute acid. This indicated the presence of flavonoids.

i) **Terpenoids:** 1 ml of extract was dissolved in 1ml of chloroform and 1ml of acetic anhydride was added following the addition of 2ml of concentrated sulphuric acid. Formation of reddish colour indicated the presence of terpenoids.

j) **Reducing sugar:** Five to ten drops of Felhing solution were added in 1 ml of dye extract. Mixture was then subjected to boiling for 15 minutes, appearance of brick red precipitate indicated the presence of reducing sugar.

3.1.7 Selection of synthetic dye*:* Dyes predominantly used for dyeing cotton fabric were taken i.e. reactive and direct dyes. Besides these, acid dyes were also taken into account to know the effect of biopolymer treatment on absorption of acid dye on cotton fabric. Percent dye absorption, colour strength (k/s) value and wash fastness rating were used for selection of one synthetic dye. Dyeing of different biopolymer treated cotton fabric with synthetic dyes was done using the following method.

i. **Dyeing with direct dye:** The fabric samples were immersed in dye bath containing 1% direct dye, 20 percent glauber's salt on the weight of fabric and soda ash (5% owf) keeping 1:40 M:L Ratio at 90 ^{0}C for 60 minute followed by wash with hot and cold water and was air dried **(Chattopadhyay and Inamdar, 2010).**

ii. **Dyeing with reactive dye:** Cotton fabric samples were treated with different biopolymers separately and dyed with reactive dye in absence of electrolyte (salts). Control sample was dyed in presence of electrolyte instead of biopolymers. The samples were dyed using aqueous bath containing 1percent Cibacron® Red LS-B (C.I. Reactive Red 270) reactive dye, 15 g/l sodium sulphate, 10 g/l sodium carbonate with M:L Ratio 1:50 and the temperature of the dyeing bath was gradually raised from 30 to 60^{0}C for 160 minutes. The dyed fabric was rinsed with hot water followed by cold water and finally dried at room temperature **(Salama *et al.*, 2015).**

iii. **Dyeing with acid dye:** Cotton fabric samples were treated with different biopolymers separately and dyed with acid dye in absence of electrolyte or salt. The control sample was dyed in presence of electrolyte or salt instead of biopolymers. Cotton fabric samples were dyed in an aqueous bath containing 1percent acid dye together with 2 percent sodium sulphate using M:L Ratio at pH 5 and temperature 40^{0}C and raised to 100^{0}C for 60 minutes. The dyed fabrics so obtained were rinsed with hot water followed by cold water and finally dried at room temperature **(Ramadan *et al.*, 2012).**

Synthetic dyes (Table 3.2) were applied on biopolymer pretreated cotton fabric for selection of one dye on the basis of dye absorption, colour strength and wash fastness.

Table 3.2: Synthetic dyes used for dyeing of cotton fabric

S. No.	Dye classes	Dye names
1.	Direct	Direct red
		Direct Chloragol Orange RS
		Direct Chlorantine Fast Yellow 5GLL
		Direct Shakuntala Green BD
		Direct Brown
2.	Reactive (hot)	Reactive red
		Turquoise HTG
		Brown H4R
3.	Reactive (cold)	Reactive blue MR
		Reactive cold M2R
		Reactive cold red M8B
4.	Acid	Acid yellow
		Acid red
		Acid black

3.2 Preliminary Properties of Cotton Fabric

Preliminary data of the selected fabric was taken using standard procedure.

3.2.1 Fabric count: The fabric count is the number of warp (ends) and filling yarns (picks) per inch in a woven fabric. Paramount pick glass with pointer was used to determine fabric count using BS 2862:1957 standard test method. It was determined by counting the number of threads per square inch in warp and weft directions at five different places in the fabric. An average of five readings was taken.

3.2.2 Fabric weight: The weight of fabric is defined as weight of a known area of the material and then computing the weight per unit area. Samples were cut at random from fabric with the help of round cutter for GSM. The samples were weighed separately on the Paramount Precision Scale for grams per square meter using ASTM –D 3776-90 test method. An average of five readings was taken and weight per unit area in grams per square meter was calculated.

3.2.3 Fabric thickness: Fabric thickness is defined as the distance between two parallel surfaces while exerting a specified pressure on the material. Paramount thickness tester was used to determine the thickness of fabric using BS 2544:1967 test method. A specimen was placed on flat surface below pressure foot of the instrument without any folds and wrinkles. The pressure foot was lowered upon the specimen gently until the pointer of the dial meter stopped moving further and the reading on the dial gauge was recorded in mm. An average of five readings was calculated as the fabric thickness.

3.3 Preparation of the Cotton Fabric

To ensure complete wetting and uniform absorbency of the extracts during the padding, it must undergo preparatory processes. Desizing and scouring treatments were given to the woven cotton fabric to remove foreign materials before imparting finish.

3.3.1 Enzymatic desizing: The cotton fabric was given desizing treatment using 2ml/l Americos Amylase 543 at 60^0C temperature for 60 minutes with 1:20 material to liquor ratio by maintaining 7 pH. The treatment liquor was drained out and given one hot rinsed and cold wash and dried. **(Vigneshwaran *et al.*, 2013)**

3.3.2 Enzymatic scouring: Desized cotton fabric was scoured in a bath containing 1.5 % (owf) Palkoscour APCL enzyme, at 60 ^{0}C for 60 minutes at material to liquor ratio 1:15 maintained at 7.0 pH. The fabric was rinsed in hot and cold water and dried **(Rajendran *et al.*, 2011).**

3.4 Standardization of Biopolymer Treatment

Biopolymers are suitable replacement materials for different chemical processes. Biopolymer pre-treatment was given to improve the dyeability of cotton fabric. Different concentrations and conditions were taken on review basis for standardization. On the basis of percent dye absorption, colour strength (k/s) value and wash fastness of treated and dyed samples, different treatment parameters were optimized. The biopolymer treatment was optimized on the following parameters:

3.4.1 Optimization of biopolymer concentration: To determine the optimum concentration of the selected biopolymer, five concentrations of biopolymer i.e. 1, 2, 3, 4, 5 percent for natural dye and five concentrations of biopolymer i.e. 1.0, 1.5, 2.0, 2.5, 3.0 percent for synthetic dye were taken. During the application of the finish, other variables (concentration of cross-linking agent: 4 %, concentration of catalyst: 4%, pH: 5.0, treatment temperature: 80 ^{0}C, treatment time: 30 minutes, drying temperature: 80 ^{0}C, drying time: 5 minutes, curing temperature: 130 ^{0}C and curing time: 2 minutes) were kept constant. The material to liquor ratio was taken as 1:20. After treatment, the samples were taken out and given a hot followed by the cold water rinsing to neutralize the treatment effect. Biopolymer treated samples were dyed with selected natural and synthetic dye and concentration of biopolymer was optimized.

3.4.2 Optimization of cross-linking agent concentration: The determination of concentration of selected cross-linking agent was carried out using five different concentrations i.e. 3, 4, 5, 6, 7 percent for natural dye and 1, 2, 3, 4, and 5 percent for synthetic dye. The optimized concentration of biopolymer keeping other variables constant (3.4.1) was given. The concentration at which maximum percent dye absorption, colour strength (k/s) and wash fastness was observed in natural and synthetic dyed samples; selected as optimum concentration of cross-linking agent for biopolymer treatment natural and synthetic dye.

3.4.3 Optimization of catalyst concentration: Biopolymer treatment was given at optimized concentration of biopolymer and cross-linking agent keeping other variables constant (3.4.1) using five different concentrations of catalyst viz. 2, 3, 4, 5 and 6 percent for natural dye and 1, 2, 3, 4 and 5 percent catalyst concentrations for synthetic dye. The concentration on the basis of maximum percent dye absorption, colour strength (k/s) and wash fastness in dyed samples was selected as optimum concentration of catalyst.

3.4.4 Optimization of treatment pH: The treatment solutions were prepared keeping different pH values i.e. 3, 4, 5, 6, 7 for natural dye and 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0 for synthetic dyes using optimized concentration of biopolymer, cross-linking agent, catalyst keeping other variables constant (3.4.1). After biopolymer treatment, samples were dyed with selected natural and synthetic dyes at pH value which exhibited maximum percent dye absorption, colour strength (k/s) and wash fastness grades was selected as optimum treatment pH.

3.4.5 Optimization of material to liquor ratio: For determination of optimum M:L Ratio of treatment solution, four different ratios i.e.1:10, 1:20, 1:30 and 1:40 were taken with optimized concentration of biopolymer, cross-linking agent, catalyst and pH value while other variables were kept constant (3.4.1). On the basis of maximum percent dye absorption, colour strength (k/s) and wash fastness values of dyed samples, M:L Ratio was optimized.

3.4.6 Optimization of treatment temperature: The treatments were carried out at five different temperatures viz. 60^0, 70^0, 80^0, 90^0 and 100^0C for natural dye and 50^0, 60^0, 70^0, 80^0 and 90 ^{0}C for synthetic dye and using optimized concentration of biopolymer, cross-linking agent, catalyst set at optimized pH value keeping optimized M:L Ratio while other variables were kept constant (3.4.1). The temperature reflecting the maximum percent dye absorption, colour strength (k/s) and wash fastness grade was selected as optimum treatment temperature.

3.4.7 Optimization of treatment time: Biopolymer treatments were given to the fabric samples for four different durations i.e. 15, 30, 45, 60 minutes for natural dye and five different durations viz. 15, 30, 45, 60 and 75 minutes for synthetic dye using optimized concentrations (biopolymer, cross-linking agent, catalyst) and conditions (pH value, M:L Ratio and treatment temperature). The fabric samples were passed between the squeezing rollers. Subsequently the treated samples were dried at 80^0C for 5 minutes and cured at 130^0C temperature for 2 minutes duration of time. The treated samples were dyed and optimum treatment time was selected on the basis of maximum dye absorption, colour strength (k/s) and wash fastness grade.

3.4.8 Optimization of drying temperature: For the optimization of drying temperature, fabric samples were treated with optimized concentration of biopolymer, cross-linking agent, catalyst and optimized conditions of pH value, M:L Ratio, treatment temperature and treatment time. The samples were passed through padding mangle for application and were dried at five different temperatures i.e. 60^0, 70^0, 80^0, 90^0 and 100^0C for 5 minutes and subsequently cured at

130^0C for 2 minutes. Temperature exhibiting maximum dye absorption, colour strength (k/s) and wash fastness grades in dyed samples was taken as optimum drying temperature.

3.4.9 Optimization of drying time: For the determination of optimum drying time, samples were immersed in padding bath consisting of optimized concentration of biopolymer, cross-linking agent and catalyst under the optimized conditions (pH, treatment temperature) using optimized M:L Ratio for optimum time of treatment. The impregnated samples passed between the rollers of padding mangle. Drying of treated samples was carried out at five different time durations i.e. 3, 4, 5, 6 and 7 minutes at optimum drying temperature and were cured at 130^0C temperature for 2 minutes. Samples were dyed with selected natural and synthetic dye. Optimum drying time reflecting maximum dye absorption, colour strength (k/s) and fastness to wash was taken as optimum.

3.4.10 Optimization of curing temperature: For the optimization of curing temperature, fabric samples were treated using optimized concentration of biopolymer, cross-linking agent, catalyst and optimized conditions of pH, M:L Ratio, treatment temperature and time, drying temperature and time and curing treatment was carried out at five different temperature ranges i.e. 110^0, 120^0, 130^0, 140^0, 150^0C for 2 minutes of curing time. Temperature giving maximum dye absorption, colour strength (k/s) and wash fastness was selected as optimum curing temperature.

3.4.11 Optimization of curing time: Fabric samples were treated using the optimized concentrations of biopolymer, cross-linking agent and catalyst with the optimized conditions of pH value, M:L Ratio, treatment temperature and time, drying temperature and time, curing temperature and time. After application of biopolymer treatment, the padded samples were cured at four different durations of time i.e. 1, 2, 3 and 4 minutes for natural dye and five different durations viz. 1, 2, 3, 4 and 5 minutes for synthetic dye. The time exhibiting the maximum percent dye absorption, colour strength (k/s) and wash fastness was selected as optimum curing time.

Application of biopolymer through standardized treatment process on cotton fabric: The biopolymer treatment was given on scoured cotton fabric through pad dry cure method using different optimized treatment variables. Each cotton sample was impregnated in a solution containing biopolymer, cross-linking agent and catalyst in optimized proportion and was pressed between the squeezing rollers of the padding mangle. The pressure of 2kg/cm was maintained and a 70-75% expression was achieved. The samples were dried and cured at optimized temperature for optimum duration.

3.5 Standardization of Dyeing Process for Natural Dye

The dyeing process was standardized for biopolymer treated fabric. Experiments were undertaken to optimize dye concentration, dyeing pH, dyeing temperature, dyeing time and material to liquor ratio on the basis of the dye absorption, colour strength (k/s) and wash

fastness properties. The dyeing process was standardized for optimization of following parameters:

3.5.1 Dye concentration: Five different concentrations of natural dye powder i.e. 3, 4, 5, 6 and 7 percent were taken on the weight of fabric (owf) and soaked overnight in five different beakers containing 100 ml distilled water each. These beakers were kept in water bath for 1 hour and the temperature was set at 100^0C for complete extraction of dye. These solutions in different beakers were stirred after regular interval of 15 minutes. The dye solution was allowed to stand for half an hour to bring it at normal room temperature. The residual material was strained out through nylon cloth and centrifuged for obtaining the clear dye extract. The pH of dye extracts was maintained at 5.5 using 60 percent sodium hydroxide. The 2 ml dye extract was taken from each beaker containing different concentrations of dye material for determination of optical density. The biopolymer treated cotton samples were soaked in water for 10 minutes for wetting out and immersed in dye bath having 1:30 M:L Ratio. The dyeing process was started at 60° C, and temperature was gradually raised to 100° C, dyeing continued for 60 minutes with frequent stirring for uniform dyeing. The dyed samples were rinsed with warm water followed by the cold water and finally dried in shade. The concentration of the dye material giving maximum dye absorption, colour strength (k/s) and wash fastness was selected as an optimum dye concentration.

Percent dye absorption of different natural dyes was measured using optical density (OD) of the dye extract. The exhaustion values of dye bath were measured by taking the absorbance of the dye liquor (before and after dyeing) using UV-visible spectrometer. Before and after dyeing process, 2 ml of dye solution from each beaker was taken out, and optical density was taken on spectrophotometer at 400 nm wavelength and percent dye absorption was calculated using the following formula

$$\text{Percent dye absorption} = \frac{\text{OD before dyeing} - \text{OD after dyeing}}{\text{OD before dyeing}} \text{ X } 100$$

3.5.2 Dyeing pH: The pH of a dye bath is an important influencing factor for the absorption of natural dye on cotton. The pH of dye solutions in different pH ranges i.e. 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.5 was adjusted with glacial acetic acid. The effect of pH on the absorption of selected natural dye on cotton fabric, with optimized dye concentration while keeping other variables constant (3.5.1) was observed. The pH value which gave maximum dye absorption and wash fastness was selected as optimum pH for dyeing with natural dye.

3.5.3 Material to liquor ratio: The effect of material to liquor ratio on the absorption of dye on biopolymer treated cotton cloth was investigated keeping different M:L Ratios i.e. 1:20, 1:30, 1:40 and 1:50 using optimized dye concentration and pH while other variables were kept constant (3.5.1). M:L Ratio exhibiting maximum dye absorption and wash fastness was taken as optimum M:L Ratio for dyeing biopolymer treated cotton fabric.

3.5.4 Dyeing temperature: The cotton samples which were pretreated with biopolymer, dyed in dye baths containing optimized concentration of natural dye and the dyeing process was performed at optimized conditions pH, M:L Ratio while other variables were kept constant (3.5.1) at different temperatures i.e. 60^0, 70^0, 80^0, 90^0 and 100^0C. The temperature showing the maximum dye absorption, colour strength (k/s) and wash fastness was taken as optimum dyeing temperature.

3.5.5 Dyeing time: The dyeing time and its impact on the dye absorption and wash fastness was studied in order to determine the optimum dyeing time. The biopolymer treated fabrics were dyed with selected natural dye for different durations i.e. 30, 45, 60, 75 and 90 minutes with optimized dyeing parameters (dye concentration, pH, M:L Ratio, dyeing temperature). The time showing maximum dye absorption, colour strength (k/s) and wash fastness, was selected as optimum dyeing time.

Application of selected natural dye using optimized process on biopolymer treated cotton fabric: Dyeing was carried out in a water bath, keeping M:L Ratio 1:30. Before dyeing, the cotton fabric samples were given biopolymer treatment with optimized process. Biopolymer treated sample was dyed in the dye bath containing optimized concentration of dye set at optimized pH. The temperature of dye bath was raised gradually from 60^0 to 100^0C and kept constant at 100^0C for one hour with gentle stirring and dye bath was allowed to cool for 15 minutes. The material was removed from dye bath, rinsed with hot water followed by cold water to remove the unfixed and hydrolyzed natural dye, squeezed and dried at room temperature in shade. The fabric samples were conditioned at 27 ± 2ºC with relatively humidity of 65 ± 2% for at least 24 hours prior to further use.

3.6 Standardization of Dyeing Process for Synthetic Dye

The dyeing process for selected synthetic dye was standardized for biopolymer treated fabric. Experiments were conducted to optimize dye concentration, dyeing pH, dyeing temperature, time and material to liquor ratio on the basis of percent dye absorption, colour strength (k/s) value and wash fastness properties. The following dyeing parameters were optimized:

3.6.1 Dye concentration: Five different concentrations of selected synthetic dye i.e. 1.0, 1.5, 2.0, 2.5, 3.0 percent were taken (owf) and soaked in five different beakers maintaining 1:30 material to liquor ratio. The biopolymer treated samples were wetted out in water for 10 minutes, transferred into each beaker containing the dye liquor and kept in water bath. The dyeing process was started at 50° C and was gradually raised to 60° C. The dyeing continued for 45 minutes with frequent stirring. The dyed samples were rinsed with warm water followed by the cold water and finally dried in shade. Before and after dyeing process, 2 ml of dye solution from each beaker was taken out, and optical density was taken on spectrophotometer at 400 nm wavelength and percent dye absorption was calculated. The

concentration of the dye material exhibiting maximum dye absorption and wash fastness grade was selected as an optimum dye concentration.

3.6.2 Dyeing pH: For the optimization of pH, dye bath were set at pH 3.5, 4.0, 4.5, 5.0 and 5.5 with glacial acetic acid. The biopolymer treated samples were dyed with optimized dye concentration while other variables were kept constant (3.6.1). The pH value which showed maximum dye absorption and wash fastness value was selected as optimum dyeing pH for selected synthetic dye.

3.6.3 Material to liquor ratio: Material to liquor ratio is another important parameter which influence the exhaustion of dye. The effect of material to liquor ratio on the absorption of selected dye on biopolymer treated cotton fabric was investigated keeping different material to liquor ratios i.e. 1:20, 1:30, 1:40 and 1:50 using optimized dye concentration, dyeing pH, keeping other variables constant (3.6.1). Material to liquor ratio having maximum dye absorption and wash fastness was taken as optimum material to liquor ratio for dyeing biopolymer treated cotton fabric.

3.6.4 Dyeing temperature: The biopolymer treated cotton samples were dyed in dye baths containing optimized concentration of synthetic dye, pH, using optimized M:L Ratio keeping dyeing time constant (3.6.1). The dyeing temperature was varyed i.e. 50^0, 60^0, 70^0 and 80^0C. The temperature at which maximum dye absorption and wash fastness was obtained, taken as optimum dyeing temperature.

3.6.5 Dyeing time: The biopolymer treated fabrics were dyed with selected dye for different durations i.e. 15, 30, 45, 60 and 75 minutes using optimized dyeing parameters. The optimum dyeing time was selected on the basis of maximum percent dye absorption and wash fastness grades.

Application of synthetic dye on cotton fabric using optimized process parameters: The dyeing of the cotton fabric was done after biopolymer treatment. The dye was applied on cotton fabric through exhaust dyeing method using optimized dye concentration and dyeing conditions. After dyeing, the fabric was taken out and washed with hot water followed by cold water to remove the unfixed dye and shade dried.

3.7 Measurement of Total Dissolved Solids (TDS)

The presence of total dissolved soilds (TDS) was measured in the used dye liquor. TDS values were measured using the digital HM Digital TDS-3 Handheld TDS Meter which was highly accurate due to its advanced microprocessor technology with measurement range from 0-9990 ppm showing temperature along with TDS value. When the sensor rods of TDS meter were dipped into the solution to be tested, displayed the readings. The TDS values of left over dye liquors of samples pretreated with alum, alkali and biopolymer and dyed with selected natural and synthetic dyes were measured. An average of three readings for each sample was taken.

3.8 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier transform infrared spectroscopy (FTIR) analysis was done to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. The characterization in terms of interactions and chemical composition of selected biopolymer, natural and synthetic dye powder was measured using potassium bromide (KBr). FTIR analysis of dye powders was got done from ***SAIF PU, Chandigarh***. The FTIR analysis of biopolymer treated, natural and synthetic dyed cotton fabrics was got done at ***SAIF, IIT Madras***.

3.9 Assessment of Colour Properties of the Dyed Fabrics

The dyed fabrics were assessed for colour properties i.e. colour measurements and colour fastness. The colour of dyed samples measured in terms of percent dye absorption, colour coordinates and colour strength was assessed against different agencies i.e. wash, light, perspiration and rubbing fastness.

3.9.1 Colour measurement: The methods of measuring colour numerically were established by the Commission International del 'Eclairage (CIE) in 1931 and 1976. These methods provide uniform colour differences in relation to visual differences. Also the measurement of colour is precise and colour is specified by a set of numbers, which can be used to re-create the original colours at any other time and place i.e. reproduction. Measurement of colour increases the objectivity of the experimental results of dyeing (Giles, 1974 and Valia, 1987).

The colours of dyed samples were measured numerically through computerized colour matching machine. The reference spectra of dyed samples were observed by using spectrophotometer SS5100A, K/S value and CIE LAB co-ordinates L*, a* and b* were noted down directly from the computer screen. This spectrophotometer uses CIE LAB (1976) colour space, D65 illuminate matching and appraisal and 420 nm wavelength to measure the actual colour and change in colour. The kubelka munk theory was used to predict the colour value.

$$K/S= (1-R)^2 /2R$$

Where,

K= constant about the light absorption of the dyed fabric

S= constant about the light scattering of the dyed fabric

R= reflectance of the dyed fabric, expressed in fractional form

The CIE LAB colour space uses L*, a* and b* scales to describe colour. L* is a measure of darkness/lightness of colour of an object and range from 0 (black) to 100 (white), a* of redness (+ve a*) or greenness (- ve a*), b* of yellowness (+ve b*) or blueness (-ve b*), C* of dullness/brightness and H* is a measure of hue.

3.9.2 Assessment of colour fastness properties of dyed fabrics*:* Fastness is the ability of dye to retain its colour after exposure to sun, perspiration, rubbing, washing or other colour destroying agents (Wingate, 1988). Natural destructive agents like, weather, oxygen and other

atmospheric gases can fade and destroy certain dyes. All the dyed samples were evaluated for colour fastness to wash, rubbing, light and perspiration using the methods prescribed by bureau of Indian standards.

i. **Fastness to washing:** Wash fastness test was carried out as per recommendation of IS: 3361-1979 method (BIS, 1979). The dyed samples were placed between two pieces of bleached fabrics measuring 10cmX 4cm (in parallel lengths). One piece was of the same material as of dyed sample i.e. cotton and other piece was of wool fabric. Two pieces of fabric were stitched together, taking the sample in between the stitches. The composite specimen were weighed and required quantity of soap solution at the rate of 5 gm/litre water was prepared keeping material to liquor ratio 1:50. One composite specimen was placed in each of eight containers of launder-o-meter and the soap solution was added to it. The specimen were treated for 45 minute at 50 ± 2^0 C in the launder-o-meter, removed and rinsed in cold water. The samples were squeezed and the stitching along the two long sides and one short side was removed. The samples were opened and dried in air with remaining line of stitching. The change in colour of dyed samples was assessed with grey scale no.1 as per the recommendation of the ISO 105 method.

   The nine- step scale consisting of half fastness rating was used. A piece of original dyed sample and the test specimen was placed side by side in the same plane. The light was incident upon the surfaces at approximate angle of 45^0 and the direction of viewing approximately perpendicular to the plane of surface. The visual differences were compared between the original and tested material with the difference represented by the Grey Scale. The fastness rating of the specimen was the number of grey scale which has a perceived colour difference nearest in magnitude to perceived colour difference between the original piece and the tested specimen. Also the degree of staining on the bleached cloth was assessed with the help of grey scale No. 2 for staining.

ii. **Fastness to sunlight:** Light fastness is defined as the resistance to fade or hue change of a coloured object when exposed to light source, most notably sunlight or the resistance of a material to change its colour characteristics as a result of exposure of the material to sunlight or the artificial light source. The apparatus used for testing of fastness to sunlight was the exposure rack. The fastness to sunlight was carried out according to IS: 686 - 1985 method (BIS, 1985). The test specimens were mounted in exposure rack in such a way that half of each specimen was covered and the other half was exposed to light. The samples were exposed to daylight everyday from sunrise to sunset in the month of June, keeping the exposure rack at an angle of 45^0 and the total exposure time being 48 hours. The change in colour of the exposed portion was compared with that of the unexposed portion using grey scale.

iii. **Fastness to perspiration:** The fastness to perspiration was tested using the test IS: 971 - 1983 method prescribed by the Bureau of Indian Standards (BIS, 1983). The acidic test liquor was prepared by dissolving 0.5 gm of L-Histidine monohydrochloride monohydrate, 5gm of sodium chloride and 2.2 gm of sodium dihydrogen orthophosphate dehydrate in one liter of water. The solution was brought to pH 5.5 with 0.1 N acetic acid solution. The alkaline test liquor was prepared by dissolving 0.5 gm of L-Histidine monohydrochloride monohydrate, 5gm of sodium chloride and 2.5 gm of disodium hydrogen orthophosphate dehydrate in one liter of water. The solution was brought to pH 8.0 with 0.1 N sodium hydroxide solution. The composite specimens were prepared in the same manner as for the wash fastness test (3.9.2.1). The test specimen were soaked in the acidic and alkaline test solutions separately with material to liquor ratio 1:50 for 40 minutes at room temperature. The treated samples were kept between two acrylic plates of perspirometer under a force of 5 kg. The loaded apparatus was kept in hot air oven for four hours at 37 ± 2^0C. The test samples were removed from the oven and air dried with temperature not exceeding 60 ^{0}C. The numerical grading for colour change of the test pieces and for staining of the two adjacent pieces was done using Grey Scale.

iv. **Fastness to rubbing:** Fastness to rubbing means the resistance of textile material to every type of rubbing and staining from the textiles in actual use. The fastness to rubbing was carried out according to IS: 776 -1986 method (BIS, 1988). The samples were made for carrying out the dry as well as wet rubbing tests. One test sample was taken and fixed to rubbing device of crock meter. The bleached cotton sample of size 2x2cm was fixed to the finger of rubbing device of crock meter. The test specimen was rubbed to and fro with the bleached piece with a download force of 900 gm in straight line, along a track of 10 cms for 10 times in 10 seconds. The test specimen was graded for the change in colour and staining using the grey scale. The test was carried out similarly for wet rubbing fastness using wet bleached white cotton fabric for fixing to the finger of rubbing device of crock meter.

3.10 Testing of Physical and Functional Properties

Physical and functional properties of samples (controlled, treated, dyed and washed) were measured as per the standard methods. The fabric samples were exposed to standard conditions for at least 24 hours before the final measurement as recommended by B.S. Handbook. The standard conditions were maintained as:

Relative humidity (%) : 65±2

Temperature : 27 ± 2^0c

The fabric samples were assessed measuring the following properties using standard test procedure.

3.10.1 Physical properties of different treated and dyed samples

Physical (preliminary, mechanical and performance) of controlled, alum and alkali pretreated dyed fabric and chitosan pretreated dyed samples were tested using standard test methods.

i. **Preliminary properties of different treated and dyed samples:** The fabric count, weight and thickness of the treated and washed fabrics were tested as per procedure mentioned in section (3.2) respectively.

ii. **Mechanical properties of different treated and dyed samples**

a. **Bending length:** Bending length is the length of fabric that will bend under its own weight to a definite extent. The bending length of the samples was determined by the paramount stiffness tester using BS 3356.1961 standard test method. Samples of size 25×200 mm were cut from warp and weft directions with the aid of template and conditioned. 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 the plate form. The template was moved slowly over 41.50 slope along with the strip till the top of the specimen viewed in the mirror cut in between both index lines. The bending length for both directions was read from the scale, which coincided with the front edge of the top plate. Each sample was tested five times at each edge.

b. **Tensile strength:** Tensile strength is the ability of the fabric to withstand the load of force usually expressed as kilograms and percent elongation of fabric corresponding to the tensile strength is the length of the sample at breaking point. Tensile strength along with elongation of samples was determined on the paramount digital tensile strength tester for textile, using IS 4169 standard test method. The samples of size 6×4 ± 0.05 inches were cut out from warp and weft directions of the fabric with the help of template. The samples were mounted between the jaws with approximately 1.5 inch of fabric protruding from each side of the jaws at a distance of 3 inches .The speed of upper jaw was adjusted at 300±10mm/min. The machine was started and the upper jaw moved in upward direction. The readings were taken from the digital display at sample break. The samples were slightly tensioned for getting accurate elongation at break. Five readings of the samples from both the directions (warp and weft) were taken and the averages were calculated.

c. **Elongation:** Elongation is the ability of the fabric to be stretched, extended or lengthened. Elongation of the fabric measured along with tensile strength through the digital monitor screen fitted on the tensile strength tester which gives elongation reading along with tensile strength of the fabric. The elongation was measured to calculate the elongation percent of the fabric by following the standard test method IS 4169 used for tensile strength testing.

iii. Performance properties of different treated and dyed samples

a. Crease recovery angle: Wrinkle recovery is the resistance to and recovery from creasing. Resistance to creasing depends on the rigidity while recovery depends on the elasticity. The measure of crease recovery is the angle at which the sample recovers from creasing. The wrinkle recovery was determined on the Shirley crease recovery tester using BS 3086:1972 test method. Samples were cut both in warp and weft directions from the fabrics with a template measuring 0.5 cm × 2.5cm and were tested after conditioning. The test specimen was carefully creased by folding in half and was placed between the two glass plates .The specimen was creased for 3 minutes under 2 kg weight. The specimen was removed and transferred to the fabric clamp in the instrument and allowed to recover from the crease for 3 minutes. As it recovers, the dial of the instrument was rotated to keep the free edge of the specimen in line with the knife-edge. The recovery angle in degree was noted from the engraved scale. Warp and weft way recovery was observed separately to the nearest degree from the mean values of the five readings in each direction.

b. Moisture regain: Moisture regain was measured using BS1051:1960. The amount of moisture in a sample of material may be expressed in terms of regain of moisture content. Moisture regain is defined as the weight of the water in a material expressed as percentage of the oven dry weight. The oven dry weight is defined as the constant weight obtained by drying at a temperature of 105 ± 3^0C. The oven was preheated for 10-15 minutes to reach the controlled temperature and the samples were placed in dry oven at 105 ± 3^0C for 3 hours. The closed container was transferred to desiccator when the container and the specimen were kept at room temperature. The samples were weighed and an average mean of five readings was calculated. The percentage of moisture regain was calculated using the following formula:

$$\text{Percentage moisture regain} = \frac{\text{Original weight} - \text{Oven dry weight}}{\text{Oven dry weight}} \text{ x } 100$$

c. Air permeability test: Air permeability is the property of the fabric to allow air passing through under the effect of different pressure .The corresponding measurement was that of the quantity of the air passing through a surface of defined magnitude, under a defined pressure difference and within a determined period of time. The samples were tested and placed it on the opening on the test cylinder under the clamping place. The clamp was tightened to the sample firmly and was checked that all the valves fitted to the three rotameter were tightly closed and vacuum pump was switched on. The readings were taken out from the rotameter.

$$\text{Air Permeability} = \frac{\text{Rate of Air Flow}}{\text{Exposed Area}}$$

Table 3.3: Conversion of rotameter reading in cubic m/m^2/minute

Exposed area of the test specimen (in cm2)	Conversion factor K to get air permeability			
	In cubic m/m^2/minute		In cubic ft/ft^2/minute	
	For reading of rotameter's in			
	LPH	Cubic m/hour	LPH	Cubic m/hour
10	0.01667	16.667	0.05468	54.68
20	0.00833	8.333	0.02734	27.34
50	0.00333	3.333	0.01094	10.94
100	0.00167	1.667	0.00547	5.47

Where LPH stands for liters per hour

For adapter discs of different areas, the following formula was used.

$$\text{Air Permeability} = K \times \text{Rotameter Reading}$$

Where K is a conversion factor

This formula was used to assess the air permeability of different fabrics. The 10cm^2 area of fabric was exposed for checking the air permeability in cubic m/m^2/minute.

3.10.2 Functional properties of different treated and dyed samples: Functional properties of controlled, alum and alkali treated dyed fabrics, biopolymer treated and treated dyed samples were tested for the following properties:

i. **Antibacterial property**: Colony forming unit (CFU) were determined to know the microbial load on controlled, treated and dyed fabric.

   The bacterial resistance of the control and treated samples against Gram-positive bacteria (*Staphylococcus aureus)* and Gram-negative bacteria (*Escherichia coli)* was quantitatively tested by AATCC Test Method 100. The sterilized fabric sample swatches of 2"x 2" were taken from the untreated controlled samples and treated samples. 50ml Luria Bertani broth was poured in sterile 500ml conical flasks under Laminar Air Flow. The untreated fabric samples i.e. control and the biopolymer treated samples dyed with natural and synthetic dyes and washed samples were aseptically transferred into separate conical flasks with media. Each flask was inoculated with the bacterial concentration of 10^5/ml using a pipette. These were incubated at 37^0C for 24 hours in a shaker incubator at 121rpm.

For preparation of the bacterial concentration of 10^5/ml from the pure culture of the bacteria, the serial dilutions were made in a series of 8 sterile tubes containing 90µl LB broth. 10µl of the pure culture was inoculated in the first tube and then subsequently serial dilutions were made with 10µl until the dilution was 10^{-8}. From each tube 50 µl of diluted culture was taken aseptically and poured onto marked petri plates of LB agar and was spread by using L shaped rod. The plates were incubated in inverted position at 37^0C for 18 hours and number of colonies was counted. Thereafter dilution factor was determined on the basis of the total colony forming units which yielded a bacterial concentration of 10^5/ml.

The conical flasks were removed from the incubator and serial dilutions were made. A series of 8 sterile test tubes containing 4.5 ml sterile water was taken. 0.5ml of the culture from the conical flask containing fabric swatch, 50 ml Luria Bertani broth inoculated with the bacterial concentration of 10^5/ml incubated for 24 hours was aseptically transferred into the first test tube. Serial dilution was carried out until its reduced dilution was 10^{-8}. Agar plates were aseptically prepared with LB agar and solidified for further use. 20 µl of diluted culture from each tube was taken aseptically and poured onto marked separate petri plates. This was spread by using L rod. The plates were incubated in inverted position at 37^0C for eighteen hours. The colonies of bacteria were counted manually and total colony forming units were calculated using following formula:

Colony Forming Units = (**no. of colonies x dilution factor**) / **volume of culture plate**

ii. Ultra-Violet protection property: Ultra-Violet protection factor of the samples was determined to measure the ultra-violet protection property of the controlled, alum treated, alkali treated and dyed fabrics, biopolymer treated and dyed fabric using standard test method.

UPF of dyed experimental fabric was determined using SDL UV penetration and protection measurement system (Compsec M 350 UV- Visible Spectrometer), according to test method UVR TRANSMISSION AATCC- 183:2004. The UPF is computed as the ratio of erythemally weighted ultraviolet radiation (UV-R) irradiance at the detector with no specimen to the erythemally weighted UV-R irradiance at the detector with specimen present. Four specimens from each sample were tested for dry testing. Specimens of 5 x 5 cm were cut from each sample, conditioned, under standard atmosphere and placed against the sample transmission port opening in the sphere. UV transmission was taken with the specimen oriented in one direction, a second measurement at 0.79 rad (450) to the first and third at 0.79 rad (450) to the second. Individual measurements were recorded. Average spectral transmittance was calculated for the three measurements per specimen with a total of five specimens representing each fabric sample. UPF was computed using mean percent transmission in the UVA range (320 – 400 nm) and mean percent transmission in the UVB range (280-320 nm).

The UPF of each specimen was calculated using following equation:

$$UPF = \frac{\sum E\lambda \, X S\lambda \, X \Delta\lambda}{\sum E\lambda \, X \, S\lambda X \, T\lambda X \Delta\lambda}$$

Where,

$E\lambda$ = relative erythemal spectral effectiveness

$S\lambda$ = solar spectral irradiance

$T\lambda$ = average spectral transmittance of the specimen (measured)

$\Delta\lambda$ = measured wavelength interval (nm)

The UV protection category was determined by the UPF values described by Australia / New Zealand Standards AS/NZS4399 (1996) given in Table 3.4.

Table 3.4: UPF rating and UPR protection category

UPF Range	UPR Protection Category	UPF Rating
15- 24	Good protection	15,20
25-39	Very good protection	25,30,35
40-50, 50 +	Excellent protection	40,45,50,50+

3.11 Retention of Physical and Functional Properties of Dyed Fabrics after Washing

The different treated and dyed samples were subjected to different washing cycles to study its effect on physical and functional properties of samples. It was analyzed by laundering all the samples in laundrometer by using IS: 3361-979 test standard method giving 5, 10, 15 and 20 washing cycles. For washability testing the solution was prepared using 5g of soap and 2g of sodium carbonate per liter. The bath was filled with water up to the overflow level (little below the axis of the rotor). Each jar was filled with necessary amount of soap solution with 20:1M:L Ratio. The jars were fitted with lids and fixed in the rotor at their respective positions and locked the nuts tightly setting temperature at 30^0C for 30 minutes. The equipment was allowed to run for the set time to enable the test liquid to attain the test temperature. The jars were opened and placed the specimen in each jars containing test liquid. After the completion of the washing cycle, all the jars were removed and specimens were removed from each jar. The specimens were rinsed twice in cold water, dried in the air and subjected to physical and functional testing.

3.12 Statistical Analysis

Data were analyzed using appropriate statistical techniques and methods.

a) Mean: Arithmetic mean calculated by obtaining the sum of all the observations, divided by total number of observations in the set. Mean was used for the standardization of finish.

$$\mathbf{A.M.} = \boldsymbol{\varepsilon X/n}$$

b) Standard Error: The standard error of the mean (SEM) is the standard deviation of the sample-mean's estimate of a population mean. In the study the standard error was used to calculate the error in the mean in the physical properties of different fabrics. SEM is usually estimated by the sample estimate of the population standard deviation (sample standard deviation) divided by the square root of the sample size (assuming statistical independence of the values in the sample):

$$SE_{\bar{x}} = \frac{s}{\sqrt{n}}$$

c) Coefficient of Variance: To compare the variability of two or more sets of data which have different means and different units of measurement then C.V. is used for knowing

the consistency of the data the coefficient of variation was used. C.V. was used to check the change in the physical properties and expressed in percentage.

$$C.V. = \frac{\mathbf{S.D.}}{\mathbf{A.M.}} \times \mathbf{100}$$

d) Analysis of variance (ANOVA): Analysis of variance (ANOVA) determine whether the means of three or more groups are different. ANOVA uses F-tests to statistically test the equality of means. F-statistics are based on the ratio of mean squares. To use the F-test to determine whether group means are equal, it's just a matter of including the correct variances in the ratio. One way ANOVA was used to determine the f-value. In one-way ANOVA, the F-statistic ratio:

F = variation between sample means / variation within the samples

CHAPTER -IV

RESULTS

The present study entitled "Effect of biopolymer treatment on dyeing efficiency of cotton fabric" was undertaken to apply the biopolymer on the cotton fabric to enhance the dyeability of treated fabrics avoiding the use of metal based mordants and excess salts which affect the environment adversely. To achieve the objectives of the study, biopolymer was selected on the basis of dye absorption, colour strength and wash fastness and fabric was treated with biopolymer using optimized conditions and dyed with selected dyes. The effect of biopolymer on the dyeability, colour properties and physical properties of natural and synthetic dyes was assessed. The results of the study have been explained under the following sections:

4.1 Preliminary properties of selected fabric

4.2 Selection of biopolymers and dyes

4.3 Standardization of biopolymer treatment and dyeing process for natural dye

4.4 Standardization of biopolymer treatment and dyeing process for synthetic dye

4.5 Measurement of total dissolved solids (TDS)

4.6 Fourier transformation infrared spectroscopy (FTIR) analysis

4.7 Assessment of colour properties of dyed fabrics

4.8 Testing of physical and functional properties of dyed fabrics

4.9 Retention of physical and functional properties of dyed fabrics after washing

4.10 Comparative analysis of functional properties of fabrics dyed with natural and synthetic dyes

4.1 Preliminary Properties of Selected Fabric

The selected cotton fabric was enzymatically desized and scoured, resultant fabric was assessed for fabric count, weight and thickness.

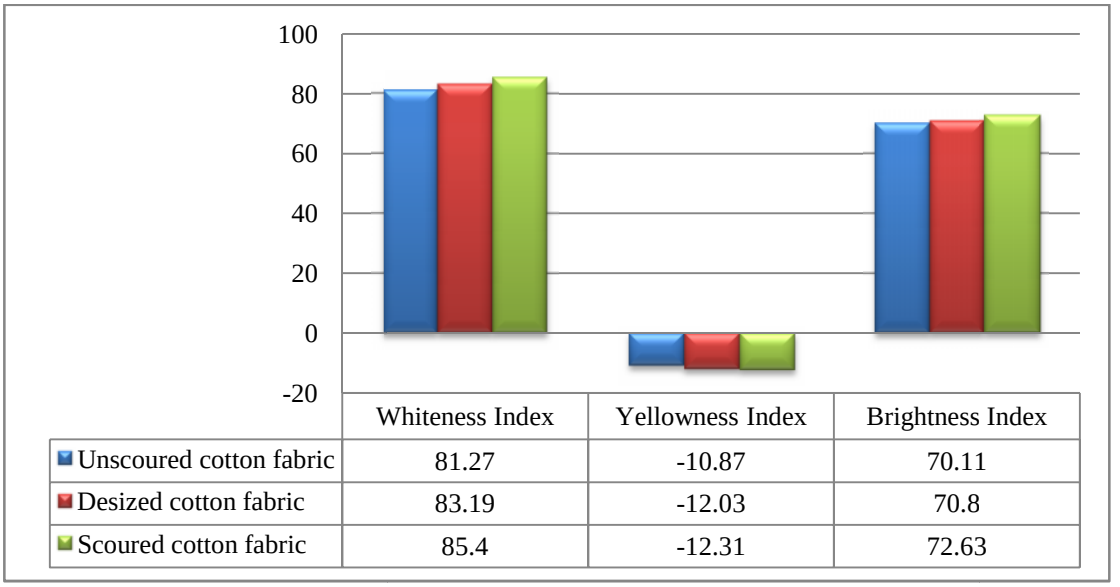
The data on preliminary properties in Table1 indicate that the fabric count of unscoured cotton fabric used for the study was 44 x 40 ends and picks per inch, weighing 140.4 g/m^2 with thickness 0.284 mm whereas the fabric count of desized and scoured fabric was 46 x 41 and 47x 43 ends and picks per inch, weighing 136.4 and 135.0 g/m^2 with thickness 0.276 and 0.232mm respectively.

Table 1: Preliminary properties of the cotton fabric

Samples	**Preliminary properties**			
	Fabric Count (ends and picks/ inch)		**Weight (g/m^2)**	**Thickness (mm)**
	Warp /Ends	Weft /Picks		
Unscoured	44	40	140.4	0.284
Desized	46	41	136.4	0.276
Scoured	47	43	135.0	0.232

4.1.1 Effect of enzymatic desizing and scouring on the whiteness and brightness index:

The effect of enzymatic desizing and scouring treatment on the whiteness and brightness index of cotton fabric is presented through Figure 1. It was observed that after enzymatic desizing of cotton fabric, whiteness index increased from 81.27 to 83.19, brightness index from 70.11 to 70.80 whereas yellowness index decreased from -10.87 to -12.03. It was also noticed from the figure that after enzymatic scouring, the whiteness index increased from 81.27 to 85.40, brightness index from 70.11 to 72.63 and yellowness index decreased from -10.87 to -12.31.



	Whiteness Index	Yellowness Index	Brightness Index
Unscoured cotton fabric	81.27	-10.87	70.11
Desized cotton fabric	83.19	-12.03	70.8
Scoured cotton fabric	85.4	-12.31	72.63

Figure 1: Effect of enzymatic preparatory processes on the whiteness and brightness of cotton fabric

4.2 Selection of Biopolymers and Dyes

4.2.1 Selection of biopolymer and natural dye: The scoured cotton fabric was pretreated with three different biopolymers i.e. beta-cyclodextrin, chitosan and sericin separately as given under sections 3.1.3 (ii) and dyed with eight natural dyes viz. banana leaves, guava leaves, mango leaves, marigold petals, onion skin, peanut skin, pomegranate rind and teak leaves separately as mentioned in section 3.1.5 (ii). The controlled samples were pretreated with aluminium potassium sulphate (alum) and dyed with all the eight natural dyes. Selection of biopolymer and natural dye was done on the basis of colour properties i.e. dye absorption, colour strength and wash fastness of the dyed samples.

It is clear from the Table 2 that amongst all three biopolymer treated samples dyed with natural dyes, chtosan treated samples exhibited highest percent dye absorption, colour strength and wash fastness grades with all the eight natural dyes. The percent dye absorption and colour strength values of chitosan pretreated dyed samples with all the natural dyes were also found higher as compared to alum treated samples.

The chitosan treated samples had the highest percent dye absorption (66.06), colour strength (15.37) and very good (4/5) wash fastness rating with onion dye followed by beta-cyclodextrin treated and dyed fabric (64.84 %, 14.70 k/s value, 4 wash fastness rating) and sericin treated onion skin dyed fabric (64.24 %, 14.53 k/s value, 4 wash fastness rating) whereas alum treated onion skin dyed fabric showed the lowest dye absorption (63.63 %), colour strength (12.32) with comparable wash fastness grade (4). Chitosan treated sample exhibited highest dye absorption, colour strength and wash fastness with all natural dyes, hence chitosan was selected as biopolymer for further work.

Table 2: Selection of biopolymer and natural dye on the basis of colour properties

S. No.	Natural dyes	Alum treated fabric (control)			Biopolymers treated fabrics								
					Beta cyclodextrin			Chitosan			Sericin		
		% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades
1.	**Banana leaves**	25.00	4.82	3	24.13	2.61	3	25.86	6.97	3/4	25.00	2.74	3
2.	**Guava leaves**	45.36	8.10	3/4	44.32	7.77	3/4	46.39	12.86	4	42.26	7.00	3/4
3.	**Mango leaves**	43.45	7.38	3/4	41.07	4.35	3/4	44.04	9.05	4	42.26	4.40	3/4
4.	**Marigold petals**	50.25	9.68	4	49.22	8.84	3/4	50.25	10.51	4	49.74	8.87	4
5.	**Onion skin**	63.63	12.32	4	64.84	14.70	4	**66.06**	**15.37**	**4/5**	64.24	14.53	4
6.	**Peanut skin**	60.93	13.99	4	60.93	13.25	4	64.06	14.14	4/5	59.37	12.80	4
7.	**Pomegranate rind**	56.86	12.58	4	53.92	11.20	4	56.86	13.79	4	55.88	12.09	4
8.	**Teak leaves**	61.40	12.95	4	59.64	12.87	4	62.28	14.03	4/5	57.01	12.73	4

Amongst all the natural dyes, onion skin dye showed the highest dye absorption (66.06 %), colour strength (15.37) and wash fastness grade (4/5) followed by peanut skin (64.06 %, 14.14 k/s value and 4/5), teak leaves (62.28 %, 14.03 k/s value and 4/5), pomegranate rind (56.8 6%, 13.79 k/s value and 4), guava leaves (46.39 %, 12.86 k/s value and 4), marigold petals (50.25 %, 10.51 k/s value and 4), mango leaves (44.04 %, 9.05 k/s and 4) and banana leaves (25.86 %, 6.97 k/s value and 3/4) respectively.

Thus chitosan as biopolymer and onion skin as natural dye were selected for further work.

4.2.2 Selection of biopolymer and synthetic dye: The cotton fabric was pretreated with three different biopolymers i.e. beta-cyclodextrin, chitosan, and sericin as given under sections 3.1.3 (ii) and dyed with different synthetic dyes viz. acid dyes (red, yellow, black), direct dyes (red, brown, Chlorantine Fast Yellow 5GLL, Chloragol Orange (RS), Shakuntala Green BD), hot brands of reactive dye (Red, Brown H4R, Turquoise HTG), cold brands of reactive dye (Red M8B, Blue MR, Orange M2R) separately. The controlled samples were pretreated with sodium sulphate, sodium carbonate and sodium chloride according to the requirement of alkali for particular dye as mentioned in section 3.1.7 and dyed with fourteen dyes from three different classes of synthetic dyes i.e. direct dye, reactive dye and acid dye

for comparison with biopolymer treated dyed samples. Selection of biopolymer and synthetic dye was done on the basis of colour properties i.e. dye absorption, colour strength and wash fastness.

It is clear from Table 3 that amongst all three biopolymer treated fabric samples, dyed with synthetic dyes, the chitosan treated dyed fabrics showed highest percent dye absorption, colour strength and wash fastness rating as compared to the alkali treated dyed fabrics for all the synthetic dyes. The chitosan treated fabric showed the highest percent dye absorption (83.84), colour strength (14.56) and very good (4/5) wash fastness rating with hot reactive red dye followed by alkali treated reactive red dyed fabric (71.61 %, 10.92 k/s value, 4), beta-cyclodextrin treated reactive red dyed fabric (63.75%, 8.71 k/s value, 4) and sericin treated reactive red dyed fabric (61.13%, 8.38 k/s value, 3/4) respectively.

Table 3: Selection of biopolymer and synthetic dye on the basis of colour properties

S. No.	Synthetic dyes		Alkali treated fabrics (Control)			Biopolymer treated fabrics								
						Beta- Cyclodextrin			Chitosan			Sericin		
			% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades
1.	Direct	Red	70.31	9.90	4	68.75	9.19	4	74.21	11.62	4	64.84	8.79	4
		Brown	72.07	11.13	4	76.62	11.73	4	79.22	12.13	4	68.18	8.94	4
		Chlorantine FastYellow 5GLL	79.04	12.04	4	79.64	12.67	4	82.63	12.92	4	68.26	9.06	3/4
		Chloragol Orange RS	71.58	10.50	4	72.13	11.05	4	77.04	11.86	4	67.75	8.82	4
		Shakuntala Green BD	63.45	8.52	3/4	63.95	8.75	4	77.66	11.92	4	62.43	8.42	4
2.	Reactive (hot)	Red	71.61	10.92	4	63.75	8.71	4	**83.84**	**14.56**	**4/5**	61.13	8.38	3/4
		Brown H4R	70.25	10.02	4	68.53	9.10	4	82.32	12.84	4/5	60.34	8.00	3/4
		Turquoise HTG	63.90	8.64	4	64.39	8.89	3/4	83.44	14.23	4/5	63.41	8.79	3/4
3.	Reactive (cold)	Red M8B	47.52	3.98	3	48.01	5.07	3	58.41	5.14	3/4	24.75	1.00	2/3
		Blue MR	42.51	3.01	3	43.71	4.13	3	56.28	5.35	3/4	50.89	4.00	3
		Orange M2R	43.41	3.12	3	45.73	5.17	3	55.03	5.23	3/4	40.31	2.93	3
4.	Acid	Red	39.47	2.49	2/3	38.59	2.40	2/3	54.38	5.13	3/4	30.70	1.02	2/3
		Yellow	32.57	1.06	2/3	24.24	0.98	2/3	57.57	5.46	3/4	37.87	2.60	2/3
		Black	44.29	3.56	2/3	42.95	3.51	2/3	58.38	5.74	3/4	51.67	4.08	2/3

Amongst all the synthetic dyes, hot reactive red dyed fabric showed the highest dye absorption (83.84 %), colour strength (14.56) and very good (4/5) wash fastness grade with chitosan treatment followed by reactive Turquoise HTG (83.44%, 14.23 k/s value and 4/5), direct

Plate 1: Shades Obtained with Different Natural Dyes on Alum and Biopolymers Treated Fabrics

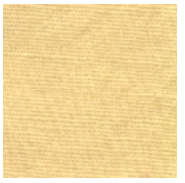
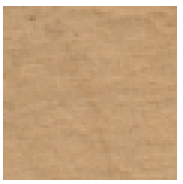
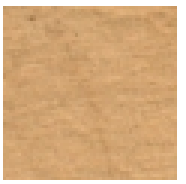
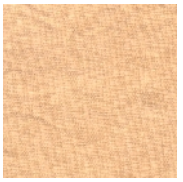
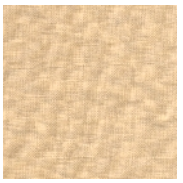
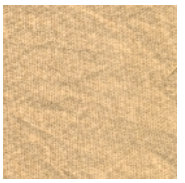
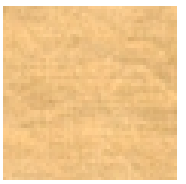
S. No.	Plants Name	Treated fabrics			
		Alum	Beta-cyclodextrin	Chitosan	Sericin
1.	**Banana** Botanical Name: *Musa balbisiana* Family: Musaceae				
2.	**Guava** Botanical Name: *Psidium guava* Family: Myrtaceae				
3.	**Mango** Botanical Name: *Mangifera indica* Family: Anacardiaceae				
4.	**Marigold** Botanical Name: *Calendula officinalis* Family: Calendulaeae				
5.	**Onion** Botanical Name: *Alleum cepa* Family: Amaryllaidaceae				
6.	**Peanut** Botanical Name: *Arachis hypogeae* Family: Fabaceae				
7.	**Pomegranate** Botanical Name: *Punica granatum* Family: Punicaceae				
8.	**Teak** Botanical Name: *Tictona grandis linn* Family: Lamiaceae				

PLATE 2: Colours Obtained with Different Natural Dyes on Chitosan Treated Cotton Fabric

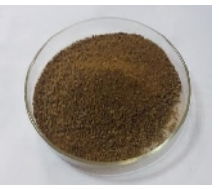
S. No.	Plants Name	Parts Used	Dye materials	Dyed Samples
1.	**Banana**	Leaves		
2.	**Guava**	Leaves		
3.	**Mango**	Leaves		
4.	**Marigold**	Petals		
5.	**Onion**	Skin		
6.	**Peanut**	Skin		
7.	**Pomegranate**	Rind		
8.	**Teak**	Leaves		

PLATE 3: Shades Obtained with Different Synthetic Dyes on Alum and Biopolymers Treated Fabrics

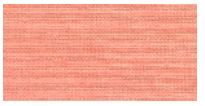
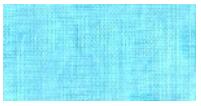
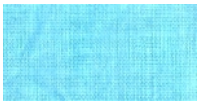
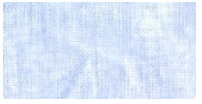
S. No.	Synthetic dyes		Treated fabrics			
			Alkali (Control)	Beta Cyclodextrin	Chitosan	Sericin
1.	Direct	Red				
		Brown				
		Chlorantine FastYellow 5GLL				
		Chloragol Orange RS				
		Shakuntala Green BD				
2.	Reactive (hot)	Red				
		Brown H4R				
		Turquoise HTG				
3.	Reactive (cold)	Red M8B				
		Blue MR				
		Orange M2R				
4.	Acid	Red				
		Yellow				
		Black				

Plate 4: Colours Obtained with Different Synthetic Dyes on Chitosan Treated Cotton Fabric

S. No.	Dyes	Dyed samples		
1.	Direct			
		Red	Chloragol Orange RS	Chlorantine FastYellow5GLL
				
		Shakuntala Green BD	Brown	
2.	Reactive (Cold)			
		Blue MR	Orange M2R	Red M8B
3.	Reactive (Hot)			
		Red	Turquoise HTG	Brown H4R
4.	Acid			
		Yellow	Red	Black

Chlorantine Fast Yellow 5GLL (82.63 %, 12.92 k/s value and 4), reactive Brown H4R (82.32 %, 12.84 k/s value and 4/5), direct Brown dye (79.22 %, 12.13 k/s value and 4), direct Shakuntala Green BD (77.66 %, 11.92 k/s value and 4), direct Chloragol Orange RS (77.04 %, 11.86 k/s value and 4) , direct Red dye (74.21 %, 11.62 k/s value and 4) respectively.

Amongst different classes of synthetic dye, the hot reactive dye showed highest dye absorption, colour strength value and wash fastness rating followed by direct dyes, acid dyes and cold reactive dyes with chitosan treatment. Thus the chitosan was selected as biopolymer and reactive red dye (hot brand) as synthetic dye for further work.

4.2.3 Selection of cross-linking agent for chitosan treatment: This sub section comprises the selection of cross-linking agent for chitosan treatment for selected natural (onion skin) and synthetic (reactive red) dye. Selection was done on the basis of dye absorption, colour strength and wash fastness properties of dyed samples.

The effect of different cross-linking agents i.e. Butan- tetra carboxylic acid, citric acid and glyoxal in terms of percent dye absorption, colour strength (k/s) and wash fastness ratings of the onion skin dyed cotton fabric is presented in Table 4. The onion skin dyed sample with butan- tetra carboxylic acid (BTCA) as a cross-linking agent in chitosan application showed the highest dye absorption (64.48 %) and colour strength (12.72) followed by citric acid (dye absorption 64.17 % and k/s 12.21) and glyoxal (dye absorption 61.96 % and k/s 10.42).

Table 4: Selection of cross linking agent for chitosan application

S. No.	Cross-linking agents	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
			L*	a*	b*	C*	H*		
	Onion skin dye								
1.	Butan tetra carboxylic acid (BTCA)	64.48	53.05	11.57	16.26	19.95	54.53	12.72	4/5
2.	Citric acid	64.17	53.59	10.67	15.92	19.17	56.14	12.21	4/5
3.	Glyoxal	61.96	54.49	10.28	15.96	18.98	57.19	10.42	3/4
	Reactive red dye (hot)								
1.	Butan- tetra carboxylic acid (BTCA)	64.81	33.92	43.86	-7.40	44.48	350.42	14.36	4/5
2.	Citric acid	64.08	34.06	44.59	-6.84	45.11	351.27	14.14	4/5
3.	Glyoxal	61.00	34.26	44.51	-7.74	45.18	350.13	13.56	4

The L* value was found lower for the butan-tetra carboxylic acid (53.05) followed by citric acid (53.59) and glyoxal (54.49) which showed that the samples were darker in colour where the butan-tetra carboxylic acid and citric acid used as catalyst in biopolymer application than glyoxal. The positive a* and b* values showed that the dyed samples were redder and yellower in tone. The chroma values indicated the brightness which was higher for the butan-tetra carboxylic acid (19.95) treated dyed sample followed by citric acid (19.17)

and glyoxal (18.98). The hue angle (H*) was below 90^0 with positive a* and b* values for all the dyed samples depicting brown and yellowish khaki colour of the samples. The lowest wash fastness rating (3/4) was found with glyoxal whereas the citric acid and butan-tetra carboxylic acid exhibited very good wash fastness rating (4/5).

The table depicts that in the reactive red dyed sample where the butan- tetra carboxylic acid (BTCA) was used as a cross-linking agent in chitosan application showed the highest dye absorption (64.81%) and colour strength (14.36) followed by citric acid (dye absorption 64.08 % and k/s value 14.14) and glyoxal (dye absorption 61.00 % and k/s value 13.56). The L* value was found lower for the butan-tetra carboxylic acid (33.92) followed by citric acid (34.06) and glyoxal (34.26) which showed that the samples were darker in colour when the butan-tetra carboxylic acid and citric acid were used as cross-linking agents in biopolymer application than glyoxal. The positive a* and negative b* values showed that the dyed samples were redder and bluer in tone. The chroma(C*) values depicted the brightness which was higher (45.18) for the glyoxal treated dyed sample followed by citric acid (45.11) and butan-tetra carboxylic acid (44.48). The hue angle (H*) was between 270^0 to 360^0 with positive a* and negative b* values for all the dyed samples which showed the reddish blue (magenta) colour of the samples. The lowest wash fastness grade i.e. good (4) was found with glyoxal whereas the citric acid and butan-tetra carboxylic acid showed very good wash fastness rating (4/5).

It is evident from the table that there were no remarkable differences in the percent dye absorption and colour strength value of dyed samples of onion skin and reactive red dye in which citric acid and butan-tetra-carboxylic acid were used as cross-linking agents in chitosan application. Hence the citric acid was selected as cross-linking agent for chitosan application for both natural (onion skin) and synthetic (hot reactive red) dyes because use of citric acid is cost effective and safe.

4.2.4 Selection of catalyst for chitosan treatment: This sub-section deals with the selection of catalyst for chitosan treatment on the basis of dye absorption, colour strength and wash fastness properties of onion skin and reactive red dyed samples.

Table 5 reflects the effect of different catalysts i.e. Magnesium chloride, phosphoric acid and sodium hypophosphite on the dye absorption, colour strength and wash fastness rating of onion skin and reactive red dyed fabric. The data in the table illustrate that the highest dye absorption (65.54 %), colour strength (12.60) and wash fastness rating (4/5) was achieved by onion skin dyed samples which was treated with chitosan with sodium hypophosphite as catalyst followed by the magnesium chloride and phosphoric acid. The lowest L* value found for sodium hypophosphite (53.74) indicated more darkeness in colour of onion skin dyed sample followed by magnesium chloride (54.24) and phosphoric acid (56.18). The hue angle was below 90^0 with positive a* and b* values for all the samples

which depicted brown and yellowish khaki colour of the samples. The chroma (C*) value showed brightness of dyed sample was found highest for sodium hypophosphite (19.17) followed by magnesium chloride (17.59) and phosphoric acid (17.54). The wash fastness rating of onion skin dyed sample was very good (4/5) for sodium hypophosphite whereas good (4) wash fastness rating was observed for magnesium chloride and phosphoric acid for chitosan application for onion skin dye.

Table 5: Selection of catalyst for chitosan application

S. No.	Catalysts	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
			L*	a*	b*	C*	H*		
	Onion skin dye								
1.	Magnesium chloride	64.29	54.24	8.86	15.19	17.59	59.71	10.92	4
2.	Phosphoric acid	63.63	56.18	10.13	14.31	17.54	54.68	10.80	4
3.	Sodium hypophosphite	65.54	53.74	11.01	15.68	19.17	54.89	12.60	4/5
	Reactive red dye								
1.	Magnesium chloride	67.63	33.22	42.96	-6.65	43.47	351.20	12.87	4
2.	Phosphoric acid	64.00	33.27	42.00	-7.04	42.59	350.48	11.70	4
3.	Sodium hypophosphite	72.00	33.15	45.95	-7.14	46.51	351.16	14.78	4/5

The data in table illustrate that in case of reactive red dye, the highest dye absorption (72.00 %), colour strength (14.78) and wash fastness rating (4/5) was obtained by dyed samples with sodium hypophosphite as a catalyst followed by the magnesium chloride and phosphoric acid.

The lowest L* value was found for sodium hypophosphite (33.15) depicting higher darkeness in colour of reactive red dyed sample followed by magnesium chloride (33.22) and phosphoric acid (33.27) and. The hue angle (H*) was between 270^0 to 360^0 with positive a* and negative b* value for all the dyed samples which showed the reddish blue (magenta) colour of the samples. The chroma (C*) value which showed brightness of dyed sample was highest with sodium hypophosphite (46.51) followed by magnesium chloride (43.47) and phosphoric acid (42.59).

The wash fastness rating was very good (4/5) for the sodium hypophosphite whereas good (4) wash fastness rating was observed for reactive red dyed samples treated with the magnesium chloride and phosphoric acid as catalyst. Sodium hypophosphite was selected as catalyst for chitosan treatment for onion skin and reactive red dye.

4.2.5 Selection of extraction method for selected natural dye

Extraction of natural dye was done in three different mediums i.e. aqueous, ethanol and methanol and the presence of phytochemicals was analyzed.

Table 8 depicts that the presence of anthraquinone, cardiacgycocids, flavonoids and tannins was observed in all the three medium of extraction whereas the presence of terenoids was found in ethanol and methanol extraction medium. The aqueous and methanol extract exhibited the presence of reducing sugar.

By considering the cost of extraction of dye, simplicity of the method and presence of phytochemicals, the aqueous method of extraction was selected for extraction of dye from plant material for dyeing of cotton fabric for further study.

Table 6: Phytochemical analysis of onion skin dye

S. No.	Phytochemicals	Extraction mediums		
		Aqueous	Ethanol	Methanol
1.	Alkaloids	-	-	-
2.	Anthraquinone	+	+	+
3.	Cardiacgycocids	+	+	+
4.	Flavonoids	+	+	+
5.	Phenol	-	-	-
6.	Reducing Sugar	+	-	+
7.	Saponins	-	-	-
8.	Steroids	-	-	-
9.	Tannins	+	+	+
10.	Terenoids	-	+	+

4.3 Standardization of Biopolymer Treatment and Dyeing Process for Natural Dye

Different variables of chitosan biopolymer treatment and dyeing process were optimized to enhance the dyeing efficiency of cotton fabric with natural dye using the biopolymer instead of metal based mordants.

4.3.1 Standardization of biopolymer treatment for natural dye: For Standardization of biopolymer (chitosan) treatment for the natural dye (onion skin), different concentrations and conditions were optimized for the following parameters:

4.3.1.1 Optimization of chitosan concentration: For the determination of optimum concentration of chitosan, five different concentrations of chitosan i.e. 1, 2, 3, 4 and 5 percent were taken and optimization was done on the basis of colour properties i.e. dye absorption, colour strength and wash fastness. Data presented in the Table 7 reveal that at 1.0 percent concentration of chitosan, the percent dye absorption was 60.71 with colour strength (k/s) 13.88 and wash fastness rating 3/4.

Table 7: Optimization of chitosan concentration on the basis of colour properties of onion skin dye

Chitosan concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1	60.71	68.47	-0.219	21.87	21.87	90.61	13.88	3/4
2	62.50	57.38	13.49	27.81	30.91	64.09	13.77	3/4
3	64.88	51.92	15.46	15.44	21.85	44.95	15.77	4
4	**66.07**	**49.85**	**15.50**	**24.49**	**28.98**	**57.65**	**16.28**	**4**
5	66.13	46.75	16.36	24.09	29.12	55.79	16.30	4

As the concentration of chitosan increased from 1.0 to 5.0 percent, L* value decreased from 68.47 to 46.75 indicating darkness of colour increased. The a* value was found positive for all the chitosan concentrations except at 1 percent which depicted that the dyed samples had redder tone and sample of 1 percent concentration had greener tone. The b* value was positive for all the concentrations of chitosan which showed the yellow tone. The C* depicted the chroma value which was highest (30.91) at 2 percent of chitosan followed by 5 (29.12), 4(28.98), 1(21.87) and 3(21.85) percent concentration. The hue angle (H*) was below 90^0 with positive a* and b* values depicting the brown and yellowish khaki colour of the sample for all concentrations of chitosan whereas the a* value was negative with hue angle above 90^0 at one percent concentration of chitosan indicating the greenish khaki colour of the dyed sample.

It is also clear from the table that as the concentration of chitosan increased from 1 to 5 percent, dye absorption increased from 60.71 to 66.13 percent, colour strength (k/s) value from 13.88 to 16.30. The wash fastness rating was fairly good (3/4) at 1 and 2 percent whereas it was found good (4) at 3, 4 and 5 percent concentrations of chitosan.

It was observed that there was no considerable difference in dye absorption, colour strength and wash fastness rating at 4 and 5 percent concentrations of chitosan. Therefore 4 percent concentration of chitosan was selected as optimum concentration for biopolymer treatment.

4.3.1.2 Optimization of cross-linking agent concentration: Five concentrations of citric acid i.e. 3, 4, 5, 6 and 7 percent were used for determination of optimized concentration of citric acid (Table 8). It was observed that 3 percent concentration of citric acid when applied with optimized concentration of chitosan for the biopolymer treatment, the percent dye absorption was 60.12 having colour strength value 11.53 along with good (4) wash fastness rating. As the concentration of citric acid increased from 3 to 7 percent, there was increase in dye absorption from 60.12 to 64.35 percent, colour strength value from 11.53 to 16.05 with good (4) wash fastness rating. As the concentration of citric acid increased from 3 to 7 percent, L* value decreased from 64.00 to 51.14, depicting darkness of colour. The a* and b*

values were found positive for all dyed samples indicating redder and yellower tone with different concentrations of citric acid in biopolymer treatment. The C* value depicted the chroma value which was highest (27.90) at 6 percent concentration of citric acid followed by 5 (26.13), 3(25.77), 7 (25.72) and 4 (25.45) percent. The hue angle (H*) was below 90^0, with positive a* and b* values for all the dyed samples depicting brown and yellowish khaki colours of the samples.

Table 8: Optimization of citric acid concentration on the basis of colour properties of onion skin dye

Citric acid concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3	60.12	64.00	8.92	24.18	25.77	69.72	11.53	4
4	61.90	59.27	10.22	23.30	25.45	66.28	12.85	4
5	62.50	57.96	13.69	22.25	26.13	58.36	13.90	4
6	**64.29**	**54.78**	**14.97**	**23.54**	**27.90**	**57.51**	**16.03**	**4**
7	64.35	51.14	16.14	20.03	25.72	51.11	16.05	4

It is evident from table that with the increase of citric acid, the dye absorption and colour strength increased without affecting wash fastness. It was revealed that no considerable difference was found in dye absorption, colour strength value and wash fastness of dyed samples with 6 and 7 percent concentration of citric acid. Six percent concentration of citric acid was taken as optimum concentration for fixation of chitosan on cotton fabric with dye absorption 64.35 percent, colour strength value 16.05 and wash fatness rating good (4)

4.3.1.3 Optimization of catalyst concentration: Sodium hypophosphite was selected as catalyst along with cross-linking agent to facilitate the fixation of chitosan on the cotton fabric. Table 9 shows that five different concentrations of sodium hypophosphite i.e. 2, 3, 4, 5 and 6 percent were taken for the optimization of catalyst concentration with optimized ratio of chitosan and citric acid. When 2 percent concentration of sodium hypophosphite was applied along with cross-linking agent and chitosan followed by dyeing with onion skin, dye absorption was 61.31 percent having colour strength value 12.35 along with fairly good (3/4)wash fastness rating.

It is evident from the table that as the concentration of sodium hypophosphite increased from 2 to 6 percent, there was increase in percent dye absorption from 61.31 to 64.23, colour strength (k/s) value from 12.35 to 15.89 whereas L* value decreased from 49.66 to 31.08 indicating increased darkness with increase in sodium hypophosphite concentration. The wash fastness rating of the dyed samples was good (4) with 4, 5, 6 percent concentration whereas fairly good (3/4) was noticed at 2 and 3 percent. The a* and b* values were found positive for all the samples dyed with onion skin dye after biopolymer treatment with different concentrations of sodium hypophosphite which indicated that all the dyed samples

had redder and yellower tone. The chroma **(**C*) value was higher (21.83) at 5 percent concentration of catalyst followed by 4 (19.72), 2 (15.77), 3 (16.21) and 6 (19.59) percent. The hue angle (H*) was below 90^0 with positive a* and b* values depicting brown and yellowish khaki colour of the samples.

Table 9: Optimization of sodium hypophosphite concentration on the basis of colour properties of onion skin dye

Sodium hypophohite concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
2	61.31	49.66	8.42	13.32	15.77	57.66	12.35	3/4
3	63.10	36.83	8.76	13.63	16.21	57.24	14.65	3/4
4	63.69	35.23	10.54	16.67	19.72	57.68	15.05	4
5	**64.17**	**34.08**	**10.60**	**19.08**	**21.83**	**60.91**	**15.83**	**4**
6	64.23	31.08	11.14	16.12	19.59	55.38	15.89	4

Five percent concentration of sodium hypophosphite was chosen as optimum concentration with dye absorption 64.17 percent, colour strength value 15.83 and wash fatness rating (4) as there was no considerable difference in colour properties of dyed samples at 5 and 6 percent concentration of sodium hypophosphite.

4.3.1.4 Optimization of pH for biopolymer treatment: Five different pH ranges i.e. 3, 4, 5, 6 and 7 were maintained for optimization. It is clear from Table 10 that when pH of treatment bath was maintained at 3, dye absorption was 60.12 percent, having colour strength (11.20) along with fairly good (3/4) wash fastness rating.

Table 10: Optimization of treatment pH on the basis of colour properties of onion skin dye

pH	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3	60.12	53.09	-1.09	6.41	6.51	99.71	11.20	3/4
4	61.31	52.86	-1.43	7.41	7.55	100.95	12.70	4
5	**61.90**	**49.80**	**-3.81**	**8.07**	**8.92**	**108.95**	**14.45**	**4**
6	60.71	51.07	-2.16	6.31	6.67	115.30	9.71	3/4
7	59.52	53.59	-3.17	7.15	7.82	113.95	8.65	3/4

As the pH of dye bath increased from 3 to 5, there was increase in dye absorption from 60.12 to 61.90 percent, colour strength value from 11.20 to 14.45 and wash fastness rating from fairly good (3/4) to good (4) but further increase in pH from 6 to 7 showed decrease in dye absorption from 60.71 to 59.52 percent, colour strength from 9.71 to 8.65 and fairly good (3/4) wash fastness rating. The L* value decreased from 53.09 to 49.80 as the pH of dye bath increased from 3.0 to 5.0 indicating increased darkness of shade whereas L* value increased indicating darkness of the samples reduced after pH 5.

The a* values were negative but b* values were positive at all the treatment pH, indicating the samples had greener and yellower tone. The chroma(C*) value was higher (8.92) at pH 5.0 followed by 7 (7.82), 4 (7.55), 6 (6.67) and 3 (6.51). The hue angle (H*) was found between 91.37 and 115.30 with negative a* and positive b* values for all onion skin dyed samples which depicted greenish khaki colour of the samples. On the basis of percent dye absorption (61.90), colour strength (14.45) and very good wash fastness rating, pH 5.0 was taken as optimum for formulation of bath for chitosan treatment.

4.3.1.5 Optimization of material to liquor ratio for biopolymer treatment: The different material to liquor ratios (owf) i.e. 1:10, 1:20, 1:30 and 1:40 were used for optimization material to liquor ratio (M:L Ratio) of treatment bath for biopolymer treatment and data regarding colour properties of onion skin dyed samples are presented in the Table 11. It is evident from the table that at 1:10 M:L Ratio, the dye absorption was 60.71 percent, colour strength 13.41, fairly good wash fastness rating (3/4). As the M:L Ratio increased from 1:10 to 1:30, the percent dye absorption increased from 60.71 to 60.89 percent, colour strength value from 13.41 to 15.03, wash fastness rating from fairly good (3/4) to good (4) whereas L* value decreased from 68.93 to 68.01 which indicated the darkness of colour. At 1:40 M:L Ratio, decrease in dye absorption and colour strength value was noticed whereas L* value increased which showed lightness of colour. The a* and b* values were positive at all the M:L Ratios used for treatment of chitosan which depicted that all the samples had redder and yellower tone. The chroma **(**C*) value was highest (21.47) at 1:30 M:L Ratio followed by 1:10 (21.36), 1:20 (20.88), and 1:40 (18.09). The hue angle (H*) was found below 90^0 with positive a* and b* value, depicting brown and yellowish khaki colours of the samples.

Table 11: Optimization of material to liquor ratio on the basis of colour properties of onion skin dye

M:L Ratio	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1:10	60.71	68.93	10.06	18.84	21.36	61.86	13.41	3/4
1:20	60.83	68.85	9.20	18.74	20.88	63.82	13.63	4
1:30	**60.89**	**56.17**	**9.57**	**19.22**	**21.47**	**63.16**	**15.03**	**4**
1:40	60.77	68.01	15.09	9.86	18.09	63.48	14.55	3/4

It is apparent from the table that at 1:30 M:L Ratio there was highest percent dye absorption (60.89), colour strength (15.03) and good wash fastness rating (4) hence was taken as optimum M:L Ratio for chitosan treatment on cotton fabric.

4.3.1.6 Optimization of treatment temperature: The samples were treated in chitosan solution at five different temperatures i.e. 60^0, 70^0, 80^0, 90^0 and 100^0C to optimize treatment temperature for achieving the maximum dye absorption (Table 12).

The table elucidates that when chitosan treatment was carried out at 60 ^{0}C, dye absorption was 58.93 percent, colour strength 8.01and fairly good wash fastness rating (3/4). The samples when treated in biopolymer solution from 60^0 to 100^{0}C temperature, the dye absorption increased from 58.93 to 62.08 percent, colour strength from 8.01 to 14.83 for the dyed samples whereas L* value decreased from 60.03 to 49.73 which indicated the increased darkness of colour. The good (4) wash fastness rating was found for all the onion skin dyed samples pretreated with chitosan at different temperatures except at 60 ^{0}C. The a* and b* values were positive at all the treatment temperatures which showed that all the samples had redder and yellower tone. The chroma value (C*) was highest (26.88) at 90^{0}C followed by the 80^0 (24.99), 60^0 (24.40), 70^0 (22.46), and 100^{0}C (19.56). The hue angle (H*) was below 90 degree which depicted brown and yellowish khaki colour of samples.

Table 12: Optimization of treatment temperature on the basis of colour properties of onion skin dye

Treatment temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
60	58.93	60.03	8.17	23.00	24.40	70.41	8.01	3/4
70	59.52	54.95	9.47	20.36	22.46	65.02	10.75	4
80	61.90	51.76	14.41	20.41	24.99	54.76	14.15	4
90	**62.02**	**51.70**	**13.53**	**23.23**	**26.88**	**59.75**	**14.75**	**4**
100	62.08	49.73	6.11	23 .34	19.56	50.19	14.83	4

For biopolymer treatment percent dye absorption 62.02 percent, colour strength value 14.75 and good wash fatness rating (4) at 90 ^{0}C was taken as optimum treatment temperature as there was no remarkable difference between 90^0 and 100^{0}C treatment temperature.

4.3.1.7 Optimization of treatment time: The biopolymer treatment was given for four different durations of time i.e. 15, 30, 45 and 60 minutes. It is apparent from Table 13 that when the biopolymer treatment was carried out for 15 minutes, the dye absorption obtained was 58.33 percent, colour strength 6.09 and wash fastness rating, fairly good (3/4).

Table 13: Optimization of treatment time on the basis of colour properties of onion skin dye

Treatment time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
15	58.33	67.70	6.90	16.23	17.64	66.92	6.09	3/4
30	60.71	64.52	9.60	14.24	17.17	55.95	9.28	4
45	**61.96**	**54.02**	**12.32**	**23.32**	**26.38**	**62.10**	**14.45**	**4/5**
60	61.90	56.63	9.21	15.51	18.03	59.27	14.41	4

As the time duration of biopolymer treatment increased from 15 to 45 minutes, increase in the dye absorption was noticed from 58.33 to 61.96 percent, colour strength value

from 6.09 to 14.45 whereas L* value decreased from 67.70 to 54.02 which means darkness of shade increased. The wash fastness rating was found to be very good (4/5) at 45 minutes, good (4) at 30 and 60 minutes whereas fairly good (3/4) at 15 minutes. A slight decrease was noticed in percent dye absorption and colour strength value with the increased treatment time (from 45 to 60 minutes). The a* and b* values were positive for different durations of treatment time showing redder and yellower tone of all samples. The chroma (C*) was higher (26.38) at 45 minute duration of treatment followed by 60 (18.03), 15 (17.64) and 30 (17.17) minutes. The hue angle (H*) was found below 90^0 with positive a* and b* values, which indicated brown and yellowish khaki colours of samples. It is clear from the table that at 45 minutes of chitosan treatment, the highest percent dye absorption (61.96), colour strength (14.45) and wash fastness rating (4/5) was observed hence was taken as optimized treatment time.

4.3.1.8 Optimization of drying temperature: Table 14 comprises the data regarding the effect of drying temperature of chitosan treated cotton fabric on dyeing with onion skin natural dye. Chitosan treated cotton fabric was dried at five different temperatures, i.e. 60^0, 70^0, 80^0, 90^0 and 100 ^{0}C. It is clear from table that at 60^0C drying temperature, the dye absorption was 60.71 percent, colour strength 11.73 along with the wash fastness rating fairly good (3/4). When the drying temperature of chitosan treated sample was raised from 60 to 100^0C, the increase in dye absorption was observed from 60.71 to 61.31 percent, colour strength from 11.73 to 14.36 whereas L* value decreased from 90.12 to 45.66 which revealed the increased darkness of colour. The wash fastness rating of the dyed samples was found very good (4/5) at 100 ^{0}C, good (4) at 70^0, 80^0, 90^0C and fairly good (3/4) at 60^0C.

Table 14: Optimization of drying temperature on the basis of colour properties of onion skin dye

Drying temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
60	60.71	90.12	0.54	4.33	4.36	82.78	11.73	3/4
70	60.77	60.84	7.11	24.13	25.16	73.54	12.84	4
80	60.89	56.22	17.08	7.08	18.49	22.50	13.10	4
90	60.95	55.62	9.79	23.40	25.37	67.26	14.34	4
100	**61.31**	**45.66**	**14.26**	**17.95**	**22.93**	**51.51**	**14.36**	**4/5**

The a* and b* values were positive at all the drying temperatures and hue angle (H*) was below 90^0 which highlighted that all dyed samples were brown and yellowish khaki in colour. The chroma (C*) was highest (25.37) at 90 ^{0}C drying temperature followed by the 70^0 (25.16), 100^0 (22.93), 80^0 (18.49), and 60^0C (4.36). The optimum drying temperature for

chitosan treatment to obtain better dyeing with onion skin natural dye was taken as 100^0C with dye absorption 61.31 percent, colour strength value 14.36 and very good (4/5) wash fatness rating.

4.3.1.9 Optimization of optimum drying time: Data regarding drying duration of chitosan treated cotton fabric is presented in the Table 15 which was carried out at five different durations of time i.e. 3, 4, 5, 6 and 7 minutes. It is apparent from the table that when the drying of chitosan treated sample was carried out for 3 minutes, dye absorption of onion skin dye was 61.43 percent, colour strength 13.36 and wash fastness rating good (4). As the duration of drying time increased from 3 to 7 minutes, increase in dye absorption was noticed from 61.43 to 63.64 percent whereas the increased darkness of colour was due to the decreased L* value from 49.14 to 45.19. The wash fastness rating was good (4) for all durations of drying time. The positive a* and b* values represented the redder and yellower tone of fabric. The hue angle (H*) was found below 90^0 with positive a* and b* value depicting brown and yellowish khaki colour of samples. The chroma (C*) value was highest (27.38) at 7 minutes duration of drying time followed by 3(27.28), 6 (27.03), 4 (26.95) and 5 (24.53) minutes. It is clear from the table that at 5 minutes duration of drying time, there was parallel dye absorption, colour strength and wash fastness to 6 and 7 minutes hence 5 minutes was taken as optimum duration of drying time for chitosan treated fabric dyed with onion skin dye at which the dye absorption was 63.57 percent, colour strength 15.61 and wash fastness rating good (4).

Table 15: Optimization of drying time on the basis of colour properties of onion skin dye

Drying time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3	61.43	49.14	14.62	23.04	27.28	57.58	13.36	4
4	61.73	48.53	14.64	22.63	26.95	57.06	14.71	4
5	**63.57**	**47.94**	**12.80**	**20.93**	**24.53**	**58.52**	**15.61**	**4**
6	63.63	47.85	15.07	22.43	27.03	56.07	15.63	4
7	63.64	45.19	17.43	21.12	27.38	50.43	15.63	4

4.3.1.10 Optimization of curing temperature: The effect of curing temperature on chitosan treated fabric, cured at five different temperatures, i.e. 110^0, 120^0, 130^0, 140^0 and 150 ^{0}C is presented in Table 16. When the curing of chitosan treated sample was carried out at 110^0C, the dye absorption of onion skin dye was 60.77 percent, colour strength 14.84 with good (4) wash fastness rating.

Table 16: Optimization of curing temperature on the basis of colour properties of onion skin dye

Curing temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
110	60.77	50.56	10.34	21.75	24.08	64.55	14.84	4
120	60.95	48.88	10.73	21.28	23.84	63.20	14.90	4
130	63.10	48.84	12.56	21.55	24.94	59.73	15.31	4
140	**64.29**	**46.94**	**12.29**	**21.39**	**24.67**	**60.09**	**15.74**	**4/5**
150	64.88	46.62	12.93	21.34	24.96	58.75	15.79	4/5

It is clear from the table that the increase in curing temperature from 110^0 to 150^0C led to increased dye absorption from 60.77 to 64.88 percent, colour strength from 14.84 to 15.79 whereas L* value decreased from 50.56 to 46.62 which showed increased darkness of colour. The wash fastness rating of the dyed samples was good (4) at 110^0, 120^0, 130^0C and very good (4/5) at 140^0 and 150 ^{0}C curing temperature. The a* and b* values were found to be positive for all the curing temperatures showing redder and yellower tone. The chroma (C*) was highest (24.96) at 150 ^{0}C curing temperature followed by the 130^0 (24.94), 140^0 (24.67), 110^0 (24.08), and 120^0C (23.84). The hue angle (H*) was below 90^0 with positive a* and b* value for all the onion skin dyed samples which depicted brown and yellowish khaki colour.

It is obvious from the table that there was no considerable difference in dye absorption and colour strength value and wash fastness was observed between 140^0 and 150 ^{0}C curing temperature. Therefore 140 ^{0}C was taken as optimum curing temperature for chitosan treated fabric for further dyeing with onion skin natural dye. At this curing temperature, dye absorption was 64.29 percent, colour strength value 15.74 with very good (4/5) wash fatness rating.

4.3.1.11 Optimization of curing time: The results related to curing of chitosan treated cotton fabric which was carried out at four different durations of time i.e. 1, 2, 3 and 4 minutes are presented in Table 17. At 1 minute duration of curing, the dye absorption was 62.50 percent, colour strength 14.43 and wash fastness rating good (4). It can be noticed from the table that as the duration of curing time increased from 1 to 4 minutes, dye absorption increased from 62.50 to 65.54 percent, colour strength from 14.43 to 15.44 whereas L* value decreased from 60.55 to 53.14 denoting the increased darkness of colour. The wash fastness rating was found good (4) at all curing time except for the sample cured for 4 minute which showed wash fastness rating very good (4/5).

All dyed samples cured for different durations of time after chitosan treatment had positive a* and b* values indicating redder and yellow tone of colour. The chroma (C*) was highest (15.19) at 2 minutes duration of curing time followed by 3 (15.01), 1(14.28) and 4

(9.58) minutes. The hue angle (H*) was found below 90^0 having positive a* and b* values, indicating brown and yellowish khaki colour of the samples.

Table 17: Optimization of curing time on the basis of colour properties of onion skin dye

Curing time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1	62.50	60.55	0.90	14.25	14.28	86.33	14.43	4
2	63.69	59.76	0.69	15.17	15.19	87.34	14.96	4
3	65.48	59.37	1.43	14.94	15.01	84.50	15.28	4
4	**65.54**	**53.14**	**5.75**	**7.66**	**9.58**	**53.06**	**15.44**	**4/5**

It is visible from the table that the highest dye absorption (65.54 %), colour strength (15.44) and wash fastness rating (4/5) was noticed at 4 minutes duration of curing hence was taken as optimized curing time.

4.3.2 Application of chitosan on cotton fabric: Chitosan was applied on scoured cotton fabric through pad dry cure method using optimized parameters as presented in Table 18 for biopolymer treatment process. Cotton fabric was first impregnated in a solution containing optimum concentrations of chitosan (4%), citric acid (6%) and sodium hypophosphite (5%) keeping 1:30 material to liquor ratio at pH 5, treatment was given at 90 ^{0}C for 45 minutes. The impregnated fabric was pressed between the squeezing rollers of the padding mangle machine, maintaining pressure of 2kg/cm and achieving 70% -75% expressions. The treated samples were dried at 100 ^{0}C for 5 minutes and cured for 4 minutes at 140 ^{0}C before dyeing with onion skin dye.

Table18: Optimized parameters of biopolymer treatment for onion skin dye

Treatment parameters	Optimized values
Concentration of chitosan (%)	4.0
Concentration of citric acid (%)	6.0
Concentration of sodium hypophosphite (%)	5.0
pH	5.0
Material to liquor ratio	1:30
Treatment temperature (^{0}C)	90
Treatment time (minutes)	45
Drying temperature (^{0}C)	100
Drying time (minutes)	5
Curing temperature (^{0}C)	140
Curing time (minutes)	4

4.3.3 Standardization of dyeing process for natural dye: The dyeing parameters were optimized for dyeing of chitosan treated cotton fabric with natural dye (onion skin) without using the salt and metal mordants. The dyeing process was optimized on the following parameters:

4.3.3.1 Optimization of dye concentration: The data in Table 19 reflect different concentrations of onion skin dye which were used for dyeing of biopolymer (chitosan) treated cotton fabric to obtain the optimized concentration of dye. Five dye baths were formulated having different concentrations of dye powder (owf) i.e. 3, 4, 5, 6 and 7 percent.

The dye absorption with 3 percent onion skin dye was 61.31 percent, colour strength value 11.36 and fairly good (3/4) wash fastness rating. As the concentration of onion skin dye increased from 3 to 7 percent, dye absorption increased from 61.31 to 64.25 percent, colour strength value from 11.36 to 16.76 whereas L* value decreased from 49.14 to 45.19 which depicted increase in darkness of colour. The wash fastness rating was noticed very good (4/5) at 5 and 6 percent, good (4) at 4 and 7 percent and fairly good (3/4) at 3 percent concentration of onion skin dye. The a* and b* values were positive for all the concentrations of onion skin dye used for optimization which showed that all the samples had redder and yellower tone. The chroma (C*) was highest (27.38) at 7 percent followed by 3 (27.28), 6 (27.03), 4 (26.95) and 5 (24.53) percent of dye concentration. The hue angle (H*) was below 90^0 with positive a* and b* value for all the dyed samples indicating yellowish khaki colour.

Table 19: Optimization of dye concentration on the basis of colour properties of onion skin dye

Dye concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3	61.31	49.14	14.62	23.04	27.28	57.58	11.36	3/4
4	63.74	48.53	14.64	22.63	26.95	57.06	14.71	4
5	64.00	47.94	12.80	20.93	24.53	58.52	15.16	4/5
6	**64.20**	**47.85**	**15.07**	**22.43**	**27.03**	**56.07**	**16.72**	**4/5**
7	64.25	45.19	17.43	21.12	27.38	50.43	16.76	4

It is apparent from the table that the wash fastness rating of samples dyed with 6 percent concentration of natural dye was higher than 7 percent. Hence was selected for dyeing of chitosan treated fabric, showing dye absorption 64.20 percent, colour strength value 16.72 and wash fatness rating very good (4/5).

4.3.3.2 Optimization of dyeing pH: The pH of dye solutions was set at i.e. 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, and 7.5 and optimum pH was selected on the basis of dye absorption, colour strength and wash fastness rating of the dyed fabrics (Table 20).

Table 20: Optimization of dyeing pH on the basis of colour properties of onion skin dye

pH	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
4.0	59.52	56.76	11.07	22.44	25.02	63.72	11.36	¾
4.5	60.71	56.17	12.15	22.52	25.59	61.62	12.84	¾
5.0	61.31	53.36	13.77	22.49	26.37	58.49	13.60	¾
5.5	**61.90**	**49.14**	**14.62**	**23.04**	**27.28**	**57.58**	**16.43**	**4/5**
6.0	60.12	45.51	12.72	18.71	22.62	55.76	15.22	4/5
6.5	58.93	58.11	9.54	21.35	23.38	65.89	12.11	4/5
7.0	55.95	60.84	7.11	24.13	25.16	73.54	9.43	¾
7.5	54.76	69.38	3.45	17.41	17.75	78.74	8.45	¾

It was noticed that at pH 4.0, the dye absorption was 59.52 percent, colour strength value 11.36 and wash fastness rating fairly good (3/4). As the pH of dye bath increased from 4.0 to 6.0, there was increase in dye absorption from 59.52 to 60.12 percent, colour strength value from 11.36 to 15.22 whereas L* value decreased from 56.76 to 45.51which revealed that as the pH of dye bath increased, darkness increased. When the pH level increased from 6.5 to 7.5, dye absorption decreased from 58.93 to 54.76 percent, colour strength value from 12.11 to 8.45 and L* value increased which showed decreased darkness of colour. The wash fastness rating was found fairly good (3/4) at all the pH level except at 5.5, 6.0, and 6.5 which showed very good (4/5) wash fastness rating. The a* and b* values were found positive at all pH used for optimization, depicting redder and yellower tone of all the onion skin dyed samples. The chroma (C*) was highest (27.28) at pH 5.5 followed by at 5.0 (26.37), 4.5 (25.59), 7.0 (25.16), 4.0 (25.02), 6.5 (23.38), 6.0 (22.62) and 7.0 (25.16). The hue angle (H*) was below 90^0 with positive a* and b* values for all the dyed samples depicting brown and yellowish khaki colour of samples. It is evident from the table that at 5.5 pH of dye bath, highest dye absorption (61.90 percent), colour strength value (16.43) and very good (4/5) wash fatness rating was observed, hence 5.5 pH was taken as optimum for formulation of dye bath.

4.3.3.3 Optimization of material to liquor ratio for dyeing: The effect of material to liquor ratio (M:L Ratio) for dyeing with onion skin natural dye on percent dye absorption, colour strength value and wash fastness is elucidated in Table 21. To achieve optimized M:L Ratio for dyeing, different M:L Ratios (owf) were used i.e. 1:20, 1:30, 1:40 and 1:50. It is evident from the table that at 1:20 material to liquor ratio, the percent dye absorption was 61.31 percent, colour strength 12.24 with good (4) wash fastness rating.

As the M:L Ratio increased from 1:20 to 1:30, increase in dye absorption was noticed from 61.31 to 63.03 percent, colour strength value from 12.24 to 14.95 and wash fastness grade 4 to 4/5 but L* value decreased from 57.12 to 51.20 which showed the darkness of colour. The progressive increase in M:L Ratio i.e. 1:30 to 1:50 registered the decrease in dye

absorption from 63.03 to 57.68 percent and colour strength value from 14.95 to 12.09 whereas L* value increased from 51.20 to 60.05 which showed the lightness in colour. The wash fastness rating was observed very good (4/5) at 1:30 and 1:40 M:L Ratio where as good (4) at 1:20 and 1:50 M:L Ratio. The a* and b* values were positive for different M:L Ratios used for dyeing which showed all the samples had redder and yellower tone. The chroma (C*) was highest (22.09) at 1:40 M:L Ratio followed by at 1:30 (21.64), 1:50 (20.41), 1:20 (20.23). The hue angle (H*) was below 90^0 along with positive a* and b* values depicting brown and yellowish khaki colour of samples.

Table 21: Optimization of M:L Ratio for dyeing on the basis of colour properties of onion skin dye

M:L Ratio	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1:20	61.31	57.12	8.48	18.37	20.23	65.18	12.24	4
1:30	**63.03**	**51.20**	**10.60**	**18.87**	**21.64**	**60.65**	**14.95**	**4/5**
1:40	62.28	51.68	11.91	18.60	22.09	57.34	14.58	4/5
1:50	57.68	60.05	7.43	19.00	20.41	68.60	12.09	4

It is clear from the table that at 1:30 M:L Ratio, the dye absorption (63.03 %), colour strength (14.95) and wash fastness (4/5) was highest, hence taken as optimized material to liquor ratio.

4.3.3.4 Optimization of dyeing temperature: To investigate the effect of dyeing temperature on the dyeing of chitosan treated cotton fabric with onion skin natural dye, five different temperatures, i.e. 60^0, 70^0, 80^0, 90^0 and 100^0C were tried. It is clear from the Table 22 that at 60 ^{0}C dyeing temperature, the dye absorption was 58.93 percent, colour strength 13.52 and wash fastness rating good (4).

Table 22: Optimization of dyeing temperature on the basis of colour properties of onion skin dye

Dyeing temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
60	58.93	65.70	0.37	11.90	11.91	91.82	13.52	4
70	59.52	65.51	0.27	12.36	12.36	88.68	13.72	4
80	61.31	65.36	1.36	11.69	11.77	83.32	14.87	4
90	**62.50**	**64.46**	**1.35**	**11.76**	**11.84**	**83.40**	**15.99**	**4/5**
100	62.56	55.89	3.03	11.09	11.49	74.69	16.02	4/5

With the increase in dyeing temperature from 60^0 to 100^0C, the increase in dye absorption from 58.93 to 62.56 percent, colour strength from 13.52 to 16.02 and decreased L* value from 65.70 to 55.89 indicated the darkness in colour of samples. The wash fastness

rating was 4 for all the dyed samples except dyed at 90^0 and 100^0C showing very good (4/5) wash fastness rating. The a* and b* values were positive at all treatment temperatures which showed redder and yellower tone of all dyed samples. The chroma **(**C*) was highest (12.36) at 70^0C followed by 60^0 (11.91), 90^0 (11.84), 80^0 (11.77) and 100^0C (11.49). The hue angle (H*) was below 90^0 with positive a* and b* values for all the dyed samples which indicated brown and yellowish khaki colour of dyed samples. It is obvious from the table that wash fastness rating at 90^0 and 100 ^{0}C was same with marginal difference in dye absorption and colour strength hence 90 ^{0}C was taken as optimum dyeing temperature for dyeing of chitosan treated cotton fabric with onion skin dye with dye absorption 62.50 percent, colour strength value 15.99 and wash fatness rating very good (4/5).

4.3.3.5 Optimization of dyeing time: The data regarding the dyeing time and its impact on percent dye absorption, colour strength and wash fastness rating is presented in Table 23. The dyeing of chitosan treated cotton fabric with onion skin was carried out at five different durations of time i.e. 30, 45, 60, 75 and 90 minutes. The dye absorption was 57.74 percent, colour strength 11.36 and wash fastness rating good (4) when dyeing was carried out for 30 minutes.

As the duration of dyeing time increased from 30 to 75 minutes, increase in dye absorption was noticed from 57.74 to 62.44 percent, colour strength value from 11.36 to 16.76 whereas L* value decreased from 49.14 to 45.19 which represented the darkness of shade. Further increase in dyeing time from 75 to 90 minutes showed the decrease in dye absorption from 62.44 to 62.38 and colour strength value from 16.76 to 16.72 but the L* value increased from 45.19 to 47.85 indicating lightness of colour. Wash fastness rating of dyed samples was good (4) for all durations of dyeing time except at 90 minutes. The a* and b* values were positive which showed redder and yellower tone of samples. The chroma (C*) was highest (27.38) at 75 minute duration of dyeing time followed by 30 (27.28), 90 (27.03), 45(26.95) and 60 (24.53) minutes. The hue angle (H*) below 90^0 with positive a* and b* value depicted brown and yellowish khaki colour.

Table 23: Optimization of dyeing time on the basis of colour properties of onion skin dye

Dyeing time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness Grades
		L*	a*	b*	C*	H*		
30	57.74	49.14	14.62	23.04	27.28	57.58	11.36	4
45	59.52	48.53	14.62	22.63	26.95	57.06	14.71	4
60	61.90	47.94	12.80	20.93	24.53	58.52	15.16	4
75	**62.44**	**45.19**	**17.43**	**21.12**	**27.38**	**50.43**	**16.76**	**4**
90	62.38	47.85	15.07	22.43	27.03	56.07	16.72	¾

The optimized dyeing time 75 minutes for dyeing of chitosan treated cotton fabric using onion skin natural dye, with dye absorption 62.38 percent, colour strength 16.72 and wash fastness rating good (4) was taken .

4.3.4 Dyeing of biopolymer treated cotton fabric with natural dye: The biopolymer treated cotton fabric was dyed with onion skin dye with exhaust method using optimized parameters of dyeing as given in Table 24.

Table 24: Optimized dyeing parameters for onion skin dye

Dyeing parameters	Optimized concentration/conditions
Dye concentration (%)	6
Dyeing pH	5.5
Dyeing temperature(^{0}C)	90
Dyeing time (minutes)	75
Dyeing material to liquor ratio	1:30

Plate: 5 Onion skin dye

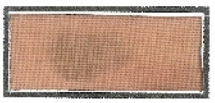
4.4 Standardization of Biopolymer Treatment and Dyeing Process for Synthetic Dye

Different variables of chitosan treatment and dyeing process for synthetic dye (reactive red dye) were optimized to enhance the dyeing efficiency of cotton fabric using biopolymer instead of chemical auxiliaries.

4.4.1 Standardization of biopolymer treatment for synthetic dye: For standardization of chitosan treatment for the reactive red dye different concentrations and conditions were optimized on the basis of colour properties of dyed samples.

4.4.1.1 Optimization of chitosan concentration: Five different concentrations of chitosan i.e. 1.0, 1.5, 2.0, 2.5 and 3.0 percent were applied for the determination of optimum concentration of chitosan for cationization of cotton fabric for enhancing the dye absorption of reactive dye without using chemicals and salts during the dye process (Table 25).

Plate 6: Shades of Onion Skin Dye Obtained During Standardization of Chitosan Treatment

Concentrations of Chitosan				
				
1%	2%	3%	4%	5%
Concentrations of Citric Acid				
				
3%	4%	5%	6%	7%
Concentrations of Sodium Hypophosphite				
				
2%	3%	4%	5%	6%
Treatment pH				
				
3.0	4.0	5.0	6.0	7.0
Material to Liquor Ratio				
				
1:10	1:20	1:30	1:40	
Treatment Temperature				
				
60^0C	70^0C	80^0C	90^0C	100^0C
Treatment Time				
				
15 minutes	30 minutes	45 minutes	60 minutes	

Drying Temperature				
				
60^{0}C	70^{0}C	80^{0}C	90^{0}C	100^{0}C
Drying Time				
				
3 minutes	4 minutes	5 minutes	6 minutes	7 minutes
Curing Temperature				
				
110^{0}C	120^{0}C	130^{0}C	140^{0}C	150^{0}C
Curing Time				
				
1minute	2 minutes	3 minutes	4 minutes	

Plate 7: Shades Obtained During Standardization of Dyeing Process of Onion Skin Dye

Dye Concentration				
				
3%	4%	5%	6%	7%
Dyeing pH				
				
4.0	4.5	5.0	5.5	6.0
				
6.5	7.0	7.5		
Material to Liquor Ratio				
				
1:20	1:30	1:40	1:50	
Dyeing Temperature				
				
60^0C	70^0C	80^0C	90^0C	100^0C
Dyeing Time				
				
30 minutes	45 minutes	60 minutes	75 minutes	90 minutes

Table 25: Optimization of chitosan concentration on the basis of colour properties of reactive red dye

Chitosan concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1.0	64.00	55.97	30.69	-20.30	36.80	326.53	7.37	4
1.5	67.63	55.90	29.96	-19.66	35.84	326.73	8.32	4/5
2.0	72.36	55.05	22.30	-20.76	30.47	317.06	12.38	4/5
2.5	**76.72**	**52.31**	**33.83**	**-17.03**	**37.88**	**333.29**	**15.00**	**4/5**
3.0	77.09	52.29	33.82	-17.48	38.07	332.68	15.09	4/5

It is apparent from the table that at 1.0 percent concentration of chitosan, dye absorption was 64.00 percent, colour strength value 7.37 and good (4) wash fastness rating. With the increased concentration of chitosan from 1 to 5 percent, dye absorption increased from 64.00 to 77.09 percent, colour strength from 7.37 to 15.09 but L* value decreased from 55.97 to 52.29 demonstrating increased darkness of colour. The wash fastness rating was very good (4/5) at all concentrations of chitosan except at 1.0 percent. At all the concentrations of chitosan, positive a* and negative b* values were observed showing redder and bluer tone of samples. The chroma (C*) was highest (38.07) at 3.0 percent concentration of chitosan followed by 2.5 (37.88), 1.0 (36.80), 1.5 (35.84) and 2.0 (30.47) percent. The hue angle (H*) between 270^0 to 360^0 with positive a* and negative b* value depicted that the colour of reactive red dyed samples was reddish blue (magenta) at all concentrations of chitosan.

The highest dye absorption was 76.72, colour strength value 15.00 along with very good (4/5) fastness rating at 2.5 percent concentration of chitosan hence selected for further work.

4.4.1.2 Optimization of concentration of citric acid: For determination of optimum concentration of citric acid, five varied concentrations of citric acid viz. 1, 2, 3, 4 and 5 percent were used. Table 26 illustrates that with increase in concentration of citric acid from 1 to 5 percent, absorption of reactive red dye increased from 68.36 to 76.76, colour strength values from 4.27 to 15.16 but L* value decreased from 53.08 to 45.42. The wash fastness rating of all the dyed samples remained very good (4/5) with all the concentrations of citric acid. The chroma (C*) value was highest for 3.0 (39.02) percent concentration of citric acid followed by 4.0 (38.21), 1.0 (37.95), 2.0 (37.34) and 5.0 (37.23) percent. The hue angle (H*) between 270^0 to 360^0 with positive a* and negative b* values with all the concentrations of citric acid showed reddish blue (magenta) colour of dyed samples (Table 26).

Table 26: Optimization of concentration of citric acid on the basis of colour properties of reactive red dye

Citric acid concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1	68.36	53.08	32.90	-18.90	37.95	330.16	4.27	4/5
2	73.81	52.25	33.36	-16.77	37.34	333.32	7.61	4/5
3	75.27	45.74	35.93	-15.21	39.02	337.06	11.11	4/5
4	**76.72**	**45.70**	**34.66**	**-16.07**	**38.21**	**335.12**	**15.04**	**4/5**
5	76.76	45.42	33.43	-16.38	37.23	333.89	15.16	4/5

The 4 percent of citric acid was chosen as optimum concentration of cross-linking agent for chitosan treatment with percent dye absorption 76.72, colour strength 15.04 and very good (4/5) wash fastness rating.

4.4.1.3 Optimization of concentration of sodium hypophosphite: For optimization of sodium hypophosphite (catalyst) concentration, five different concentrations of sodium hypophosphite i.e. 1, 2, 3, 4 and 5 were taken (Table 27). The increase in dye absorption from 61.09 to 78.54 percent and colour strength value from 6.82 to 14.97 was viewed with successive increase in concentration of sodium hypophosphite from 1 to 5 percent with decreased L* from 53.96 to 46.85. The wash fastness rating was very good (4/5) at 3 to 5% concentration.

The chroma (C*) value was highest (38.56) with 1.0 percent concentration of sodium hypophosphite followed by 3.0 (37.82), 2.0 (36.69), 5.0 (34.76) and 4.0 (34.56) percent. The hue angle (H*) remained between 270^0 to 360^0 with positive a* and negative b* values with all the concentrations of sodium hypophosphite which depicted reddish blue (magenta) colour of samples. The maximum percent dye absorption (78.54) and colour strength value (14.97) was found at 5 percent concentration of sodium hypophosphite, hence it was selected as optimum concentration of sodium hypophosphite.

Table 27: Optimization of concentration of sodium hypophosphite on the basis of colour properties of reactive red dye

Sodium hypophosphite concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1	61.09	53.96	32.37	-20.95	38.56	327.10	6.82	4
2	68.00	53.92	31.20	-19.31	36.69	328.26	9.02	4
3	73.81	52.78	32.84	-18.76	37.82	330.27	11.79	4/5
4	77.18	47.85	29.82	-17.47	34.56	329.65	14.17	4/5
5	**78.54**	**46.85**	**30.07**	**-17.41**	**34.76**	**329.94**	**14.97**	**4/5**

4.4.1.4 Optimization of pH for biopolymer treatment: Seven chitosan treatment baths were prepared setting pH at 3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0. The dye absorption, colour strength values along with wash fastness ratings of chitosan treated cotton fabrics dyed with reactive red dye are presented in Table 28.

Table 28: Optimization of treatment pH on the basis of colour properties of reactive red dye

pH	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3.0	64.00	58.00	29.88	-17.74	34.75	329.31	14.79	4
3.5	67.63	55.39	32.55	-18.99	37.68	329.09	15.21	4
4.0	75.63	53.92	25.98	-25.98	36.47	315.46	16.51	4/5
4.5	78.54	53.79	31.62	-18.30	36.54	329.95	17.60	4/5
5.0	**80.81**	**52.99**	**31.20**	**-19.31**	**36.69**	**328.26**	**18.30**	**4/5**
5.5	72.36	54.15	19.72	-14.21	24.32	324.26	15.31	4/5
6.0	54.18	58.71	19.95	-16.54	25.92	320.36	12.97	4

The table reveals that as the pH increased from 3.0 to 5.0, dye absorption also increased from 64.00 to 80.81 percent, colour strength value from 14.79 to 18.30 with decreased L* value from 58.00 to 52.99 . The wash fastness rating was found very good (4/5) at all pH levels except at 3.0, 3.5 and 6.0. The decline in dye absorption from 80.81 to 54.18 percent and colour strength value from 18.30 to 12.97 was observed when pH increased from 5.0 to 6.0 whereas the L* values increased from 52.99 to 58.71. The chroma (C*) value was highest (37.68) at pH 3.5 followed by 5.0 (36.69), 4.5(36.54), 4.0 (36.47), 3.0 (34.75), 6.0 (25.92) and 5.5 (24.32). The hue angle (H*) found between 270^0 to 360^0 with positive a* and negative b* values at all the pH levels showing reddish blue (magenta) colour of samples.

At 5.0 pH the maximum percent dye absorption (80.81) and colour strength value (18.30) was found along with very good (4/5) wash fastness rating was selected as optimum pH.

4.4.1.5 Optimization of material to liquor ratio for biopolymer treatment: Chitosan treatment baths with different M:L Ratios i.e. 1:10, 1:20. 1:30 and 1:40 were used for optimization of M:L Ratio on the basis of colour properties of reactive red dyed samples. Table 29 illustrates that as the M:L Ratio increased from 1:10 to 1:30, dye absorption increased from 73.27 to 77.81 percent and colour strength value from 11.39 to 15.41 while L* decreased from 48.96 to 48.70 whereas at 1:40 M:L Ratio decrease in colour strength value (13.40) and percent dye absorption (77.45) was observed. The wash fastness rating was found good (4) at 1:10 and 1:40 M:L Ratio where as very good (4/5) at 1:20 and 1:30 M:L Ratio.

Table 29: Optimization of material to liquor ratio on the basis of colour properties of reactive red dye

M:L Ratio	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1:10	73. 27	48.96	35.08	-18.43	39.63	332.29	11.39	4
1:20	76.00	48.92	36.15	-18.18	40.46	333.31	12.28	4/5
1:30	**77.81**	**48.70**	**36.37**	**-17.08**	**40.19**	**334.84**	**15.41**	**4/5**
1:40	77.45	48.76	34.60	-18.34	39.16	332.07	13.40	4

The chroma (C*) value was highest (40.46) at 1:20 M:L Ratio followed by 1:30 (40.19), 1:10 (39.63) and 1:40 (39.16). The hue angle (H*) found between 270^0 to 360^0 with positive a* and negative b* values for all the M:L Ratios of chitosan treatment baths showed reddish blue (magenta) colour of samples. The 1:30 was chosen as optimum M:L Ratio with dye absorption 77.81 percent, colour strength value 15.41 and wash fastness rating very good (4/5).

4.4.1.6 Optimization of treatment temperature: To determine the optimum treatment temperature for chitosan application, treatment was given to scoured cotton fabric at five different temperatures viz. 50^0, 60^0, 70^0, 80^0 and 90 ^{0}C. The data in the Table 30 reveal that as the treatment temperature increased from 50^0 to 90 ^{0}C, dye absorption of reactive red dye increased from 53.81 to 73.81 percent, colour strength value from 13.12 to 17.98 and L* value decreased from 53.05 to 52.45. The wash fastness rating was found good (4) at 50 and 60^0C and very good (4/5) at 70^0, 80^0 and 90 ^{0}C treatment temperature.

The chroma (C*) value was highest (38.46) at 60^0C followed by 70^0 (37.82), 50^0 (37.73), 80^0 (37.15) and 90^0 C (36.50). The hue angle (H*) remained between 270^0 to 360^0 with positive a* and negative b* values at all the treatment temperatures illustrating reddish blue (magenta) colour of samples.

Table 30: Optimization of treatment temperature on the basis of colour properties of reactive red dye

Treatment temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
50	53.81	53.05	32.73	-18.75	37.73	330.20	13.12	4
60	67.63	52.86	33.56	-18.78	38.46	330.78	13.46	4
70	72.00	52.78	32.84	-18.76	37.82	330.27	14.61	4/5
80	73.45	52.71	32.11	-18.67	37.15	329.83	17.56	4/5
90	**73.81**	**52.45**	**31.47**	**-18.47**	**36.50**	**329.59**	**17.98**	**4/5**

The highest percent dye absorption (73.81) and colour strength value (17.98) was observed at 90^0C along with very good (4/5) wash fastness rating, hence was selected as optimum treatment temperature.

4.4.1.7 Optimization of treatment time: To achieve the optimum treatment time, samples were treated with chitosan for varied durations i.e. 15, 30, 75, 60 and 75 minutes. Table 31 illustrates that with increased treatment time from 15 to 75 minutes, dye absorption increased from 64.00 to 78.90 percent, colour strength value from 12.44 to 14.90 whereas the L* value decreased from 53.12 to 52.96. The wash fastness rating was found very good (4/5) at all the durations of treatment time except at 15 and 75 minutes. The chroma (C*) value was highest (37.95) at 45 minutes duration of chitosan treatment with slight variation at different treatment time duration. The hue angle (H*) found between 270^0 to 360^0 with positive a* and negative b* values for all the durations of treatment time which reflected reddish blue (magenta) colour of samples.

There was no considerable difference in percent dye absorption and colour strength value at 60 and 75 minutes of treatment time but the wash fastness rating was higher for 60 minutes of treatment time. Therefore 60 minutes duration was selected as optimum time for chitosan treatment with dye absorption 78.54 percent, colour strength value 14.84 having very good (4/5) wash fastness rating.

Table 31: Optimization of treatment time on the basis of colour properties of reactive red dye

Treatment time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
15	64.00	53.12	32.94	-18.80	37.93	330.29	12.44	3
30	72.00	53.09	32.80	-18.51	37.66	330.56	13.59	4/5
45	76.36	53.08	32.90	-18.90	37.95	330.16	14.11	4/5
60	**78.54**	**52.99**	**31.62**	**-18.30**	**36.54**	**329.95**	**14.84**	**4/5**
75	78.90	52.96	31.83	-18.32	36.72	330.08	14.90	4

4.4.1.8 Optimization of drying temperature: The optimum drying temperature was obtained by altering temperatures for drying the treated samples at 60^0, 70^0, 80^0, 90^0 and 100^0C. The data in Table 32 demonstrate that with rise in drying temperature from 60^0 to 100^0C, dye absorption of reactive red dye increased from 67.63 to 74.90 percent, colour strength value from 11.32 to 16.73 but L* value decreased from 47.82 to 46.85. The wash fastness rating was observed very good (4/5) at all drying temperatures except at 60^0 and 70^0C.

The chroma (C*) value was highest (35.14) at 90^0C. The hue angle (H*) remained between 270^0 to 360^0 having positive a* and negative b* values for all the drying temperatures which showed that the reactive red dyed samples were reddish blue (magenta) in colour.

It was concluded that at 100^0C drying temperature highest percent dye absorption (74.90), colour strength value (16.73) and wash fastness rating (4/5) was noticed, hence was taken as optimum drying temperature for chitosan treatment.

Table 32: Optimization of drying temperature on the basis of colour properties of reactive red dye

Drying temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
60	67.63	47.82	30.07	-17.68	34.89	239.55	11.32	4
70	69.09	47.81	29.82	-17.47	34.56	329.65	14.19	4
80	72.36	47.53	27.35	-16.14	31.76	329.46	16.32	4/5
90	74.18	47.27	29.17	-19.58	35.14	326.13	16.45	4/5
100	**74.90**	**46.85**	**30.07**	**-17.41**	**34.74**	**329.94**	**16.73**	**4/5**

4.4.1.9 Optimization of drying time: Table 33 illustrates that the five different time limits i.e. 3, 4, 5, 6 and 7 minutes were tried for drying of treated fabric to achieve the optimum drying time. It can be observed from the table that as the drying time increased from 3 to 7 minutes, the increase was noticed in dye absorption from 68.00 to 76.72 percent and colour strength value from 11.95 to 15.96 whereas L* value decreased from 53.96 to 53.19 indicating darkness of colour increased. The wash fastness rating was found very good (4/5) for all durations of drying time. The chroma (C*) value was highest (38.56) for 3minutes duration of drying time followed by 7(37.68), 4 (36.69), 6 (35.94) and 5(33.82) minutes depicting brightness of dyed samples. The hue angle (H*) found between 270^0 to 360^0 having positive a* and negative b* values for all the durations of drying time which demonstrated that colour of samples were reddish blue (magenta).

Table 33: Optimization of drying time on the basis of colour properties of reactive red dye

Drying time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3	68.00	53.96	32.37	-20.95	38.56	327.10	11.95	4/5
4	75.63	53.92	31.20	-19.31	36.69	328.26	12.16	4/5
5	76.00	53.39	27.85	-19.18	33.82	325.45	15.25	4/5
6	76.36	53.26	29.57	-20.42	35.94	325.37	15.74	4/5
7	**76.72**	**53.19**	**32.55**	**-18.99**	**37.68**	**329.09**	**15.96**	**4/5**

It is inferred that at 7 minutes drying time highest percent dye absorption (76.72), colour strength value (15.96) with very good (4/5) wash fastness rating was achieved, hence was selected as optimum drying time.

4.4.1.10 Optimization of curing temperature: The data regarding the optimization of curing temperature on the basis of dye absorption, colour strength value and wash fastness of reactive red dye are presented in Table 34. Five different temperatures i.e. 110^0, 120^0, 130^0, 140^0 and 150 ^{0}C were used for curing of chitosan treated fabrics.

It is clear from the table as the curing temperature increased from 110^0 to 150^0 C, dye absorption increased from 71.27 to 81.45, colour strength from 16.60 to 18.65 and L* value decreased from 48.10 to 47.57 indicating increased darkness of colour. The wash fastness rating was found very good (4/5) at all the curing temperatures.

The chroma (C*) value was highest (43.79) at 150 ^{0}C. The hue angle (H*) found between 270^0 to 360^0 having positive a* and negative b* value for all the curing temperatures showed reddish blue (magenta) colour of samples.

Table 34: Optimization of curing temperature on the basis of colour properties of reactive red dye

Curing temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
110	71.27	48.10	30.71	-18.04	35.62	329.58	16.60	4/5
120	73.09	48.03	30.60	-18.74	35.88	329.58	17.18	4/5
130	77.09	48.00	29.88	-17.74	34.75	329.31	17.84	4/5
140	80.36	47.97	29.78	-18.43	35.02	328.26	18.09	4/5
150	**81.45**	**47.57**	**34.83**	**-26.54**	**43.79**	**322.69**	**18.65**	**4/5**

The highest percent dye absorption (81.45), colour strength value (18.65) and very good (4/5) wash fastness rating was achieved at 150^0C, hence was chosen as optimum curing temperature.

4.4.1.11 Optimization of curing time: To determine the optimum curing time, five different time durations i.e. 1, 2, 3, 4 and 5 minutes were used for curing the treated samples. It is clear from Table 35 that as the curing time increased from 1 to 5 minutes, dye absorption increased from 69.81 to 77.81 and colour strength value from 16.77 to 18.51 while L*value declined from 55.40 to 53.92 denoting darkness of shades. The chroma (C*) value was highest (38.07) for 1minute duration of curing time followed by 2 (37.68), 5 (36.69), 4 (36.47) and 3 (24.32) minutes depicting brightness of dyed samples. The hue angle (H*) found between 270^0 to 360^0 along with positive a* and negative b* values for all the durations of curing time depicted reddish blue (magenta) colour of reactive red dyed samples.

The wash fastness rating was found very good (4/5) at all durations of curing time. Further it was also noticed that when chitosan treated fabric was cured for 150^0C for 5 minutes, slight yellowing of fabric took place. There was no remarkable difference in colour strength value of reactive red dyed fabrics cured for 3, 4 and 5 minutes and the wash fastness rating was also same. Therefore 3 minutes curing time was selected as optimum curing time with dye absorption 76.90 percent, colour strength value 18.42 comprising wash fastness rating very good (4/5).

Table 35: Optimization of curing time on the basis of colour properties of reactive red dye

Curing time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1	69.81	55.40	32.65	-19.58	38.07	329.06	16.77	4/5
2	72.00	55.39	32.55	-18.99	37.68	329.09	16.96	4/5
3	**76.90**	**54.15**	**19.72**	**-14.21**	**24.32**	**324.26**	**18.42**	**4/5**
4	77.45	53.79	25.98	-25.98	36.47	315.46	18.45	4/5
5	77.81	53.92	31.20	-19.31	36.69	328.26	18.51	4/5

4.4.2 Application of biopolymer treatment on scoured cotton fabric: The biopolymer treatment was applied on the cotton fabric by pad dry cure method using optimized concentrations and conditions mentioned in the Table 36.

Table 36: Optimized concentration and conditions for application of chitosan for reactive red dye

Treatment parameters	Optimized concentrations/conditions
Concentration of chitosan (%)	2.5
Concentration of citric acid (%)	4
Concentration of sodium hypophosphite (%)	5
Treatment pH	5.0
Material to liquor ratio	1:30
Treatment temperature (^{0}C)	90
Treatment time (minutes)	60
Drying temperature (^{0}C)	100
Drying time (minutes)	7
Curing temperature (^{0}C)	150
Curing time (minutes)	3

Cotton fabric was first impregnated in a solution containing optimum concentrations of chitosan (2.5%), citric acid (4%) and sodium hypophosphite (5%) keeping 1:30 material to liquor ratio and pH 5.0, treated at 90^{0}C for 60 minutes. The impregnated fabric was pressed between the squeezing rollers of the padding mangle machine maintaining pressure of 2 kg/cm and achieving 70% -75% expressions. The biopolymer (chitosan) treated samples were dried at 100^{0}C for 7 minutes and cured for 3 minutes at 150 ^{0}C before dyeing with reactive red dye.

4.4.3 Standardization of dyeing process for synthetic dye

4.4.3.1 Optimization of dye concentration: Five different dye concentrations viz. 1.0, 1.5, 2.0, 2.5 and 3.0 percent were used to obtain the optimum dye concentration of reactive red dye. It is evident from Table 37 that as the concentration of dye increased from 1.0 to 3.0 percent, dye absorption increased from 56.44 to 78.64 percent and colour strength value from

6.20 to 18.76 but L* value registered the decrease from 50.28 to 47.77 indicating increase in darkness of shade.

The wash fastness rating was found fairly good (3/4) at 1 percent, good (4) at 1.5 percent and very good (4/5) at 2.0, 2.5 and 3.0 percent of dye concentration. The chroma (C*) value was highest (27.38) at 3.0 percent concentration of dye followed by 2.5 (27.00), 2.0 (26.16), 1.5 (25.47) and 1.0 (23.62) percent of concentration depicting the brightness of dyed samples. The hue angle (H*) remained between 270^0 to 360^0 having positive a* and negative b* values for all the concentrations of dye which indicated reddish blue (magenta) colour of samples.

Table 37: Optimization of dye concentration on the basis of colour properties of reactive red dye

Dye concentration (%)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1.0	56.44	50.28	23.54	-1.89	23.62	355.41	6.20	3/4
1.5	69.47	49.55	25.40	-1.85	25.47	355.82	10.65	4
2.0	77.09	48.95	26.07	-2.26	26.16	355.04	12.66	4/5
2.5	**78.13**	**47.94**	**26.84**	**-2.96**	**27.00**	**353.70**	**18.73**	**4/5**
3.0	78.64	47.77	27.18	-3.31	27.38	353.05	18.76	4/5

The 2.5 percent was selected as optimum concentration of dye with dye absorption 78.13 percent, colour strength value 18.73 along with very good (4/5) wash fastness rating as no remarkable difference was noticed in 2.5 and 3.0 percent concentration.

4.4.3.2 Optimization of dyeing pH: Five different pH i.e. 3.5, 4.0, 4.5, 5.0, 5.5 were set to attain optimum pH value of dyeing solution. It is clear from Table 38 that as the pH increased from 3.5 to 5.0, dye absorption of reactive red dye increased from 67.63 to 78.26 percent, colour strength (k/s) value from 9.74 to 14.75 whereas the L* value decreased from 58.00 to 52.99 indicating increased darkness of shade. Further increase in pH from 5.0 to 5.5 showed the decrease in dye absorption from 78.26 to 75.63 and colour strength (k/s) from 14.75 to 10.13 however the L* value increased from 52.99 to 53.96 denoting the decreased darkness. The wash fastness rating was fairly good (3/4) at 3.5 and 4.0 pH, good (4) at 4.5 and 5.0 pH and very good (4/5) at 5.0 pH.

The chroma (C*) value was highest (38.56) at pH 5 followed 4.5 (36.69), 4.0 (36.54), 5.5 (34.75) and 3.5 (33.82) indicating brightness of dyed samples. The hue angle (H*) was found between 270^0 to 360^0 with positive a* and negative b* values at all pH ranges which depicted reddish blue (magenta) colour of samples.

The highest percent dye absorption (78.26), colour strength value (14.75) with very good (4/5) wash fastness rating was found at 5.0 pH hence was selected as optimum pH value for dyeing of chitosan treated cotton fabric with reactive red dye.

Table 38: Optimization of dyeing pH on the basis of colour properties of reactive red dye

pH	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
3.5	67.63	58.00	27.85	-19.18	33.82	325.45	9.74	3/4
4.0	77.81	53.92	31.62	-18.30	36.54	329.95	12.26	3/4
4.5	78.18	53.26	31.20	-19.31	36.69	328.26	14.27	4
5.0	**78.26**	**52.99**	**32.37**	**-20.95**	**38.56**	**327.10**	**14.75**	**4/5**
5.5	75.63	53.96	29.88	-17.74	34.75	329.31	10.13	4

4.4.3.3 Optimization of material to liquor ratio (M:L Ratio): Different M:L Ratios i.e. 1:20, 1:30, 1:40 and 1:50 were used to achieve optimum M:L Ratio for dyeing of chitosan treated cotton fabric with reactive red dye. Table 39 elucidates that with the increase in M:L Ratio from 1:20 to 1:30, there was increase in dye absorption from 76.00 to 76.38 percent and colour strength (k/s) value from 14.77 to 17.43 but the L* values decreased from 66.26 to 65.67 which depicted increased darkness of shade. Further increase in M:L Ratio from 1:40 to 1:50 showed the decrease in dye absorption from 76.02 to 75.86 percent and colour strength values from 16.84 to 16.30 whereas L* values increased from 65.20 to 65.93 denoting lightness of shade. The wash fastness rating was observed fairly good (3/4) at 1:20 and 1:50, good (4) at 1:40 and very good (4/5) at 1:30 M:L Ratio.

The chroma (C*) value was highest (29.87) for 1:40 M:L Ratio followed by 1:50 (29.18), 1:30 (28.00) and 1:20 (18.82) indicating brightness of sample. The hue angle (H*) was found between 270^0 to 360^0 with positive a* and negative b* values for all the M:L Ratios showing reddish blue (magenta) colour of sample.

Table 39: Optimization of material to liquor ratio on the basis of colour properties of reactive red dye

M:L Ratio	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
1:20	76.00	66.26	18.75	-1.59	18.82	355.15	14.77	3/4
1:30	**76.38**	**65.67**	**27.86**	**-2.75**	**28.00**	**354.35**	**17.43**	**4/5**
1:40	76.02	65.20	29.66	-3.51	29.87	353.25	16.84	4
1:50	75.86	65.93	29.03	-2.90	29.18	354.28	16.30	3/4

It is concluded from the table that the percent dye absorption 76.38, colour strength (k/s) value 17.43 and wash fastness rating very good (4/5) was found highest at 1:30 M:L Ratio, hence selected.

4.3.3.4 Optimization of dyeing temperature: To determine the optimum dyeing temperature for dyeing of chitosan treated fabric with reactive red dye four different dyeing temperatures i.e. 50^0, 60^0, 70^0 and 80^0C were tried.

Table 40: Optimization of dyeing temperature on the basis of colour properties of reactive red dye

Dyeing temperature (^{0}C)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
50	74.90	48.03	32.96	-6.42	33.58	348.98	14.92	4
60	77.09	47.46	32.54	-2.01	32.60	356.45	15.76	4
70	78.18	46.41	31.28	-1.89	31.34	356.53	18.32	4/5
80	**78.54**	**45.66**	**30.66**	**-2.24**	**30.37**	**355.81**	**18.41**	**4/5**

Table 40 demonstrates that as the dyeing temperature increased from 50^0 to 80^0C , dye absorption increased from 74.90 to 78.54 percent and colour strength (k/s) values from 14.92 to 18.41 whereas L* value decreased from 48.03 to 45.66 displaying the increased darkness of shade. The wash fastness rating was found good (4) at 50^0 and 60^0C, very good (4/5) at 70^0 and 80^0C.

The chroma (C*) value was highest (33.58) at 50^0C which reduced (30.37) at 80 ^{0}C. The hue angle (H*) remained between 270^0 to 360^0 having positive a* and negative b* values for all the dyeing temperatures which showed that the colour of samples was reddish blue (magenta). It is thus envisaged that 80^0C dyeing temperature showed maximum dye absorption (78.54 %) and colour strength value (18.41) and very good (4/5) wash fastness rating, hence selected as optimum.

4.3.3.5 Optimization of dyeing time: The optimization of dyeing time was done by observing the dye absorption, colour strength value and wash fastness at five different time periods i.e. 15, 30, 45, 60 and 75 minutes.

Table 41: Optimization of dyeing time on the basis of colour properties of reactive red dye

Dyeing time (minute)	Dye absorption (%)	Colour coordinates					Colour strength (k/s)	Wash fastness grades
		L*	a*	b*	C*	H*		
15	70.54	58.71	19.95	-16.54	25.92	320.36	10.49	3/4
30	71.63	51.12	33.79	-22.30	40.49	326.58	17.18	4
45	**72.36**	**50.94**	**32.97**	**-19.71**	**38.42**	**329.13**	**17.87**	**4/5**
60	72.72	50.76	40.35	-33.03	52.28	320.84	17.92	4/5
75	72.76	50.36	30.36	-21.32	37.10	324.93	17.02	4

Table 41 elucidates that with the increase in dyeing time from 15 to 75 minutes, the dye absorption of reactive red dye on chitosan treated cotton fabric increased from 70.54 to 72.76 percent, colour strength (k/s) from 10.49 to 17.02 whereas the L* value showed decline from 58.71 to 50.36 depicting increased darkness of shade. The wash fastness rating was noticed fairly good (3/4) at 15 minutes, good (4) at 30 and 75 minutes and very good (4/5) at 45 and 60 minutes dyeing time respectively. The chroma (C*) value decreased from 52.28 at 60 minutes to 25.92 at 15 minutes indicating brightness of dyed samples. The hue angle (H*)

remained between 270^0 to 360^0 with positive a* and negative b* values for all the durations of dyeing time depicting reddish blue (magenta) colour of samples. The wash fastness rating 45 to 60 minutes was very good (4/5) with negligible variation in dye absorption and colour strength hence 45 minutes was selected as optimum dyeing time at which the dye absorption was 72.36 percent, colour strength (k/s) value 17.87 along with very good (4/5) wash fastness rating.

4.4.4 Application of reactive red dye on chitosan treated fabric: The chitosan treated cotton fabric was dyed with reactive red dye using exhaust method following the optimized values of dyeing parameters (Table 42):

Table 42: Optimized concentration and conditions for dyeing with reactive red dye

Dyeing parameters	**Optimized concentration/conditions**
Dye concentration (%)	2.5
Dyeing pH	5.0
Dyeing material to liquor ratio	1:30
Dyeing temperature (^{0}C)	80
Dyeing time (minutes)	45

4.5 Measurement of Total Dissolved Solids (TDS): The amount of total dissolved solids (TDS) was measured in dye liquor after dyeing.

Table 43 consists of data regarding the presence of total dissolved solid remained in the dye liquor after dyeing of alum, alkali and chitosan treated cotton fabrics with onion skin and reactive dyes separately. In case of natural dye, the TDS value was higher (1260 ppm) in the dye liquor left after dyeing of alum treated fabric as compared to the dye liquor left after dyeing of chitosan treated dyed fabric that exhibited presence of only 618 ppm total dissolved solids amounting half of the value in dye liquor in which alum treated sample was dyed.

The assessment of synthetic dye liquor revealed that the TDS value was lower in the dye liquor left after dyeing of chitosan treated fabric showing presence of only1019 ppm total dissolved solids which was quite less than the liquor in which alkali treated samples were dyed with reactive red dye (1830 ppm).

Table 43: Total dissolved solids present in dye bath after dyeing

S. No.	**Dye liquor**	**TDS (ppm)**
	Onion skin dye liquor after	
1.	Alum treatment	1260
2.	Chitosan treatment	618
	Reactive red dye liquor after	
3.	Alkali treatment	1830
4.	Chitosan treatment	1019

Plate 8: Shades of Reactive Red Dye Obtained During Standardization of Chitosan Treatment

Concentrations of Chitosan				
				
1.0 %	1.5%	2.0%	2.5%	3.0%
Concentrations of Citric Acid				
				
1%	2%	3%	4%	5%
Concentrations of Sodium Hypophosphite				
				
1%	2%	3%	4%	5%
Treatment pH				
				
3.0	3.5	4.0	4.5	5.0
				
5.5	6.0			
Material to Liquor Ratio				
				
1:10	1:20	1:30	1:40	
Treatment Temperature				
				
50^0C	60^0C	70^0C	80^0C	90^0C

Treatment Time				
				
15 minutes	30 minutes	45 minutes	60 minutes	75 minutes
Drying Temperature				
				
60^{0}C	70^{0}C	80^{0}C	90^{0}C	100^{0}C
Drying Time				
				
3 minutes	4 minutes	5 minutes	6 minutes	7 minutes
Curing Temperature				
				
110^{0}C	120^{0}C	130^{0}C	140^{0}C	150^{0}C
Curing Time				
				
1minute	2 minutes	3 minutes	4 minutes	5 minutes

Plate 9: Shades Obtained During Standardization of Dyeing Process of Reactive Red Dye

Dye Concentration				
				
1.0 %	1.5 %	2.0 %	2.5 %	3.0 %
Dyeing pH				
				
3.5	4.0	4.5	5.0	5.5
Material to Liquor Ratio				
				
1:20	1:30	1:40	1:50	
Dyeing Temperature				
				
50^0C	60^0C	70^0C	80^0C	
Dyeing Time				
				
15 minutes	30 minutes	45 minutes	60 minutes	75 minutes

4.6 Fourier Transformation Infrared Spectroscopy (FTIR) analysis: FTIR analysis was done for selected biopolymer, dye powders, biopolymer treated and treated dyed fabrics. The presence of functional groups at different peak ranges (cm-1) is presented in Table 44 to 49.

4.6.1 FTIR analysis of chitosan: The characteristics bands of the chitosan are presented in Table 44. The peak corresponding to the 3290.65 cm^{-1} represented the presence of hydroxyl group (H-bonded–OH- stretch). The area under the 2876.86 cm^{-1} peak of biopolymer showed the presence of alkanes, O-H stretching - alkanes, carboxylic Acids. The presence of peak at 1661. 75 cm^{-1} indicated the -C-double bond-C stretch and amide. The existence of aromatic ring stretch, secondary amine, -NH-bend was confirmed by the presence of peak at 1588.74 cm^{-1}. Peaks at 1381.74 cm^{-1}, 1151.75 cm^{-1} , 1074.68 cm^{-1} and 662.81 cm^{-1} because of -OH- bend, secondary amine –CN- stretch (tertiary alcohol, C-O stretch), -C-C- stretch, primary amine, CN stretch and aliphatic bromo compounds respectively.

Table 44: FTIR analysis of chitosan powder

S.No.	Peak ranges (cm^{-1})	Peaks	Functional groups
1.	3200-3300	3290.65	Hydroxyl group (H-bonded–OH- stretch)
2.	2800-2900	2876.86	Alkanes, O-H stretching - Alkanes, Carboxylic Acids
3.	1600-1700	1661.75	-C-double bond-C stretch, amide
4.	1500-1600	1588.74	Aromatic ring stretch, secondary amines, -NH-bend
5.	1400-1500	1421.73	Organic Sulphates
6	1300-1400	1381.74	-OH- bend
7.	1100-1200	1151.74	Secondary amine –CN- stretch, tertiary alcohol, C-O stretch
8.	1000-1100	1074.68	-C-C- stretch, primary amine, CN stretch
9.	600-700	662.81	Aliphatic Bromo compounds

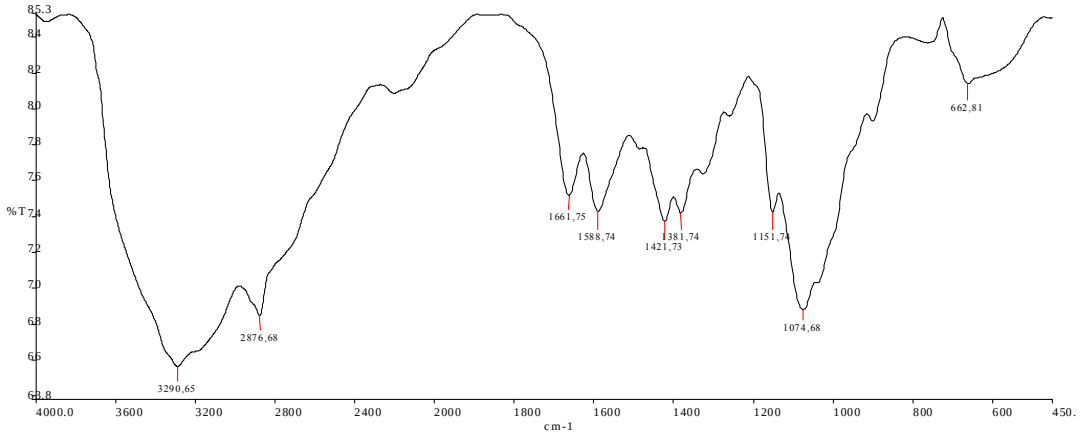


Figure 2: FTIR analysis of chitosan powder

4.6.2 FTIR analysis of onion skin dye powder: Table 45 comprises the data regarding the Fourier Transformation Infrared spectroscopy (FTIR) analysis of onion skin dye powder which was done to analyze presence of functional groups.

Table 45: FTIR analysis of onion skin dye powder

S.No.	Peak ranges (cm^{-1})	Peaks	Functional groups
1.	3200-3300	3286.52	Hydroxyl group (H-bonded–OH- stretch)
2.	2900-3000	2924.57	Methylene–CH- stretch
3.	1700-1800	1732.61	Carbonyl group, aldehyde group
4.	1600-1700	1645.56	-C-double bond-C stretch/ quinone or conjugated ketone
5.	1400-1500	1423.60	Organic Sulphates
6	1300-1400	1327.59	-OH- bend
7.	1000-1100	1050.57	-C-C- stretch,ethers
8.	700-800	771.70	Skeletal –C-C- vibrations
9.	600-700	635.68	Aliphatic Bromo compounds

This table depicts the presence of different functional groups at different peaks which are responsible for different properties. The spectrum of onion dye represents the peak at 3286.52 cm^{-1} due to the hydroxyl group (H-bonded–OH- stretch), peak at 2924.57 cm^{-1} that was because of methylene–CH- stretch and the peak at 1732.61 cm^{-1} was attributed to carbonyl group (C=O) and aldehyde group. The peaks at 1645.56 cm^{-1} and 1423. 60 cm^{-1} indicated the presence of C=C stretch, quinone or conjugated ketone and organic sulphates respectively. The peaks at 1327.59 cm^{-1} suggested the presence of OH – bend which showed water absorption characteristic. Finally the peaks at 1050.57 cm^{-1}, 771,70 cm^{-1}, and 635.68 cm^{-1} exhibited the presence of –C-C vibrates and aliphatic bromo compounds respectively.

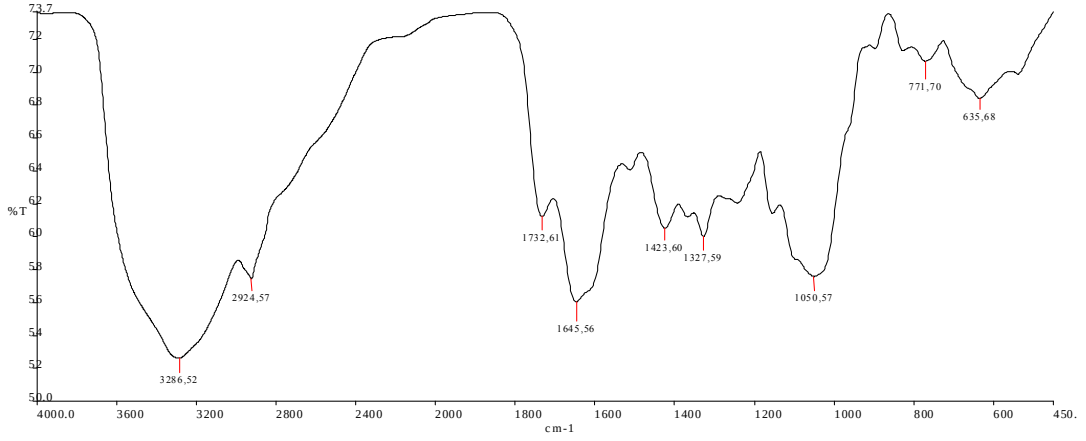


Figure 3: FTIR analysis of onion skin dye powder

4.6.3 FTIR analysis of reactive red dye: Fourier transfer infrared spectroscopy (FTIR) analysis of reactive red dye powder was done to analyze the functional groups and different characteristics due to their presence (Table 46). The region of broad absorption band at 3463.28 cm^{-1} for the reactive red dye powder was characterized with O-H stretching and H-bonded band structure that mostly contain major functional groups of phenol, alchohols and water. A small peak at 3103.37 cm^{-1} was attributed to the aromatic ring (-C-H-stretch). The

presence of -S-H- stretch exist in the region of 2503.58 cm^{-1}, which might be due to the presence of thiols. The presence of peaks at 2102.56 cm^{-1} and 1541.23 cm^{-1} indicated C-triple bond-C- stretch and Aromatic ring stretch-NH-bend respectively.

The peaks at 1477.21 cm^{-1}, 1412.33 cm^{-1} indicated the presence of organic sulphate and peaks also existed at 1323.23 cm^{-1} , 1212.17 cm^{-1} and 1051.29 cm^{-1} which might be due to the presence of –OH- bend, aromatic primary amine –CN- stretch and –C-C- stretch respectively. In addition, peaks were at 985.41 cm^{-1}, 901.55 cm^{-1} for cyclo-hexane ring vibrations. Appearance of peaks at 826.51 cm^{-1}, 681.46 cm^{-1} and 627.43 cm^{-1} and 545.51 cm^{-1} showed the aliphatic bromo compound and –C-I- stretch.

Table 46: FTIR analysis of reactive red dye

S.No.	Peak ranges (cm^{-1})	Peaks	Functional groups
1.	**3400-3500**	3463.28	O-H stretching and H- bonded band
2.	**3100-3200**	3103.37	Aromatic ring (-C-H- stretch)
3.	**2500-2600**	2503.58	Thiols (-S-H- stretch)
4.	**2100-2200**	2102.56	C-triple bond-C- stretch
5.	**1500-1600**	1541.23	Aromatic ring stretch-NH-bend
6.	**1400-1500**	1477.21	Organic Sulphates
		1412.33	
7.	**1300-1400**	1323.33	-OH- bend
8.	**1200-1300**	1212.17	Aromatic primary amine –CN- stretch
9.	**1000-1100**	1051.29	-C-C- stretch
10.	**900-1000**	985.41	Cyclo hexane ring vibrations
		901.55	
11	**800-900**	826.51	Peroxides -C-O-O-stretch
12.	**600-700**	681.46 627.43	Aliphatic Bromo compounds
13.	**500-600**	545.51	-C-I- stretch

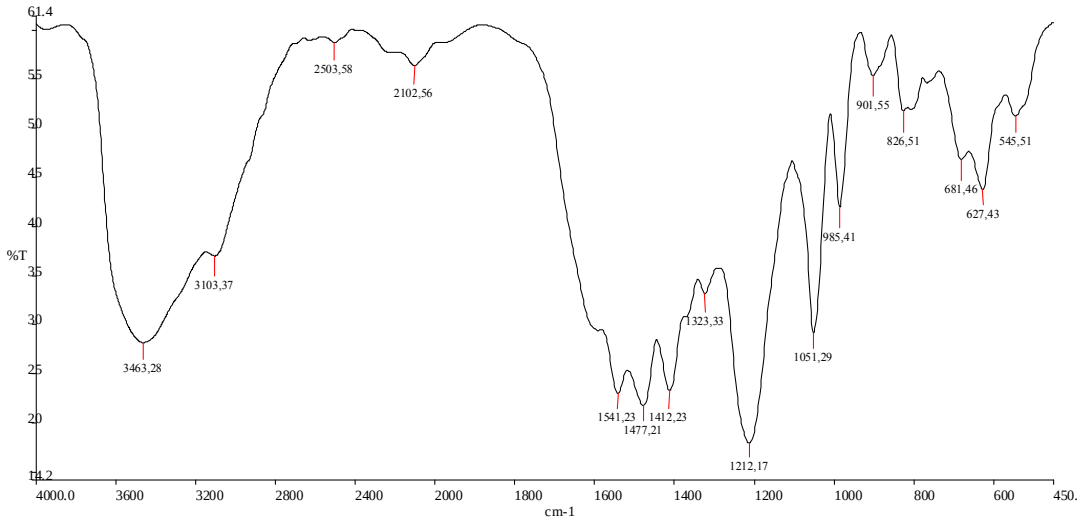


Figure 4: FTIR analysis of reactive red dye powder

4.6.4 FTIR analysis of chitosan treated cotton fabric: FTIR analysis of chitosan treated fabric was done and data related to presence of functional groups are presented in Table 47.

Table 47: FTIR analysis of chitosan treated cotton fabric

S.No.	Peak ranges (cm^{-1})	Peaks	Functional groups
1.	3200-3500	3278.38	Hydroxyl group (H-bonded–OH- stretch) Alcohol
2.	2800-2900	2895.56	C-H stretching, O-H stretching, Alkanes (CH; CH_2; CH_3), Carboxylic Acids
3.	2200-2300	2297.87	Cyano compounds,disubstituted alkynes
4.	2000-2100	2095.52	Cyanide ion and related ion
		2001.67	
5.	1600-1700	1634.07	-C-double bond-C stretch
6	1400-1500	1427.33	Organic Sulphates
7.	1300-1400	1363.84	-OH bend
		1313.86	
8.	1200-1300	1202.31	Tertiary amine, –CN- stretch
9.	1100-1200	1158.22	Secondary amine –CN- stretch
		1105.03	
10.	1000-1100	1052.74	C-O stretching - Alcohol , Carboxylic Acids, Esters, Ethers
		1026.13	
11	700-800	703.94	Skeletal –C-C- vibrations
12.	600-700	663.41	Aliphatic Bromo compounds
		607.63	
13.	500-600	555.04	-C-I- stretch

The spectrum showed characteristics (functional groups) namely hydroxyl group (H-bonded–OH- stretch) alcohol (3278.38 cm^{-1}), C-H stretching, O-H stretching, alkanes (2895.56 cm^{-1}), carboxylic acids (2895.56 cm^{-1}), cyano compounds, disubstituted alkynes (2297.87 cm^{-1}), cyanide ion and related ion (2095.52 cm^{-1} and 2001.67 cm^{-1}), -C-double bond-C stretch (1634.07 cm^{-1}), organic sulphates (1427.33 cm^{-1}), -OH bend (1363.84 cm^{-1} and 1313.86 cm^{-1}), tertiary amine –CN- stretch (1202.31cm^{-1}), secondary amine –CN- stretch (1158.22 cm^{-1} and 1105.03cm^{-1}), C-O stretching - alcohol, carboxylic acids, esters, ethers (1052.74 cm^{-1} and 1026.13 cm^{-1}) , skeletal –C-C- vibrations (703.94 cm^{-1}), aliphatic bromo compounds (663.41cm^{-1} and 607.63 cm^{-1}), -C-I- stretch (555.04 cm^{-1}) were present in chitosan treated cotton fabric.

Figure 5: FTIR analysis of chitosan treated cotton fabric

4.6.5 FTIR analysis of chitosan treated onion skin dyed cotton fabric: The data regarding FTIR analysis of chitosan treated onion skin dyed fabric in Table 48 indicated the presence of different functional groups.

The peaks at 3273.69 cm^{-1}, 2895.77 cm^{-1}, 2294.82 cm^{-1}, 2106.81$cm^{-1}$and 1631.14 cm^{-1} are associated with the presence of hydroxyl group (H-bonded–OH- stretch) alcohol, C-H stretching, O-H stretching (alkanes, carboxylic Acids), cyano compounds, C-triple bond-C-stretch and functional group C=O , -C-double bond-C stretch respectively. It confirmed the existence of different functional groups viz. organic sulphates (1426.68 cm^{-1}), -OH bend and aromatic amino stretch (1363.39 cm^{-1} and 1313.75 cm^{-1}), tertiary amine and –CN- stretch (1202.53 cm^{-1}) , secondary amine –CN- stretch (1105.67 cm^{-1}, 1153.05 cm^{-1}, 1157.81 cm^{-1}), -C-C- stretch (1026.76 cm^{-1}), skeletal –C-C- vibrations (703.07 cm^{-1}), aliphatic bromo compounds (664.19 cm^{-1} and 610.67 cm^{-1}), -C-I- stretch (555.17 cm^{-1}).

Table 48: FTIR analysis of chitosan treated onion skin dyed cotton fabric

S. No.	Peak ranges (cm^{-1})	Peaks	Functional groups
1.	3200-3300	3273.69	Hydroxyl group (H-bonded–OH- stretch) Alcohol
2.	2800-2900	2895.77	C-H stretching, O-H stretching - Alkanes (CH; CH2; CH3), Carboxylic Acids
3.	2200-2300	2294.82	Cyano compounds,disubstituted alkynes
4.	2100-2200	2106.81	C-triple bond-C-stretch
5.	1600-1700	1631.14	functional group C=O , -C-double bond-C stretch
6	1400-1500	1426.68	Organic Sulphates
7.	1300-1400	1363.39	-OH bend
		1313.75	Aromatic amino stretch
8.	1200-1300	1202.53	Tertiary amine, –CN- stretch
9.	1100-1200	1105.67	Secondary amine –CN- stretch
		1153.05	
		1157.81	
10.	1000-1100	1026.76	-C-C- stretch
11	700-800	703.07	Skeletal –C-C- vibrations
12.	600-700	664.19	Aliphatic Bromo compounds
		610.67	
13.	500-600	555.17	-C-I- stretch

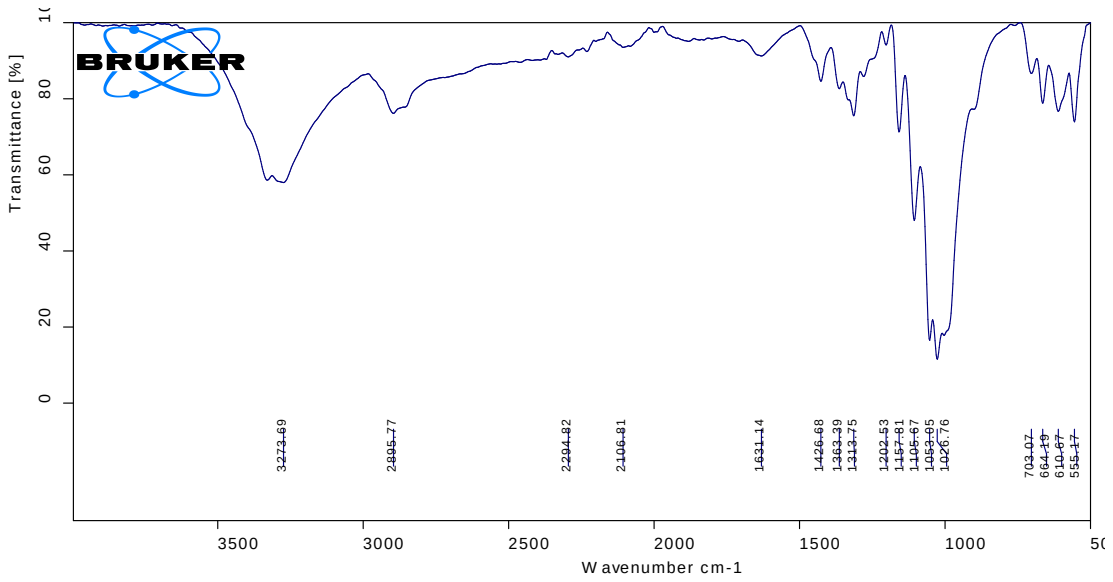


Figure 6: FTIR analysis of chitosan treated onion skin dyed cotton fabric

4.6.7 FTIR analysis of chitosan treated reactive dyed cotton fabric: The Table 49 consists of data regarding the FTIR spectrum of chitosan treated cotton fabric dyed with reactive red dye. The appearance of a strong broad band at 3276.62 cm^{-1} showed the characteristics of hydrogen group (H-bonded–OH- stretch) where as small peak at 2895.70 cm^{-1} and 2297.36 cm^{-1} depicted characteristic of alkanes and cyano compounds, distributed alkynes. Further intensification of a weak band at 2108.00 cm^{-1} showed the characteristic of C-triple bond-C-

stretch and 1636.30 cm^{-1} of -C-double bond-C stretch, primary amine and N-H bend. Characteristics of organic sulphates was found at 1426.98 cm^{-1} and -OH bend (aromatic primary amine stretch) at 1314.73 cm^{-1} as well as at 1363.66 cm^{-1}. The tertiary amine, –CN- stretch and secondary amine, –CN- stretch were noticed at 1202.68 cm^{-1} and 1105.15 cm^{-1} (and 1157.03 cm^{-1}) respectively.

There were peaks at 1024.85 cm^{-1} , 702.71 cm^{-1}, 663.84 cm^{-1}, 608.17 cm^{-1} and 555.32 cm^{-1} which illustrated the existence of -C-C- stretch, Skeletal –C-C- vibrations, aliphatic bromo compounds and -C-I- stretch correspondingly.

Table 49: FTIR analysis of chitosan treated reactive red dyed cotton fabric

S. No.	Peak ranges (cm^{-1})	Peaks	Functional groups
1.	3200-3300	3276.62	Hydroxyl group (H-bonded–OH- stretch)
2.	2800-2900	2895.70	C-H stretching, O-H stretching - Alkanes (CH; CH2; CH3), Carboxylic Acids
3.	2200-2300	2297.36	Cyano compounds, disubstituted alkynes
4.	2100-2200	2108.00	C-triple bond-C-stretch
5.	1600-1700	1636.30	-C-double bond-C stretch, primary amine, N-H bend
6	1400-1500	1426.98	Organic Sulphates
7.	1300-1400	1314.73	-OH bend, Aromatic primary amine stretch
		1363.66	
8.	1200-1300	1202.68	Tertiary amine, –CN- stretch
9.	1100-1200	1105.15	Secondary amine, –CN- stretch
		1157.03	
10.	1000-1100	1024.85	-C-C- stretch
11	700-800	702.71	Skeletal –C-C- vibrations
12.	600-700	663.84	Aliphatic Bromo compounds
		608.17	
13.	500-600	555.32	-C-I- stretch

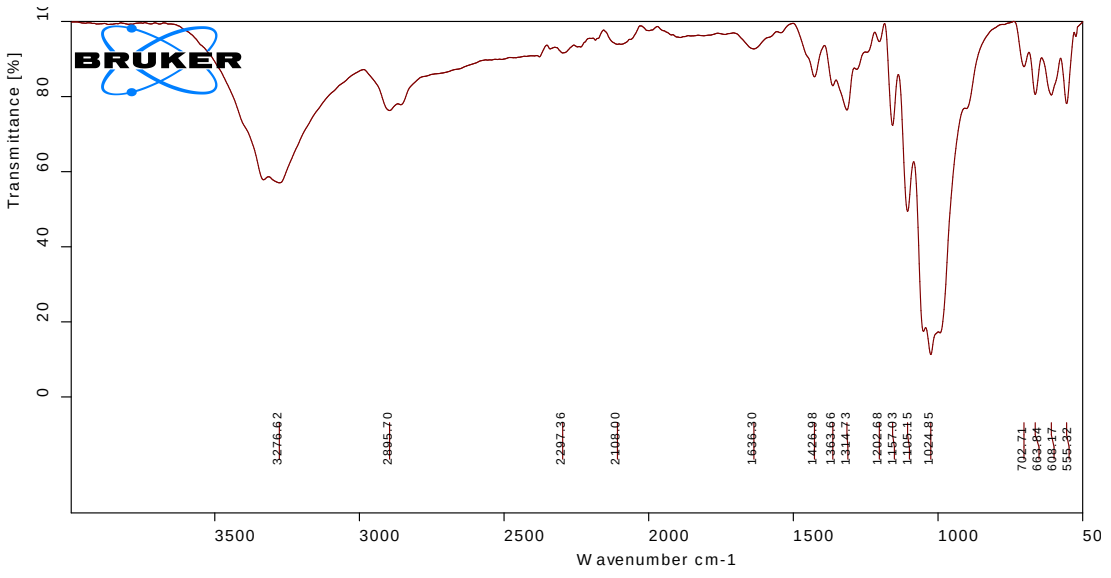


Figure 7: FTIR analysis of chitosan treated reactive red dyed cotton fabric

Page 1/1

4.7 Assessment of Colour Properties of Dyed Fabrics

The assessment of colour properties of fabrics dyed with onion skin and reactive red dye was done to know the effect of different pretreatment on the colour properties of dyed fabrics.

i. Assessment of dye absorption, colour coordinate and colour strength of dyed fabric: This section comprises the evaluation of colour properties of onion skin and reactive dyed cotton fabric which were pretreated with chitosan in terms of percent dye absorption, CIE L*, a*, b*, C*, H* and colour strength. The results regarding colour properties of dyed fabrics are presented in Table 50**.**

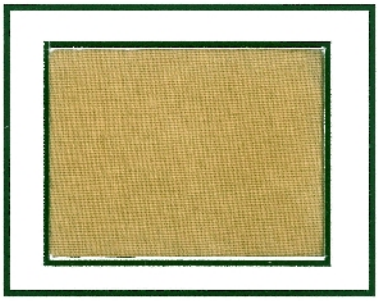
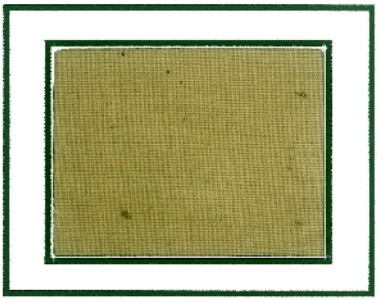
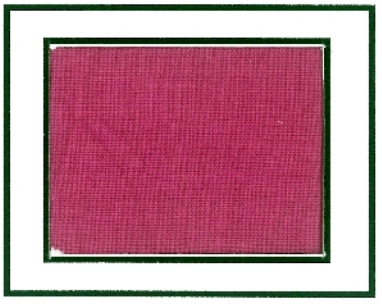
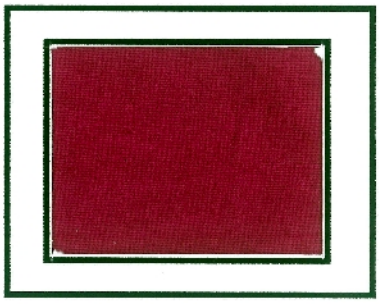
Table 50: Measurement of dye absorption, colour coordinates and colour strength of dyed fabrics

Dyed samples	Dye absorption (%)	Colour Coordinates					Colour strength (k/s)
		L*	a*	b*	C*	H*	
Onion skin dyed							
Alum treated	55.98	62.09	10.28	15.96	18.98	57.19	12.21
Chitosan treated	66.17	54.49	8.38	18.16	20.00	65.21	16.52
Reactive red dyed							
Alkali treated	68.36	54.76	20.38	-16.25	26.07	321.44	13.03
Chitosan treated	78.90	36.48	43.15	-10.53	44.42	346.30	18.72

Data in table depicts that chitosan treated fabric showed 66.17 percent dye absorption which was higher as compared to alum treated fabric (55.98). The lower L* value (54.49) of chitosan treated sample indicated its darker colour than the alum treated sample when dyed with onion skin dye. The a* and b* values were found positive for both the treated samples and the hue angle (H*) was below 90^0, depicting brown and yellowish khaki colour of the samples. The chitosan treated dyed sample was brighter than alum pretreated dyed sample as indicated by higher chroma (C*) value i.e. 20.00. The colour strength value at chitosan treated was also higher (16.52) in comparison to alum treated sample (12.21).

The percent dye absorption (78.90) and colour strength value (18.72) were higher for the chitosan pretreated reactive red dyed fabric than alkali pretreated dyed fabric (68.36) and (13.03) respectively. The lower L* value (36.48) depicted that the chitosan pretreated reactive dyed sample was darker in colour than alkali treated dyed fabric for which the L* value was higher (54.76). The a* and b* values depicted that both (alkali and chitosan) treated reactive red dyed samples had redder and bluer tone but more redder and bluer tone was observed for chitosan pretreated dyed sample. The chroma (C*) value was higher (44.42) for the reactive red dyed sample pretreated with chitosan which indicated its brightness than alkali treated dyed sample. The hue angle (H*) remained between the 270^0 to 360^0 having positive a* and

Plate 10: Shades Obtained with Natural and Synthetic Dye

Samples Dyed with Onion Skin Dye	
	
Alum treated	Chitosan treated
Samples Dyed with Reactive Red Dye	
	
Alkali treated	Chitosan treated

negative b* values for both treated and dyed cotton fabric. It depicted that the colour of sample was reddish blue (magenta).

ii. Assessment of colour fastness properties of dyed fabrics: The data consists of colour fastness properties viz. wash, light, perspiration and rubbing fastness of onion skin dyed fabric, pretreated with alum and chitosan separately and reactive red dyed samples pretreated with alkali and chitosan separately are presented in the Table 51.

It is evident from the table that the onion skin dyed sample pretreated with chitosan had very good wash fastness rating (4/5) for colour change and colour staining where as wash fastness rating was good (4) in terms of colour change and colour staining for the dyed sample pretreated with alum.

Light fastness of dyed samples pretreated with chitosan was higher (4/5) for the first two days in comparison to alum pretreated samples. Afterwards it remained good (4) for tested samples. It was inferred that chitosan treated onion skin dyed sample had very good light fastness for first two days followed by good till 7th day. However dyed sample of alum pretreatment showed good light fastness for each successive day till 7th day.

Table 51: Colour fastness grades of dyed fabrics

Dyed samples	Colour fastness grades																
	Wash		Light (Days)							Perspiration				Rubbing			
										Alkaline		Acidic		Dry		Wet	
	CC	CS	1st	2nd	3rd	4th	5th	6th	7th	CC	CS	CC	CS	CC	CS	CC	CS
Onion skin dyed																	
Alum treated	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Chitosan treated	4/5	4/5	4/5	4/5	4	4	4	4	4	4	4	4	4	4	4	4	4
Reactive red dyed																	
Alkali treated	4	4	4/5	4/5	4/5	4/5	4	4	4	4	4	4	4	4/5	4/5	4/5	4/5
Chitosan treated	4/5	4/5	4/5	4/5	4/5	4/5	4	4	4	4	4	4	4	4/5	4/5	4/5	4/5

CC= Colour Change, CS =Colour Staining

Perspiration fastness when assessed against the alkaline and acidic perspiration medium, it was found that alum and chitosan treated samples dyed with onion skin dye exhibited good (4) perspiration grades. The rubbing fastness ratings were also noticed good (4) for dry and wet samples of the chitosan and alum treated, dyed with onion skin dye. It can be concluded from the table that chitosan treated onion skin dyed samples demonstrated the higher wash fastness rating and light fastness rating for first two days than alum treated dyed sample and depicted the comparable grades for perspiration and rubbing fastness.

The reactive red dyed samples pretreated with chitosan showed very good (4/5) wash fastness rating for colour change (CC) and colour staining (CS) than dyed sample pretreated

with alkali. Light fastness rating was found very good (4/5) for reactive dyed samples pretreated with alkali and chitosan separately for first four days followed by good (4) till (7^{th}) day. The perspiration fastness was found good (4) for colour change and colour staining for chitosan and alkali treated dyed samples. The rubbing fastness was found 4/5 (very good) for both (alkali and chitosan) treated dyed fabric in terms of colour change and colour staining. It can be concluded from the table that reactive red dyed samples pretreated with chitosan showed better wash fastness properties over alkali treated dyed fabric but showed comparable results in terms of light, perspiration, and rubbing fastness.

4.8 Testing of Physical and Functional Properties of Dyed Fabrics

The physical properties of fabrics were tested after giving different treatments to study the changes in preliminary (fabric count, weight, and thickness), mechanical (bending length, flexural rigidity, tensile strength, and elongation), performance (crease recovery, moisture regain and air- permeability) and functional properties (antibacterial and ultra-violet protection property).

4.8.1 Physical properties of onion skin dyed cotton fabric: The physical properties of scoured, alum, chitosan treated and treated dyed fabric with onion skin dye are presented in Table 52 to 55.

i. Effect of chitosan and onion skin dye on preliminary properties of cotton fabric: The data regarding the effect of different treatments on preliminary properties i.e. fabric count, weight and thickness are presented in Table 52. The percent change in preliminary properties of treated and dyed fabrics from scoured fabric was also calculated.

The data in the table illustrate that the fabric count of scoured (control) cotton fabric was 47 ends and 43 picks per inch, weighing 135 g/m^2 having thickness of 0.232 mm. Fabric count increased by 2.17 percent in alum treated and 10.0 percent in chitosan treated sample. The alum and chitosan treated fabric when dyed with onion skin dye, the increase in fabric count was i.e. 8.16 and 13.46 percent respectively. It was revealed that chitosan treated dyed cotton fabric sample showed maximum (13.46) percent increase in fabric count. The significant difference in fabric count between alum and chitosan treated fabrics dyed with onion skin dye was found at 5% level of significance.

It is obvious from the table that the weight and thickness of the fabric increased after alum and chitosan treatment. The alum treated fabric showed increase in weight from 135.0 to 136.6 g/m^2 and thickness from 0.232 to 0.276 mm whereas the chitosan treated fabric showed the increase in weight from 135.0 to 137.6 $g/m^2$and thickness from 0.232 to 0.286 mm. Further weight and thickness increased for alum treated dyed fabric by 1.17 and 17.73 percent respectively. Similarly the chitosan treated dyed fabric showed 3.57 and 21.62 percent increase in weight and thickness respectively. The percent increase was found higher for the chitosan treated dyed fabric in terms of weight per unit area (3.57 %) and thickness (21.62 %)

as compared to alum treated dyed cotton fabric. A significant difference at 5% level of significance was found between treated and dyed fabrics for weight and thickness.

ii. Effect of chitosan and onion skin dye on mechanical properties of cotton fabric: It is learnt from Table 53 that there was increase in bending length of scoured fabric after alum treatment from 2.88 to 2.96 cm and further increased from 2.96 cm to 3.02 cm when alum treated fabric was dyed with onion skin dye. The flexural rigidity increased from 39.66 to 40.12 mg-cm for alum treated fabric and further increased from 40.12 to 41.17 mg-cm when dyed with onion skin dye.

Bending length of scoured cotton fabric increased from 2.88 to 3.05 cm after chitosan treatment and further increased from 3.05 to 3.09 cm after dyed with onion skin. The flexural rigidity also increased for the chitosan treated fabric from 39.66 to 41.05 mg-cm and from 41.05 to 41.88 mg-cm after dyeing with onion skin dye.

The percent increase in bending length and flexural rigidity was found slightly higher in chitosan treated dyed fabric as compared to alum treated dyed fabric. Statistically a non-significant difference was found in bending length among the means of different treated and dyed fabrics in warp and weft direction.

The table reflects that the mean tensile strength of the scoured fabric was 16.89 kg (17.60 kg for warp and 16.18 kg for weft direction) which decreased after alum treatment from 16.89 to 16.74 (0.89 %). Further reduction was found in the tensile strength of the onion skin dyed fabric pretreated with alum from 16.74 kg to 16.32 kg (3.49 % decrease).

The tensile strength decreased for chitosan pretreated fabric from 16.89 to 16.58 kg (1.86 % decrease). Tensile strength decreased for the onion skin dyed fabric pretreated with chitosan from 16.58 to 16.31 kg (3.49 % decrease). Statistically the significant difference was found in the means of tensile strength for the warp direction where as non- significant difference was found in means of weft direction of different treated and dyed fabrics.

The table demonstrates that the elongation in weft direction was greater than warp direction for all the treated and dyed samples. When the pretreatment of alum was given to the scoured fabric, elongation decreased from 13.70 to 13.46 percent (13.54 to 13.28 % for warp and from 13.86 to 13.64 % in weft direction). The percent decrease was higher for the alum treated dyed fabric (4.26 %) than alum treated fabric (1.78 %) when compared with scoured fabric.

The elongation of chitosan treated dyed cotton fabric increased from 12.57 to 12.97 percent when compared with chitosan pretreated fabric. The percent decrease in elongation was 8.98 and 5.62 for chitosan treated and onion skin dyed fabric pretreated with chitosan when compared with scoured cotton fabric.

Table 52: Effect of pretreatments and onion skin dye on preliminary properties of fabric

S. No.	Treated samples	Properties							
		Fabric count (ends and picks/ inch)				Weight per unit area (g/m^2)		Thickness (mm)	
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp+ weft)	Percent change	Mean ± S.E.(m)	Percent change	Mean ± S.E.(m)	Percent change
1.	**Scoured fabric (control)**	47 ± 0.37	43 ± 0.49	45	-	135.0 ± 1.18	-	0.232 ± 0.002	-
2.	**Alum treated**	48 ± 0.58	44 ± 0.24	46	+2.17	135.8 ± 0.49	+ 0.59	0.276 ± 0.004	+15.94
3.	**Alum treated dyed**	51 ± 0.70	46 ± 0.63	49	+8.16	136.6 ± 0.50	+1.17	0.282 ± 0.004	+17.73
4.	**Chitosan treated**	52 ± 0.54	47 ± 0.44	50	+10.0	137.6 ± 0.24	+1.89	0.286 ± 0.004	+18.88
5.	**Chitosan treated dyed**	54 ± 0.70	50 ± 0.94	52	+13.46	140.0 ± 0.63	+3.57	0.296 ± 0.004	+21.62
	C.D	1.77	1.78	-		2.04	-	0.01	-
	C.V.	2.63	2.90			1.12		2.72	
	F value	20.00*	18.97*			7.92*		54.88*	

+ = Increase, - = Decrease, S.E.(m) = Standard Error of Mean, C.V.= Coefficient of Variance, F value = Fisher Ratio, *Significant at 5% level of significance

Table 53: Effect of pretreatments and onion skin dye on mechanical properties of fabric

S. No.	Treated samples	Properties													
		Bending length (cm)				Flexural rigidity (mg-cm)	Percent Change	Tensile strength (kg)				Elongation (%)			
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp +weft)	Percent Change			Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp +weft)	Percent change	Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp +weft)	Percent change
1.	**Scoured (control)**	3.04 ± 0.08	2.72 ± 0.03	2.88	-	39.66	-	17.60 ± 0.23	16.18 ±0.28	16.89	-	13.54 ± 0.27	13.86 ± 0.20	13.70	-
2.	**Alum treated**	3.14 ± 0.09	2.78 ± 0.03	2.96	+2.70	40.12	+1.15	17.38 ± 0.08	16.10 ± 0.07	16.74	-0.89	13.28 ± 0.28	13.64 ± 0.05	13.46	-1.78
3.	**Alum treated dyed**	3.20 ± 0.06	2.84 ± 0.12	3.02	+4.63	41.17	+3.67	16.94 ± 0.12	15.70 ± 0.18	16.32	-3.49	13.04 ± 0.08	13.24 ± 0.26	13.14	-4.26
4.	**Chitosan treated**	3.20 ± 0.03	2.90 ± 0.11	3.05	+5.57	41.05	+3.39	17.14 ± 0.09	16.02 ± 0.25	16.58	-1.86	12.50 ± 0.33	12.64 ± 0.09	12.57	-8.98
5.	**Chitosan treated dyed**	3.26 ± 0.05	2.92 ± 0.37	3.09	+6.79	41.88	+5.30	16.82 ± 0.24	15.80 ± 0.08	16.31	-3.49	12.38 ± 0.19	13.56 ± 0.16	12.97	-5.62
	C.D	0.43	0.59	-	-	-	-	0.51	NA	-	-	0.73	0.51	-	-
	C.V.	4.55	6.39					2.24	2.71			4.28	2.89		
	F cal	1.66(NS)	1.05(NS)					3.39*	1.05(NS)			4.02*	7.54*		

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean, C.V. = Coefficient of Variance, F value =Fisher Ratio
*Significant at 5% level of significance, NS= Non- Significant

It can be concluded from the table that the elongation of the fabric decreased for alum and chitosan treated dyed cotton fabrics as compared to scoured fabric. Statistically the significant difference was found in elongation and tensile strength of warp direction only amongst the means of different treated and dyed fabrics at 5% level of significance.

iii. Effect of chitosan and onion skin dye on performance properties of cotton fabric:

Table 54 narrates slight increase in crease recovery angle of the alum treated (86.4^0) and alum treated dyed cotton fabric (92.3^0) in comparison to scoured fabric (84.0^0).

The chitosan treated fabric showed significant increase in the crease recovery angle of scoured cotton fabric from 84.0 to 96.5 degree which further increased from 96.5 to 103.2 degree after dyeing with onion skin dye. The percent increase in the crease recovery angle was found higher for the chitosan treated (12.95) and chitosan treated dyed (18.60) cotton fabric in comparison to alum treated (2.77) and alum treated dyed (8.99) cotton fabric. The crease recovery angle was found higher for warp direction for both alum and chitosan treated fabrics and onion skin dyed fabrics pretreated with alum and chitosan. Statistically the significant difference was found amongst the means of alum and chitosan treated dyed cotton fabrics for crease recovery angle.

This table reveals that the moisture regain of scoured fabric was 6.78 percent and decreased to 6.56 after alum treatment. When alum treated fabric was dyed, further decrease in moisture regain was found (6.56 percent). In the same way moisture regain decreased for chitosan treated fabric from 6.78 to 6.76 percent further after dyeing to 6.75 percent. The percent decrease was found higher (3.35) for alum treated dyed fabric in comparison to chitosan treated dyed fabric.

It is apparent from the table that the air permeability of alum treated and alum treated dyed cotton fabric decreased from 82.39 to 81.83 $m^3/m^2/min$ and 82.39 to 80.16 $m^3/m^2/min$ respectively. It was noticed that chitosan treated and chitosan treated dyed cotton fabric also showed the decrease in air permeability from 82.39 to 80.94 $m^3/m^2/min$ and 82.39 to 79.33 $m^3/m^2/min$ respectively. The percent decrease in air permeability was found higher for the chitosan treated dyed cotton fabric (3.85%) as compared to alum treated dyed cotton fabric (2.78 %). The significant difference was noticed in air-permeability of fabrics with different treatments at 5% level of significance.

4.8.2 Effect of chitosan and onion skin dye on functional properties of cotton fabric: The data in Table 55 exhibits that the scoured fabric showed the bacterial count mean 176.66 and 8.83 x 10^9 CFU/ml for *E. coli* bacteria and 169.93 and 8.46 x 10^9 CFU/ml for *S. aureus* bacteria. When the alum treatment was given to the scoured fabric, 12.82 percent reduction in growth of *E. coli* and 15.28 percent reduction in growth *of S. aureus* bacteria were observed.

The alum treated onion skin dyed cotton fabric showed 85.57 percent reduction in the growth of *E. coli* bacteria and 83.91 percent reduction in the growth of *S. aureus* bacteria.

The chitosan treated cotton fabric exhibited 12.33 bacterial count mean for *E. coli* bacteria with 93.02 percent reduction in the growth of bacteria whereas it showed 8.33 bacterial count mean for *S. aureus* bacteria having 95.07 percent reduction in growth as compared to control sample. Percent reduction in *E. coli* bacterial growth increased in case of chitosan treated onion skin dyed cotton fabric to 97.20 percent with bacterial count of 4.66 and 98.03 percent reduction in the growth of *S. aureus* bacteria comprising bacterial count 3.33.

Thus it is concluded from the table that the percent reduction in the growth of bacteria increased when alum and chitosan treated cotton fabrics were dyed with onion skin dye. It was also noticed that the chitosan treated dyed cotton fabric showed higher percent reduction in the growth of *E. coli* as well as *S. aureus* bacteria as compared to alum treated dyed cotton fabric.

It is discerned from the Table 55 that the UPF value of the scoured fabric was 10.50 and of alum treated fabric was 10.90 which enhanced to 66.70 when dyed with onion skin dye with excellent grade under the protection category. The UV-A Transmission decreased from 7.24 to 7.12 percent and UV-B Transmission from 9.10 to 8.76 percent of scoured cotton fabric after alum treatment. It further decreased from 7.12 to 2.02 and 8.76 to 2.19 respectively.

The chitosan treated fabric had UPF value 11.40 which was slightly higher than the scoured (10.50) and alum treated fabrics (10.90). After dyeing of chitosan pretreated fabric with onion skin dye, very high UPF value (84.80) was observed which achieved the excellent protection category. For the chitosan treated onion skin dyed cotton fabric UV-A and UV-B Transmission were 1.19 and 1.25 percent respectively which was lower than the alum treated dyed cotton fabric.

It was deduced from the table that the UPF value of the pretreated cotton fabric increased when dyed with onion skin dye indicating dyeing treatment played an important role in increasing the UPF value of cotton fabric. The chitosan treated dyed cotton fabric showed the higher UPF value (84.80) as compared to alum treated dyed cotton fabric (66.70) depicting that the chitosan treated dyed cotton fabric provided more ultraviolet protection than the alum treated dyed fabric. Furthermore it was inferred that the UV-B Transmission percent was higher than UV-A Transmission percent for all the treated and dyed cotton fabric.

Table 54: Effect of pretreatments and onion skin dye on performance properties of fabric

S. No.	Treated samples	Properties							
		Crease recovery angle (degree)				Moisture regain (%)	Percent change	Air permeability ($m^3/m^2/min$)	Percent change
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp +weft)	Percent change				
1.	**Scoured (control)**	85.4 ± 0.24	82.6 ± 0.67	84.0	-	6.78	-	82.39	-
2.	**Alum treated**	87.2 ± 0.97	85.6 ± 2.78	86.4	+2.77	6.58	-3.03	81.83	-0.68
3.	**Alum treated dyed**	93.4 ± 1.03	91.2 ± 0.58	92.3	+8.99	6.56	-3.35	80.16	-2.78
4.	**Chitosan treated**	97.2 ± 0.58	95.8 ± 0.66	96.5	+12.95	6.76	-0.29	80.94	-1.79
5.	**Chitosan treated dyed**	103.8 ± 0.37	102.6 ± 0.67	103.2	+18.60	6.75	-0.44	79.33	-3.85
	C.D **C.V.** **F cal**	2.11 3.50 110.78*	4.08 3.35 33.79*	-	-	N/A 4.62 0.42 (NS)	-	0.99 0.92 19.33*	-

+ = Increase, - = Decrease, S.E.(m) = Standard Error of Mean, C.V.= Coefficient of Variance, F value =Fisher Ratio
*Significant at 5% level of significance, NS= Non- Significant

Table 55: Effect of pretreatments and onion skin dye on functional properties fabric

S. No.	Treated samples	Properties									
		Bacterial count mean (10^6)	**CFU/ml For *E. coli***	**% reduction in *E. coli* bacterial growth**	**Bacterial count mean (10^6)**	**CFU/ml *S. aureus***	**% reduction in *S. aureus* bacterial growth**	**UV-A (Trans-mission) %**	**UV-B (Trans-mission) %**	**UPF**	**Protection category**
1.	**Scoured (control)**	176.66	8.83×10^9	-	169.93	8.46×10^9	-	7.24	9.10	10.50	No category
2.	**Alum treated**	154.0	7.70×10^9	12.82	149.66	7.48×10^9	15.28	7.12	8.76	10.90	No category
3.	**Alum treated dyed**	24.33	1.22×10^9	85.57	28.33	14.2×10^8	83.91	2.02	2.19	66.70	Excellent
4.	**Chitosan treated**	12.33	6.16×10^8	93.02	8.33	4.17×10^8	95.07	6.74	8.40	11.40	No category
5.	**Chitosan treated dyed**	4.66	2.33×10^8	97.20	3.33	1.66×10^8	98.03	1.19	1.25	84.8	Excellent

4.8.3 Physical properties of reactive red dyed cotton fabric: The physical properties of scoured, alkali and chitosan treated and pretreated fabrics dyed with reactive dye are presented in Table 56 to 59.

i. Effect of chitosan and reactive red dye on preliminary properties of cotton fabric:

Measurement of preliminary properties of treated fabrics was done to see the effect of different treatments. The data in the Table 56 comprise the fabric count, weight and thickness of treated and dyed fabric.

The data in the table present that fabric count was higher for the alkali treated (50 x 45) and chitosan treated (52 x 47) as compared to scoured cotton fabric (47x43) in warp as well as in weft direction. When the dyeing of alkali and chitosan treated fabric was done with reactive red dye, further increase in fabric count was noticed for the alkali treated dyed sample (52 x 47) and the chitosan treated dyed sample (53 x 49) for warp and weft directions respectively. It was also inferred that chitosan treated dyed cotton fabric sample showed maximum increase in fabric count (11.76 %). Statistically the significant difference was found amongst the means of different treated and dyed fabrics for fabric count.

From the table it is obvious that the weight and thickness of the fabric increased after alkali and chitosan treatment. The alkali treated fabric depicted increase in weight of scoured fabric from 135.0 to 136.0 g/m^2 and thickness from 0.232 to 0.252 mm whereas the chitosan showed the increase in weight per unit area from 135.0 to 137.8 g/m^2 and thickness from 0.232 to 0.262 mm. The weight and thickness increased from 136.0 to 137.8 g/m^2 and from 0.252 to 0.262 mm respectively when alkali treated fabric dyed with reactive red dye. Similarly the chitosan treated dyed cotton fabric showed increase in weight per unit area from 137.0 to 138.0 g/m^2 and thickness from 0.284 to 0.286 mm.

The percent increase in weight (2.17 %) and thickness (18.88 %) was higher for chitosan treated reactive red dyed fabric and as compared to alkali treated dyed fabric. Statistically the significant difference was found amongst the means of different treated fabrics for thickness but non-significant for weight.

ii. Effect of chitosan and reactive red dye on mechanical properties of cotton fabric: The data related to bending length, flexural rigidity, tensile strength and elongation of alkali and chitosan treated fabrics dyed with reactive red dye are presented in Table 57. From the table it is apparent that the bending length of scoured fabric increased from 3.04 to 3.11cm and 2.72 to 2.74 cm in the warp and weft directions respectively after the alkali treatment along with increase in flexural rigidity from 38.81 to 39.71 mg-cm where as it increased after chitosan treatment for warp direction from 3.04 to 3.18 cm and weft direction from 2.72 to 2.80 cm with flexural rigidity from 38.81 to 40.88 mg-cm. Percent increase for bending length and flexural rigidity of alkali treated dyed cotton fabric was 2.93 and 4.95 percent respectively

whereas chitosan treated dyed cotton fabric exhibited 4.00 percent increase in bending length and 5.98 percent in flexural rigidity.

The table narrates that when the scoured fabric was given alkali treatment, tensile strength decreased in warp direction from 17.60 to 16.90 kg and from 16.18 to 15.84 kg in weft direction and further decrease was also noticed when dyed with reactive red dye in warp from 16.90 to 15.96 kg and weft from 15.84 to 15.19 kg. Similarly the decrease in tensile strength was observed for chitosan treated fabric from 16.89 to 16.37 kg and further decreased from 16.73 to 16.51 kg for chitosan treated reactive red dyed sample. The percent decrease in tensile strength was found to be higher for the alkali treated dyed cotton fabric (8.42 %) in comparison to chitosan treated dyed sample. Statistically significant difference was found amongst the means of tensile strength dyed cotton fabrics having different treatments at 5% level of significance.

The elongation of the fabric decreased from 13.70 to 11.88 percent when alkali treatment was given to the scoured fabric but it increased from 11.88 to 12.70 percent after dyeing with reactive red dye. In the same way the chitosan treated sample showed decrease in elongation from 13.70 to 13.03 percent but increased from 13.03 to 13.64 percent after dyeing. The percent decrease in elongation was found highest for alkali treated fabric. Statistically the significant difference was found in tensile strength and elongation of different treated and dyed fabrics for warp and weft direction at 5% level of significance.

iii. Effect of chitosan and reactive red dye on performance properties of cotton fabric:

The data related to effect of different treatments and reactive red dyeing on the crease recovery angle, moisture regain and air permeability are presented in Table 58.

The table exemplifies that the crease recovery angle of scoured fabric increased from 84.00 to 86.30 degree after alkali treatment with increase of 2.67 percent and further increased from 86.30 to 87.90 degree i.e. 4.44 percent increase when dyed with reactive red dye. The same pattern was also observed for chitosan treated cotton fabric which showed increase in crease recovery angle from 84.00 to 91.60 degree and on dyeing further increased from 91.60 to 100.0 degree. The percent increase was found 8.29 percent for chitosan treated fabric and 16.00 percent for chitosan treated dyed fabric. It is obvious from the table that chitosan treated reactive red dyed cotton fabric showed higher crease recovery angle than alkali treated dyed cotton fabric. Statistically the significant difference was noticed amongst the means of treated and dyed cotton samples for crease recovery angle at 5% level of significance.

The table illustrates that the moisture regain of scoured fabric decreased from 6.78 to 6.32 percent after alkali treatment and from 6.78 to 6.72 percent in case of chitosan treated fabric. Moreover the moisture regain decreased in alkali treated dyed fabric from 6.32 to 6.30

percent and from 6.72 to 6.39 percent for chitosan treated dyed fabric. The percent decrease in moisture regain was found higher (7.61%) for alkali treated dyed cotton fabric. Statistically non-significant difference was noticed amongst the means of different treated dyed fabrics for moisture regain at 5% level of significance.

It is clear from the table that the air permeability of scoured fabric decreased from 82.39 to 81.63 m^3/m^2/min for alkali treated and from 82.39 to 81.21 m^3/m^2/min for chitosan treated fabric. Further the air permeability of dyed sample which was pretreated with alkali decreased from 81.63 to 81.21 m^3/m^2/min and from 81.54 to 80.04 m^3/m^2/min for chitosan pretreated dyed sample. Statistically significant difference was noticed for air permeability amongst the means of fabrics with different treatments at 5% level of significance.

4.8.4 Effect of chitosan and reactive red dye on functional properties of cotton fabric:

The effect of different treatments and reactive red dyeing on antibacterial and ultra-violet protection property of cotton fabric is presented in Table 59.

From the table it can be noted that when the alkali treatment was given to the scoured fabric, 6.00 percent reduction was found in the growth of *E.coli* bacteria and 5.64 percent in the growth of *S. aureus* bacteria. The alkali treated reactive red dyed cotton fabric showed 26.80 and 25.58 percent reduction in the growth of *E.coli* and *S.aureus* bacteria respectively.

When the chitosan treatment was applied to the scoured cotton fabric, it provided 84.14 and 84.16 percent reduction in the growth of *E.coli* and *S. aureus* bacteria respectively. Further chitosan treated dyed cotton fabric exhibited 85.50 percent reduction in the growth of *E.coli* bacteria and 84.28 percent in the growth of *S.aureus* bacteria. Thus it is envisaged that chitosan treated reactive red dyed fabric displayed the higher percent reduction in growth of *E.coli* and *S. aureus* bacteria in comparison to alkali treated dyed fabric.

The UPF value of scoured cotton fabric was found 10.50, when alkali and chitosan treatment was given to scoured fabric, negligible increase was noticed in UPF value of the alkali treated (10.7) and chitosan treated (11.4) fabrics. The UPF value of both the treated fabrics was below 15 depicting that both the treated (alkali and chitosan) fabrics did not gained any protection category. When the alkali and chitosan treated fabrics were dyed with reactive red dye, their UPF value was 27.4 and 32.1 respectively and both the dyed fabrics achieved very good protection category. Thus it is inferred that dyeing with reactive dye increased the UPF value of the alkali and chitosan treated fabrics. However chitosan treated dyed cotton fabric showed higher UPF value than that of alkali treated dyed cotton. Chitosan treated dyed cotton fabric gave better ultra-violet protection.

Table 56: Effect of pretreatments and reactive red dye on preliminary properties of fabrics

S. No.	Treated samples	Properties							
		Fabric count (ends and picks/ inch)				Weight per unit area (g/m^2)		Thickness (mm)	
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp+weft)	Percent change	Mean ± S.E.(m)	Percent change	Mean± S.E.(m)	Percent change
1.	**Scoured fabric (control)**	47 ± 0.37	43 ± 0.49	45	-	135.0 ± 1.18	-	0.232 ± 0.002	-
2.	**Alkali treated**	50 ±1.04	45 ± 0.77	48	+6.25	136.0 ± 1.14	+0.74	0.252 ± 0.006	+7.94
3.	**Alkali treated dyed**	52 ± 0.91	47 ± 0.54	50	+10.00	137.8 ± 0.73	+2.03	0.262 ± 0.007	+11.45
4.	**Chitosan treated**	52 ± 0.54	47 ± 0.66	50	+10.00	137.0 ± 0.54	+1.45	0.284 ± 0.002	+18.31
5.	**Chitosan treated dyed**	53 ± 0.70	49 ± 0.70	51	+11.76	138.0 ± 0.70	+2.17	0.286 ± 0.004	+18.88
	C.D	2.25	1.91			NA		0.014	
	C.V.	3.33	3.13			0.89		4.05	
	F cal	9.46*	11.32*			1.96 (NS)		22.50*	

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean, C.V.= Coefficient of Variance, F value =Fisher Ratio
*Significant at 5% level of significance, NS= Non- Significant

Table 57: Effect of pretreatments and reactive red dye on mechanical properties of fabric

S. No.	Treated samples	Properties													
		Bending length (cm)				Flexural rigidity (mg-cm)	Percent Change	Tensile strength (kg)				Elongation (%)			
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp + weft)	Percent Change			Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp + weft)	Percent Change	Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp + weft)	Percent Change
1.	**Scoured (control)**	3.04 ± 0.08	2.72 ± 0.03	2.88	-	38.81	-	17.60 ± 0.23	16.18 ± 0.28	16.89	-	13.54 ± 0.27	13.86 ± 0.20	13.70	-
2.	**Alkali treated**	3.11± 0.02	2.74 ± 0.05	2.92	+1.67	39.70	+2.24	16.90 ± 0.23	15.84 ± 0.29	16.37	-3.17	11.49 ± 0.17	12.27 ± 0.27	11.88	-7.87
3.	**Alkali treated dyed**	3.15 ± 0.01	2.78 ± 0.03	2.96	+2.93	40.83	+4.95	15.96 ± 0.18	15.19 ± 0.22	15.57	-8.42	12.20 ± 0.16	13.21 ± 0.31	12.70	-15.31
4.	**Chitosan treated**	3.18 ± 0.10	2.80 ± 0.032	2.99	+3.67	40.88	+5.06	17.30 ± 0.24	16.16 ± 0.08	16.73	-0.96	12.50 ± 0.34	13.58 ± 0.26	13.03	-0.43
5.	**Chitosan treated dyed**	3.22 ± 0.04	2.78 ± 0.04	3.00	+4.00	41.28	+5.98	16.90 ± 0.23	16.12 ± 0.12	16.51	-2.30	13.54 ± 0.28	13.74 ± 0.31	13.64	-5.14
	C.D	NA	NA					0.66	0.64			0.70	0.80		
	C.V.	4.39	3.19	-	-	-	-	2.94	3.06	-	-	4.24	0.27	-	-
	F cal	1.22 (NS)	0.69 (NS)					7.68*	3.66*			9.73*	4.55*		

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean, C.V. = Coefficient of Variance, F value =Fisher Ratio
*Significant at 5% level of significance, NS= Non- Significant

Table 58: Effect of pretreatments and reactive red dye performance properties of fabric

S. No.	Treated samples	Properties							
		Crease recovery angle (degree)				Moisture regain (%)	Percent change	Air permeability ($m^3/m^2/min$)	Percent change
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp +weft)	Percent change				
1.	Scoured fabric (control)	85.4 ± 0.24	82.6 ± 0.67	84.00	-	6.78	-	82.39	-
2.	Alkali treated	88.4 ± 0.68	84.2 ± 0.66	86.30	+2.67	6.32	-7.27	81.63	-0.92
3.	Alkali treated dyed fabric	89.4 ± 0.51	86.4 ± 0.51	87.90	+4.44	6.30	-7.61	81.21	-1.43
4.	Chitosan treated	92.4 ± 0.58	90.8 ± 0.81	91.60	+8.29	6.72	-0.89	81.54	-1.03
5.	Chitosan treated dyed fabric	100.6 ± 0.92	99.4 ± 0.74	100.0	+16.0	6.39	-6.10	80.04	-2.85
	C.D C.V. F cal	1.86 1.54 83.86*	2.05 1.73 100.04*	-	-	N/A 5.07 2.40 (NS)	-	1.17 1.08 4.73*	-

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean, C.V. = Coefficient of Variance, F value =Fisher Ratio
*Significant at 5% level of significance, NS= Non- Significant

Table 59: Effect of pretreatments and reactive red dye functional properties of fabric

S. No.	Treated samples	Properties									
		Bacterial count mean(10^6)	**CFU/ml For *E. coli***	**% reduction in *E. coli* bacterial growth**	**Bacterial count mean(10^6)**	**CFU/ml *S. aureus***	**% reduction in *S. aureus* bacterial growth**	**UV-A (Trans-mission) %**	**UV-B (Trans-mission) %**	**UPF**	**Protection category**
1.	**Scoured Fabric (Control)**	176.66	8.83×10^9	-	169.93	8.46×10^9	-	7.24	9.10	10.5	No category
2.	**Alkali treated**	166.0	8.30×10^9	6.00	160.33	8.01×10^9	5.64	7.36	9.56	10.7	No category
3.	**Alkali treated dyed**	129.30	6.47×10^9	26.80	126.00	6.30×10^9	25.58	3.54	4.13	27.4	Very good protection
4.	**Chitosan treated**	28.00	1.40×10^9	84.14	33.66	16.9×10^8	84.16	6.74	8.40	11.4	No category
5.	**Chitosan treated dyed**	25.67	1.28×10^9	85.50	26.66	13.3×10^8	84.28	2.78	3.20	32.1	Very good protection

4.9 Retention of Physical and Functional Properties of Dyed Fabrics after Washing

Effect of different pretreatments and dyeing on the retention of physical (preliminary, mechanical, performance) and functional properties was studied to see the changes after washing.

4.9.1 Physical properties of onion skin dyed fabric after washing: The physical properties in terms of preliminary, mechanical and performance properties of alum and chitosan pretreated fabrics dyed with onion skin dye were assessed after 5, 10, 15 and 20 washing cycles to analyze the effect of treatments. It was noticed that there was no remarkable difference in percent change in preliminary properties of alum and chitosan pretreated fabrics dyed with onion skin dye [Annexure- 3 (Table 1-3)].

4.9.2 Functional properties of onion skin dyed fabric after washing: The data regarding the retention of antibacterial and ultra-violet protection properties on alum and chitosan treated onion skin dyed fabrics after washing are presented in Table 60.

It is evident from the table that the alum treated dyed cotton fabric showed decrease in percent reduction in growth of *S. aureus* bacteria from 80.14 to 70.21 percent and *E.coli* bacteria from 78.70 to 67.49 percent with progressive increase in washing cycles from 5 to 20. It was also noticed that efficacy of alum treated dyed cotton fabric for *E.coli* and *S. aureus* bacteria decreased with increase in number of washing cycles.

It is visible from the data presented in the table that the increase in washing cycles from 5 to 20 led to decrease in percent reduction in the growth of *S. aureus* from 96.84 to 80.14 percent and of *E.Coli.* bacteria from 93.20 to 80.74 percent for chitosan treated dyed cotton fabric. It was also observed that chitosan treated dyed cotton fabric showed higher percent reduction in growth of *S. aureus* (80.14) and *E. coli* (80.74) bacteria in comparison to alum treated dyed fabric after 20 washing cycles.

It is clear from the table that the UPF value of alum treated onion skin dyed sample was 66.70 and got excellent protection category. When the number of washing cycles increased from 5 to 20, decrease was noticed in the UPF value from 64.10 to 61.92 but remained under the excellent protection category.

The similar trend was observed for chitosan treated onion skin dyed fabric, UPF value decreased from 83.10 to 82.31 with progressive increase in washing cycles from 5 to 20 but remained under the excellent protection category. The percent decrease after 20 washing cycles was only 3.02 percent for chitosan treated dyed sample which was quite lower than the alum treated dyed fabric (7.71%).

Thus it is concluded that though the UPF value of the alum and chitosan treated onion skin dyed fabric decreased with the increase in washing cycles but chitosan treated dyed cotton fabric retained its ultra-violet protection property more than alum treated dyed fabric even after 20 washing cycles.

Table 60: Retention of functional properties on onion skin dyed fabric after washing

S. No.	Treated samples		Properties										
			Bacterial count mean (10^6)	**CFU/ml for *S. aureus***	**% reduction in *S.aureus.* bacterial growth**	**Bacterial count mean (10^6)**	**CFU/ml For *E. coli.***	**% reduction in E. coli. bacterial growth**	**UV-A (Trans-mission) %**	**UV-B (Trans-mission) %**	**UPF**	Percent change	**Protection category**
1.	**Scoured fabric (control)**		169.33	8.46×10^9	-	176.66	8.83×10^9	-	7.24	9.10	10.50	-	No category
2.	**Alum treated dyed**	**Unwashed**	24.33	1.22×10^9	85.57	28.33	14.2×10^8	83.91	2.02	2.19	66.70	-	Excellent
		Washing cycles											
		5	33.66	1.68×10^9	80.14	37.60	18.8×10^8	78.70	2.18	2.67	64.10	-4.05	Excellent
		10	42.00	2.10×10^9	75.17	44.00	22.0×10^8	75.08	2.32	2.89	63.21	-5.52	Excellent
		15	46.66	2.33×10^9	72.45	50.67	25.3×10^8	71.35	2.70	3.98	61.83	-7.87	Excellent
		20	50.33	3.51×10^9	70.21	57.33	28.7×10^8	67.49	1.98	2.13	61.92	-7.71	Excellent
3.	**Chitosan treated dyed**	**Unwashed**	3.33	16.6×10^7	98.03	4.66	23.3×10^7	97.20	1.19	1.25	84.80	-	Excellent
		Washing cycles											
		5	5.33	26.7×10^7	96.84	12.00	60.0×10^7	93.20	1.25	1.32	83.10	-2.04	Excellent
		10	18.66	93.3×10^7	88.97	19.00	95.0×10^7	89.24	1.31	1.55	83.02	-2.14	Excellent
		15	23.00	11.5×10^8	86.41	25.00	12.5×10^8	85.84	1.61	1.78	82.19	-3.17	Excellent
		20	33.66	16.8×10^8	80.14	34.00	17.0×10^8	80.74	1.98	2.13	82.31	-3.02	Excellent

+ = increase, - = decrease

4.9.3 Physical properties of reactive red dyed fabric after washing: The physical properties in terms of preliminary, mechanical and performance properties of alkali and chitosan pretreated fabrics dyed with reactive red dye were assessed after 5, 10, 15 and 20 washing cycles to analyze the effect of treatments. It was noticed that there was no remarkable difference in percent change in preliminary properties of alkali and chitosan pretreated fabrics dyed with reactive red dye after washing [Annexure- 4 (Table 1-3)].

4.9.4 Functional properties of reactive red dyed fabric after washing: The data in Table 61 demonstrate the retention of functional properties i.e. antibacterial and ultra-violet protection of alkali and chitosan pretreated fabrics dyed with reactive red dye after wash.

The alkali treated dyed fabric showed the decreased percent reduction in growth of *S.aureus* bacteria from 22.45 to 3.73 percent and for *E.coli* decreased from 22.18 to 0.58 percent with progressive increase in washing cycles from 5 to 20.

For the chitosan treated dyed cotton fabric, the percent reduction in the growth of *S.aureus* decreased from 84.28 to 73.53 percent where *E.coli*, it decreased from 83.80 to 69.19 percent with increase in number of washing cycles from 5 to 20. It is also clear from the table that the chitosan treated dyed cotton fabric provided greater resistance to the growth of *E.coli* and *S.aureus* bacteria after 20 washing cycles.

It is obvious from the table that the UPF value for the alkali treated reactive red dyed sample was 27.40 (very good protection category). When the number of washing cycles increased from 5 to 20, the UPF value decreased from 26.03 to 23.97 but retained very good protection value.

The similar trend was noticed for chitosan treated reactive red dyed fabric, the UPF value decreased from 30.96 to 29.92 with progressive increase in washing cycles from 5 to 20 and remained under the very good protection category. It is inferred that the UPF value of the alkali and chitosan treated reactive red dyed fabric decreased with the increase in washing cycles. The percent decrease in UPF value was only 7.28 percent for chitosan treated dyed cotton fabric which was lower than the alkali treated dyed fabric (14.30 %) after 20 washing cycles indicating that the chitosan treated dyed fabric retained its ultra-violet protection property better than alkali treated dyed fabric hence provided better protection against U-V radiations.

Table 61: Retention of functional properties on reactive red dyed fabrics after washing

S. No.	Treated samples		Properties										
			Bacterial count mean (10^6)	**CFU/ml for *S. aureus***	**% reduction in *S. aureus* bacterial growth**	**Bacterial count mean (10^6)**	**CFU/ml For *E. coli.***	**% reduction in *E. coli.* bacterial growth**	**UV-A (Trans-mission) %**	**UV-B (Trans-mission) %**	**UPF**	Percent change	**Protection category**
1.	**Scoured (control)**		169.33	8.46×10^9	-	176.66	8.83×10^9		7.24	9.10	10.50	-	No category
2.	**Alkali treated dyed**	**Unwashed**	126.00	6.30×10^9	25.58	129.30	6.47×10^9	26.80	3.54	4.13	27.40	-	Very good protection
		Washing cycles											
		5	131.30	6.57×10^9	22.45	137.46	6.86×10^9	22.18	3.48	4.24	26.03	-5.26	Very good protection
		10	146.00	7.30×10^9	13.77	151.33	7.56×10^9	14.33	3.59	4.61	25.16	-8.90	Very good protection
		15	159.33	7.96×10^9	5.90	164.00	8.20×10^9	7.16	3.67	4.78	23.78	-15.22	Very good protection
		20	163.00	8.15×10^9	3.73	175.63	8.78×10^9	0.58	4.08	4.93	23.97	-14.30	Very good protection
3.	**Chitosan treated dyed**	**Unwashed**	26.66	13.3×10^7	84.28	28.00	1.28×10^9	85.50	2.78	3.20	32.10	-	Very good protection
		Washing cycles											
		5	28.66	14.3×10^8	83.09	28.66	14.3×10^8	83.80	2.89	3.38	30.96	-3.68	Very good protection
		10	31.33	15.7×10^7	81.49	25.67	19.7×10^8	77.69	3.16	3.88	29.89	-7.39	Very good protection
		15	39.33	19.7×10^7	76.71	39.33	23.5×10^8	73.38	3.46	4.03	29.96	-7.14	Very good protection
		20	41.33	20.6×10^8	73.53	54.33	27.2×10^9	69.19	3.56	4.17	29.92	-7.28	Very good protection

4.10 Comparative analysis of Functional Properties of Fabrics Dyed with Natural and Synthetic Dyes

Comparative analysis of onion skin and reactive red dyed fabrics was done on the basis of protection provided against bacterial growth and ultra-violet radiation.

i. Comparative analysis of antibacterial property of fabrics: The comparison between the onion skin dyed fabric and reactive red dyed fabric is presented in Figure 8 which illustrates that alum treated onion skin dyed fabric exhibited 85.57 and 83.91 percent reduction in growth of *E. coli* and *S. aureus* bacteria which was higher than the alkali treated reactive red dyed cotton which registered only 26.80 and 25.58 percent reduction respectively. It is also apparent from the figure that chitosan treated onion skin dyed cotton fabric showed the highest percent reduction in the growth of *E. coli* (97.2 %) and *S. aureus* (98.03 %) bacteria than the chitosan treated reactive red dyed fabric which demonstrated 85.50 percent reduction for *E. coli* and 84.28 percent for *S. aureus bacteria*. Thus it can be concluded that the onion skin dye provided the highest antibacterial property to the alum and chitosan treated fabric against *E. coli* and *S. aureus* bacteria in comparison to reactive red dyed fabric pretreated with alkali and chitosan.

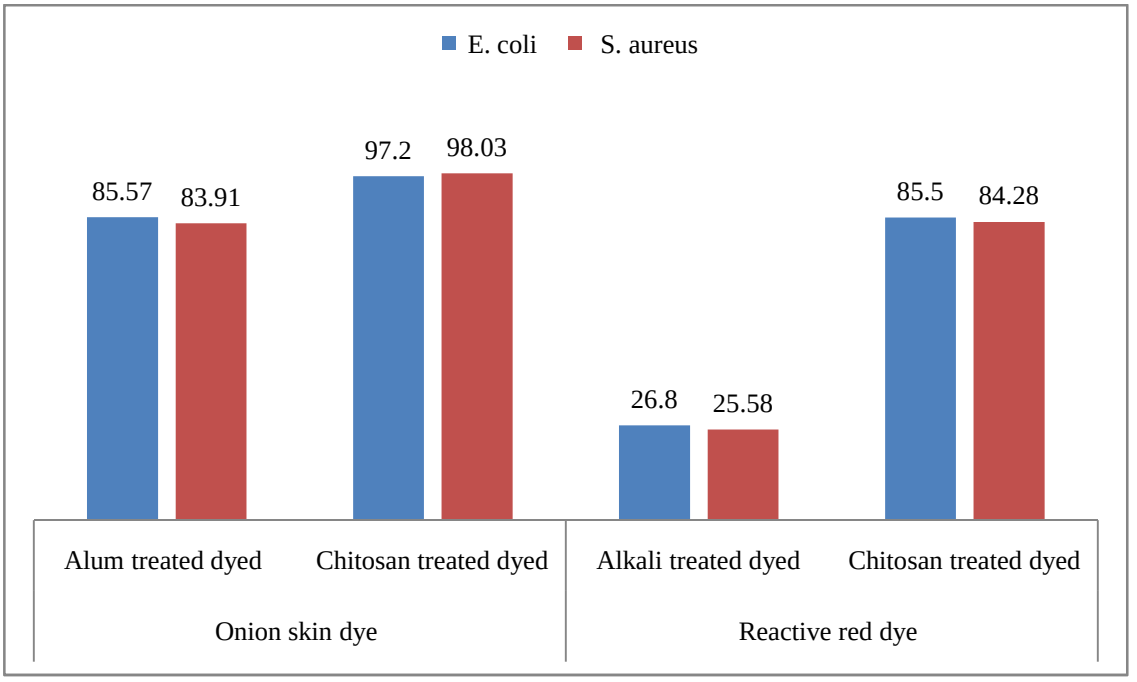
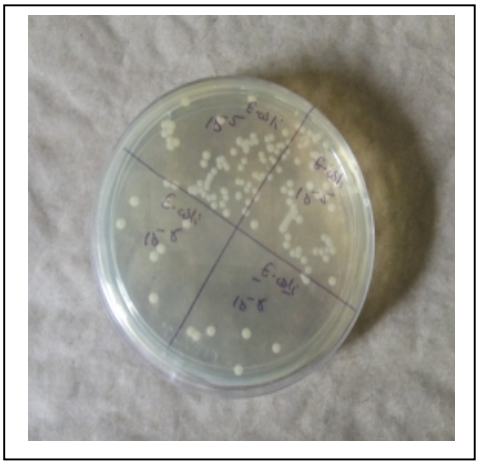


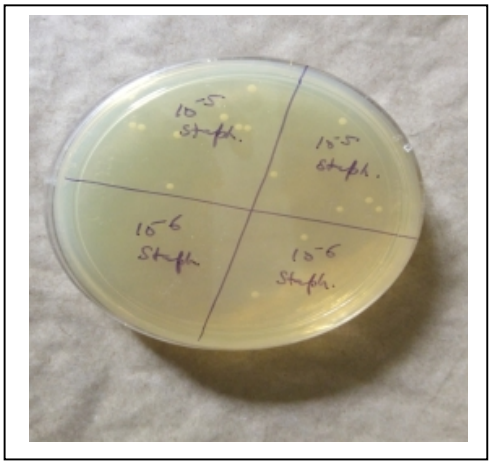
Figure 8: Comparison between antibacterial property of natural and synthetic dyes

ii. Comparative analysis of ultra-violet protection property of fabrics: The ultra-violet protection properties of onion skin and reactive red dyed fabric are demonstrated in the Figure 9 which depicted that both alum and chitosan treated fabrics dyed with onion skin showed the highest UPF values (66.70 and 84.80 respectively) than the alkali and chitosan treated fabric dyed with reactive red dye (27.4 and 32.1).

Plate 11: Bacterial Growth on Chitosan Treated Dyed Fabrics

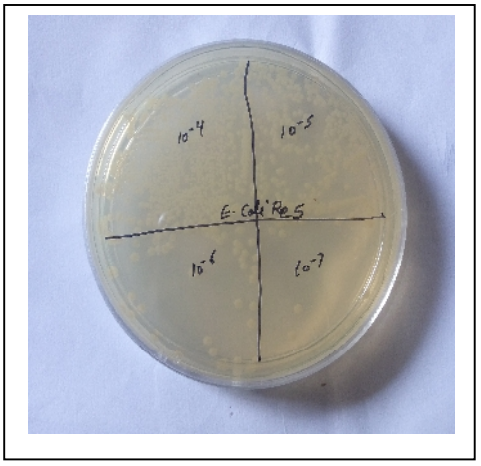


***E. coli* growth**

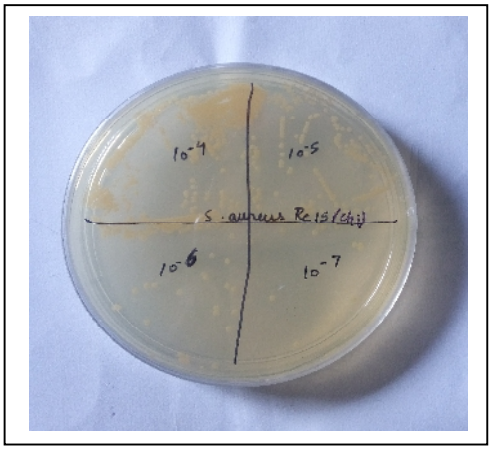


***S.aureus* growth**

Chitosan Treated Onion Skin Dyed Fabrics



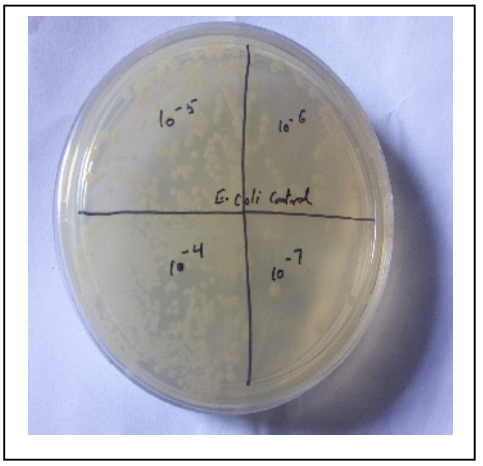
***E. coli* growth**

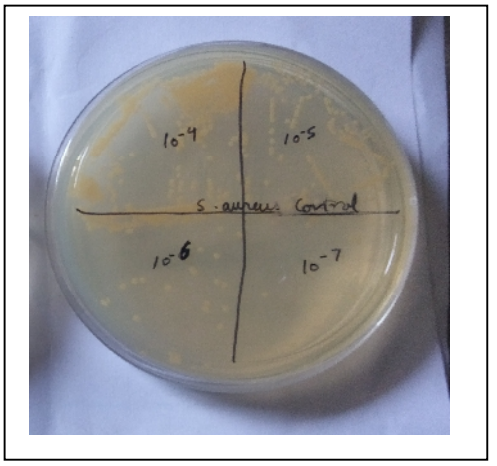


***S.aureus* growth**

Chitosan Treated Reactive Red Dyed Fabrics

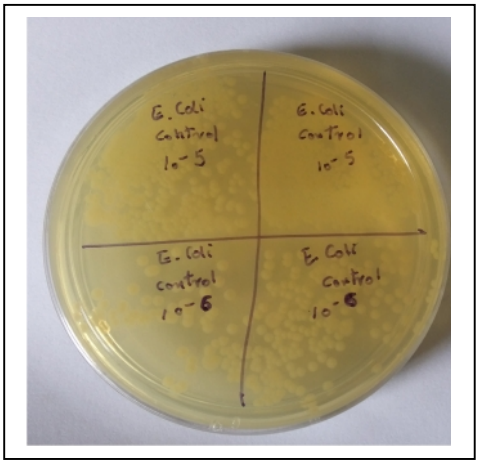
Plate 12: Bacterial Growth on Alum and Alkali Treated Dyed Fabrics

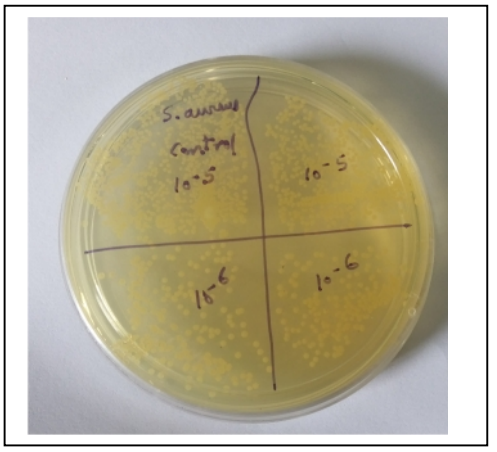




***E. coli* growth** ***S.aureus* growth**

Alum Treated Onion Skin Dyed Fabrics





***E. coli* growth** ***S.aureus* growth**

Alkali Treated Reactive Red Dyed Fabrics

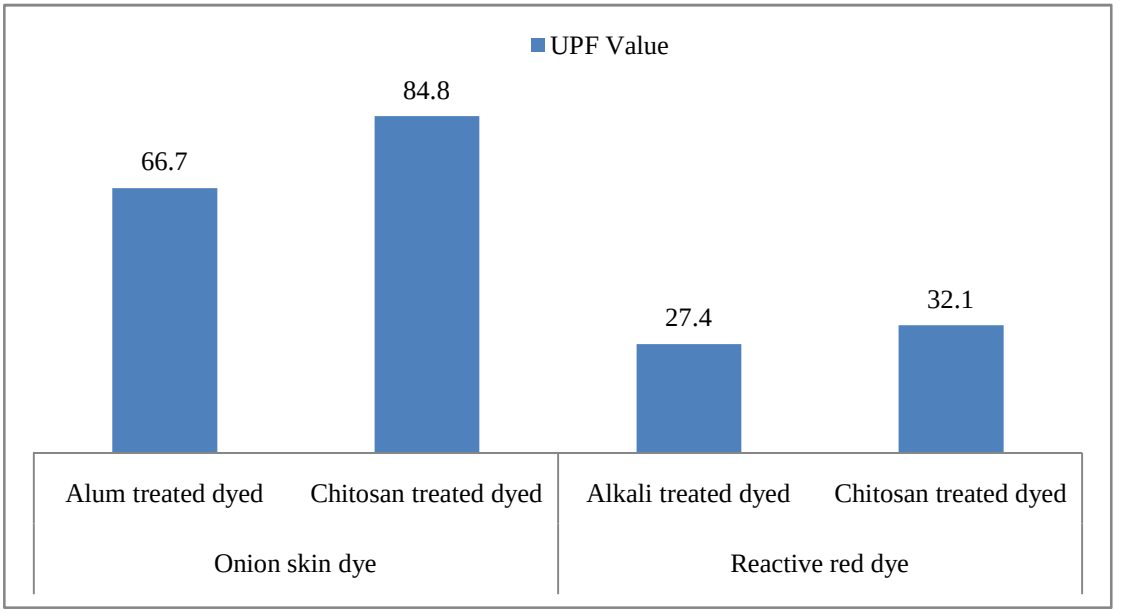


Figure 9: Comparison between ultra-violet protection property of natural and synthetic dyes

It is deduced that the onion skin dye play a significant role in enhancing the UPF value of the alum and chitosan treated fabrics which achieved the excellent UV properties after dyeing whereas reactive red dyed fabrics got category of very good protection.

CHAPTER -V

DISCUSSION

This chapter presents the discussion regarding the findings of the study. The relevant discussion have been presented under the following sub headings:

5.1 Selection of biopolymer, dyes and other auxiliaries

5.2 Standardization of biopolymer treatment and dyeing process for natural dye

5.3 Standardization of biopolymer treatment and dyeing process for synthetic dye

5.4 Measurement of total dissolved solids (TDS)

5.5 Fourier transformation infrared spectroscopy (FTIR) analysis

5.6 Assessment of colour properties of dyed fabrics

5.7 Testing of physical and functional properties of dyed fabrics

5.8 Retention of functional properties of dyed fabrics after washing

5.9 Comparative analysis of functional properties of fabrics dyed with natural and synthetic dye

5.1 Selection of Biopolymer, Dyes and other Auxiliaries

i. **Selection of biopolymer:** The use of biopolymer instead of metal based mordants and salts is a promising option and environmental benign route for the dyeing of cotton fabric with natural and synthetic dye. The pretreatment to cotton fabric was given with alum and alkali and compared with three biopolymers i.e. chitosan, sericin, beta-cyclodextrin for natural and synthetic dyes. Among these biopolymers the chitosan showed the highest dye absorption, colour strength and wash fastness rating with natural as well as for synthetic dye. This might be due to that the amino groups of chitosan were cationic in nature reacted more with dye anions. **Kavitha *et al.* (2007)** stated that chitosan can be considered as multifunctional textile finishing agent because of its dyeing improvement function which can be combined with other functions such as antimicrobial and antistatic activity. **Bashar and Khan (2013)** also found that the cotton fibres form cross-linking with chitosan facilitating positive dye sites on the fibre surface. As a result anionic dyes such as direct, acid and reactive can easily be absorbed by electrostatic attraction due to the formed cationic nature.

ii. **Selection of natural dye:** Amongst different natural dyes, onion skin dye was selected on the basis of percent dye absorption and wash fastness on chitosan treated fabric. This may be due to the fact that onion skin dye was anionic in nature when it came in contact with chitosan treated cotton fabric with cationic characters in dye liquor, the ionic interaction between dye anions and cations of chitosan treated cotton fabric took place as a result dye absorption inside the structure of the cotton fabric occurred and the dye absorption increased. When the phytochemical analysis of onion dye extract was carried out, it

indicated the presence of tannins, antraquinone, flavonoids, cadiacgycocides and reducing sugars in aqueous medium. Among these phytochemicals the antraquinone, tannins and favonoids play an important role in imparting and enhancing the colour to cotton fabric. Results are also supported by the finding of **Das *et al.* (2015)** that onion is edible and the papery skin of onion is discarded as a waste during consumption of onion as food, but this papery skin contains pelargonidin (tetrahydroxy anthocyanidin) as colouring pigment in its structure. **Zhou *et al.* (2012)** revealed that uptake of annatto dye on modified cotton fabric occurs through electrostatic attractions between the anions of the dye and cationic segment on the modified cotton fibres. It was also reported by **Tepparin *et al.* (2012)** that tannins could improve the colour yield and colour fastness properties of the dyed fabrics. Antraquinone and flavonids helps in imparting the colour to any substrate besides this the presence of these phytochemical provided antimicrobial and antioxidant properties.

iii. **Selection of synthetic dye:** Among different classes of three synthetic dyes (reactive, direct and acid dye), the reactive red dye showed the maximum percent dye absorption and very good (4/5) wash fastness rating after chitosan treatment hence it was selected. Reactive dyes are anionic in nature and water soluble because of the presence of sulphonic (SO^-_3) groups in the chemical structure and cotton also carry the anionic character in water, these dyes have low intrinsic affinity towards the cotton fibre due to the repulsive charges between the dye and cotton. It can be overcome by treating the cotton fabric with cationic agents i.e. chitosan. When the chitosan treatment was given to the cotton it imparted its cationic character to cotton and enhanced the attachments of dye anions on cotton fabric through ionic attraction. Thus the colour strength value found to be increased in the chitosan treated sample dyed with reactive dye. The findings of the study are found in line with **Bashar and Khan (2013)** findings revealed that the chitosan can easily adsorb anionic dyes such as direct, acid and reactive dyes by electrostatic attraction due to its cationic nature**. Houshyar and Amirshahi (2002)** reported that treatment of cotton with chitosan increased the dye absorption with reactive dye.

iv. **Selection of cross-linking agent and catalyst:** Three cross-linking agents i.e. butan tetra carboxylic acid (BTCA), citric acid and glyoxal and three catalysts i.e. Sodium hypophosphite, magnesium chloride and phosphoric acid were used. It was observed that the butan tetra carboxylic acid (BTCA) showed comparatively better results than the citric acid in terms of percent dye absorption and colour strength value. This might be due to the fact that BTCA consists of four carboxylic groups in its structure due to the four carboxylic groups BTCA could react more with chitosan and increased the attachment on cotton whereas the citric acid contains only three carboxylic group in its structure and chitosan attachment was less as a result dye absorption was slightly less. But the citric acid was selected as cross-linking agent for chitosan treatment due to its cost

effectiveness over butan tetra carboxylic acid (BTCA) as well as parallel properties in terms of percent dye absorption and colour strength value and the wash fastness rating was same 4/5 (very good) for both. Amongst three catalysts, the sodium hypophosphite was found more effective which demonstrated the highest percent dye absorption, colour strength value and wash fastness rating so selected as catalyst for chitosan treatment. The finding of the study are found in line with findings of **Lu and Yang (1999)** revealed that the citric acid (CA), one of the polycarboxylic acids used as cross-linking agent for cotton, is cost-effective and environment friendly. **Gillingham *et al.* (1999)** emphasized that sodium hypophosphite was more effective as catalyst for cross-linking reaction of PCAs compared to other catalysts. Sodium di hydrogen phosphate (SDP) and Sodium hypophosphite (SHP) were used as catalysts for simultaneous dyeing and finishing of cotton fabric using reactive dyes and citric acid as a cross linking agent enhanced the dyeability of cotton fabric **(Malik and Kumar, 2005).**

5.2 Standardization of Biopolymer Treatment and Dyeing Process for Natural Dye

5.2.1 Standardization of chitosan treatment for onion skin dye: The standardization of chitosan treatment for onion skin dye was done on the following parameters:

i. **Optimization of chitosan concentration:** On the basis of dye absorption, colour strength and wash fastness, 4 percent concentration of chitosan was selected for biopolymer treatment. It was found that with increased chitosan concentration, the dye absorption and colour strength increased. The reason might be that natural dyes contain unsaturated moiety bearing ionisable groups such as hydroxyl and carboxylic groups and become more water soluble due to their presence in anionic forms. Cotton by its nature is negatively charged in water, thus exhibiting poor dye absorption for natural dyes due to the repulsive forces between dye and cotton anions in water. The application of chitosan helped in improving the absorption of natural dye by its cationic nature and as capable of forming ionic interaction with cotton cellulose, rendering cotton cellulose positively charged. Chitosan treated cotton fabrics favoured the absorption of natural dyes through the ionic attraction forces between the dye anions and chitosan treated fibre cations. As a result dye absorption and colour strength value increased with chitosan concentration which facilitated more sites for the attachment of dye molecules. Findings of the study are supported by the **Kittinaovarat (2004)** that the chitosan treated cotton fabric showed more functional groups (amino and methyl groups) than the untreated cotton fabric. This phenomenon depicted that chitosan provided more sites to attach dye and form functional hydrogen bonds to improve dyeing properties. **Saravanan *et al.* (2013)** found that with the increase in concentration of chitosan, colour strength value of natural dyed cotton fabric increased.

ii. **Optimization of citric acid and sodium hypophosphite concentration:** The 6 percent of citric acid and 5 percent of sodium hypophosphite concentration was selected as optimum. It was noticed that as the concentration of citric acid and sodium hypophosphite increased, there was increase in percent dye absorption, colour strength value and the wash fastness ratings. This might be due to that as the concentration of citric acid increased, degree of cross-linking increased which enhanced the attachment of chitosan on the cotton fabric and the sodium hypophosphite acted as catalyst which fastened the reaction of cross-linking and enhanced the effectiveness of cross-linking with the help of citric acid. The more deposition of chitosan took place on the cotton fabric with the increase in concentration of citric acid and sodium hypophosphite which attracted more dye molecules resulting increased dye absorption and colour strength value. The study is supported by the findings of **Khattak *et al*. (2014)** that cross-linking did better job in enhancing the colour strength and colour fastness of cotton fabric dyed with marigold. **Vukusic *et al.* (1999)** studied finishing of cotton fabric with butan- tetra carboxylic acid and citric acid along with sodium hypophosphite as single and in combination with phosphoric acid. It was observed that the sodium hypophosphite was best catalyst for the fixation of chitosan on cotton fabric.

iii. **Optimization of treatment pH:** Five varied pH of treatment solution were set and pH 5 was selected as optimum. It was noticed that as the pH of dye bath increased from 3.0 to 5.0, there was increase in dye absorption from 60.12 to 61.90 percent, colour strength value from 11.20 to 14.45 and wash fastness rating from 3/4 to 4 afterwards progressive increase in the pH range from 5 to 7 showed the decrease in dye absorption from 61.90 to 59.52 percent colour strength value from 14.45 to 8.65 and also showed decrease in the wash fastness rating from 4 to 3/4. This might be due to that in acidic condition chitosan attained the polycationic form because of protonation of amino groups. The findings of study are supported by **Munna *et al.* (2017)** that the chitosan is insoluble in water, but soluble in dilute aqueous acidic solutions below its constant (pKa)~6.3, wherein it is able to convert into the soluble protonated form ($-NH_3$). **Rattanaphani *et al.* (2007)** highlighted that the chitosan amino groups,$-NH_2$- would be in protonated cationic form ($-NH_3^+$-) in acidic solution. After pretreatment of cotton fabric with chitosan under acidic conditions, the protonated amino ($-NH_3^+$) groups of chitosan could interact with the surface of the cellulose. Chitosan could then act as an organic mordant to enhance the absorption of lac dye on the cellulose surface resulting in dye sorption on the cotton.

iv. **Optimization of material to liquor ratio (M:L Ratio):** The optimum material to liquor selected was 1:30. It was noticed that as the M:L Ratio increased from 1:10 to 1:30, the percent dye absorption and colour strength value increased but with further increase in

M:L Ratio decrease in percent dye absorption and colour strength value was recorded. This might be due that for the complete wetting of fabric within the treatment bath the sufficient amount of material to liquor ratio is required. When the M:L Ratio was to too less, incomplete absorption of finish within the fabric might have taken place. When M: L Ratio was too high, the hydrolysis would higher which decreased the absorption of finish as a result chitosan attachment was poor. Thus the absorption of dye on fabric pretreated with chitosan above and below the sufficient M: L Ratios would be low.

v. **Optimization of treatment, drying, curing temperature and time:** On the basis of dye absorption, colour strength and wash fastness rating, the optimized temperatures and durations for biopolymer treatment were 90^0C treatment, 100^0C drying and 140^0C curing temperature for 45 minutes, 5 minutes and 4 minutes durations respectively. It was observed that as the treatment, drying and curing temperature increased for prolonged durations of time, dye absorption and colour strength and wash fastness rating increased. This might be due to the fact that rise in treatment temperature with adequate duration of time facilitated the swelling of fibre structure which made the easy penetration of chitosan finish inside the fabric structure and got trapped resulting increased dye absorption, colour strength and wash fastness rating. The treatment time also played an important role in achieving the dye equilibrium which accelerated the percent dye absorption till equilibrium, after achieving the equilibrium hydrolysis of dye started which caused decline in wash fastness and colour strength value due to less dye absorption and another reason could be that the dye which deposited on fabric surface got hydrolyzed thus the wash fastness decreased. The drying temperature supported the fibre structure swelled due to treatment temperature came into its previous compact state and the finish got fixed in the interior of fabric structure. The drying temperature and time helped in attaining the maximum finish into fibre structure through gradual drying. Further increase in drying time did not affect reaction between fibre and finish as a result dye absorption and colour strength value increased for certain time after that became constant. The results of the study supported by **Mohanraj *et al.* (2012)** used leaf extract for treatment of cotton fabric using 8 percent citric acid by pad dry cure method and samples were dried at 100^0- 105 ^{0}C. It was perceived that with increasing curing temperature and time dye absorption and colour strength value increased. The reason might be that for maximum cross-linking high temperature was required. During curing, high temperature was provided to chitosan treated fabric for sufficient time which increased the rate of cross-linking reaction and facilitated the more fixation of chitosan within the cotton fabric. The chitosan attachment provided cationic character to cotton fabrics and attracted more dye molecules as a result the dye absorption and colour strength value of fabric increased. The findings of the study are supported by **Aly *et al.***

(2004) that the fixation of chitosan increased with increasing curing temperature and time and found that 150 °C curing temperature with 5 minutes curing time were optimum for giving antibacterial property.

5.2.2. Standardization of dyeing process for onion skin dye: Right-first-time, right-on-time, and right-every-time are the goal of the dyer, because it is the lowest cost of dyeing system that provides quick response for customer. This is only possible by standardizing the dyeing process to get the optimum concentration and conditions for dyeing.

Six percent concentration, 5.5 pH, 90^0C treatment temperature, 75 minutes dyeing time and 1:30 M:L Ratio were taken as optimum concentration and conditions for onion skin dye on the chitosan treated fabric. It was observed that with increase in dye concentration, dyeing temperature and dyeing time, the dye absorption and colour strength value increased. This might be due to the fact that as the dye concentration increased, the availability of the dye molecules in the dye bath also increased hence more dye molecule could attach to the fiber. It was also noticed that as the pH of dyeing increased from 3.5 to 5.0, increase was noticed in dye absorption and colour strength, after that it declined with further increase in pH value of dye liquor because chitosan treated fabric showed more cationic nature in acidic condition. The increase in dyeing temperature enhanced the movement of dye molecules in dye liquor and dye anions speedily moved towards the cationic charged chitosan treated fabric consequently the dye absorption and colour strength increased. With the increase in dyeing time, more colour strength was obtained. Less colour strength took place when dyeing was done for short period of time because of incomplete dyeing where insoluble impurities compete with the colourants to sorb onto cotton fabric rather than colourant. As the time of dyeing increased from less to more duration, more and more colour strength was attained by fabric. The results are found in line with **Waly *et al.* (2016)** that by increasing the concentration of the natural dye in dye bath and dyeing temperature a gradual increase in colour yield expressed as k/s was attained on the cotton fabrics. It was also reported that higher k/s was realized at acidic medium (pH 4) for most of natural dyes and dyeing time gave the opportunity to natural dye to penetrate and diffuse inside the fabrics attaining maximum dye absorption capacity when reached the dyeing equilibrium state.

5.3 Standardization of Biopolymer Treatment and Dyeing Process for Synthetic Dye

5.3.1 Standardization of chitosan treatment for reactive red dye: The standardization of chitosan treatment for reactive red dye was done on the following parameters:

i. **Optimization of chitosan concentration:** Five different concentrations of chitosan were used and 2.5 percent concentration was selected as optimum. It was observed that as the concentration of chitosan increased, dye absorption and colour strength value of the dyed fabric increased. The reason might be that as the chitosan concentration increased, the more chitosan attachment took place on cotton fabric which provided more cationic

character to the cotton fabric hence attracted more dye anions. Thus more dye absorption and colour strength value took place. The result of the study supported by **Bhuiyan *et al.* (2014)** that increased concentration of chitosan provided higher depth of shade. The enhancement of dye absorption occurred due to the formation of additional hydroxyl groups. It was found by **Karthikeyan and Ramachandran (2015)** and **Pavlidon (2005)** that by increasing in chitosan concentration, there was a significant improvement in color strength (k/s) of cotton fabric pretreated with chitosan and enhanced the possibility of dyeing cotton with reactive dyes without addition of salt.

ii. **Optimization of citric acid concentration:** The 5 percent concentration of citric acid and sodium hypophosphite was taken as optimum. It was found that as the concentration of citric acid and sodium hypophosphite increased, there was increase in percent dye absorption and colour strength value of dyed cotton fabric. The reason may be that the sodium hypophosphite helped in cross-linking of citric acid for chitosan attachment which increased the degree of cross-linking as a result attachment of chitosan on the cotton fabric increased which favoured the more attachment of dye anions on cotton fabric pretreated with chitosan. Hence the dye absorption and colour strength of dyed sample increased. The result of the study are supported by **Singha *et al.* (2012)** stated that the dyeing of cotton with reactive dyes using chitosan with cross-linker in the dye bath improved the dye ability of cellulosic fabrics with reactive dye. **Malik and Kumar (2005)** used Sodium di-hydrogen phosphate (SDP) and Sodium hypophosphite (SHP) as catalysts for simultaneous dyeing and finishing of cotton fabric using reactive dyes and citric acid as a cross linking agent. The findings of the study are found in line with **Welch *et al.* (1993)** revealed that the sodium hypophosphite was most effective cross-linking catalyst in terms of speed and completeness of curing, fabric whiteness obtained and durability of the resultant durable press finish to alkaline laundering.

iii. **Optimization of treatment pH:** Seven different pH of treatment soloutions were set and the optimum pH value was found 5.0. It was observed that as the pH of chitosan treatment solution increased from 3.0 to 5.0, increase was noticed in percent dye absorption and colour strength value of cotton fabric after that it decreased. This may be due to that at 5.0 pH, chitosan showed the more cationic character in acidic medium which helped in absorption of more anionic dye molecules. Thus the percent dye absorption and colour strength increased. The result of the study are supported by findings of **Suitcharit *et al.* (2010)** that chitosan favoured active sites in acidic solution which enhanced the dye absorption as well as film formation on the fibre surface. **Sayed and Sharma (2016)** reported that chitosan could also be used in the dye bath, because due to the unimolecular structure it has an extremely high affinity for many classes of

dyes including disperse, direct, reactive, acid, vat, sulphur and basic etc. At lower pH chitosan free amines were protonated attracting anionic dyes.

iv. **Optimization of material to liquor ratio (M:L Ratio):** Four different M:L Ratios were tried and 1:30 was selected as optimum M:L Ratio. It was noticed that as the material to liquor ratio increased from 1:10 to 1:30, percent dye absorption and colour strength value increased however further increase in M:L Ratio recorded the decrease in percent dye absorption and colour strength value. This might be due to that 1:30 M:L Ratio was sufficient for providing the complete exhaustion of finish uniformly inside fabric structure in treatment bath which provided maximum fixation of chitosan on fabric whereas too low M:L Ratio i.e. 1:10, 1:20 were insufficient for complete wetting of cotton and finish got adsorbed on the surface unevenly which showed the low absorption, uneven dyeing and low wash fastness but 1:40 M:L Ratio was too high in which finish remained more disperse form and took very long time to get absorbed causing slight less dye absorption but higher than 1:10 and 1:20 M:L Ratios**.**

v. **Optimization of treatment, drying, curing temperature and time:** The 90^0C treatment, 100^0C drying and 150^0C curing temperature for 60 minutes, 7 minutes and 3 minutes duration of time were taken optimum on the basis of dye absorption, colour strength and wash fastness rating. It was found that increased treatment temperature enhanced the dye absorption and colour strength value of reactive red dye on chitosan treated fabric. This might be due to that the rise in treatment temperature helped in the opening up the structure of fibre and provided the more amorphous region for the absorption of chitosan finish and made easy penetration of chitosan inside the fabric structure and prolong treatment of chitosan provided the better absorption of chitosan on the cotton which accelerated the percent dye absorption and colour strength value of dyed fabric resulted increase in dye absorption and colour strength value. It was noticed that the rise in drying temperature and time increased colour properties of dyed fabrics. This may be due to that sufficient drying temperature and time supported the fibre structure to come its crystalline stage from amorphous stage after absorbing maximum chitosan finish which got fixed in fibre structure. The maximum chitosan attachment favoured the increased dye absorption, colour strength and wash fastness rating. It was observed that as the curing temperature and time increased, dye absorption, colour strength value, wash fastness rating increased due to the maximum cross-linking reaction took place at high curing temperature and more attachment of cationic chitosan on cotton fabric which attracted more anionic dye molecules of reactive red dye. **Srisuk and Srikulkit (2008)** dried the chitosan treated samples at 100°C, for 10 minutes followed by curing at 150°C for 3 minutes showed the maximum dye uptake. **Hebeish and El-Hilw (2001)** used montmorillonite and chitosan (MMT/ CTS) slurry containing citric acid and

sodium hypophosphite (SHP) for the treatment of cotton fabric and dried at 80^0C for 5 minutes then cured at 150^0C for 3 minutes for cross-linking for ease care properties.

5.3.2. Standardization dyeing process for reactive red dye: The exhaustion of reactive dyes on cellulosic substrate is determined by number of factors and the most important are pH of dye bath, the temperature of dyeing, concentration of electrolyte, time of dyeing and liquor ratio.

The 2.5 concentration of dye, 5.0 pH, 80^0C dyeing temperature, 60 minutes dyeing time and 1: 30 M:L Ratio were selected as optimum concentration and conditions for dyeing of chitosan treated fabric with reactive red dye. It was observed that with increase in dye concentration dyeing temperature and time, dye absorption and colour strength value increased. But for the pH and M: L Ratio, dye absorption increased to specific range and time after that it started decline. **Ibrahim and Reda (2015)** found that in the exhaust dyeing process, most of the reactive dyes were easily absorbed and diffused into modified cotton by opposite charges attraction. The absorption could greatly increase the concentration of reactive dyes inside treated cotton, which enhanced dye-fiber fixation reaction in the dye-fixation process. The findings of study are supported by **Haggag *et al.* (2014)** found that increase in dye concentration led to increase in colour strength (k/s) value. **Samanta (2009)** used a completely isolated technique in which a mixture of chitosan and PEG was used to pre-treat the cotton muslin fabric that led to a salt-free reactive dyeing in acid bath. **Tamirat *et al.* (2007)** revealed that higher temperature increased the kinetic energy of the dye molecules and thereby enhanced the rate of penetration of dye in to the vicinity of the substrate. The increase in dyeing temperature increased the molecular vibrations both in the fiber and dye, which induced favorable fixation kinetics and the increase in time of dyeing increased dye exhaustion. This was because of availability of appropriate time for adsorption and fixation of dye from the solution to the fabric. Increase in the time above peak limits led to the hydrolysis of dye and showed slight decrease in dye absorption. **Alam *et al.* (2008)** exposed that the dye absorption by cotton fabric linearly increased with dyeing time and reached to maximum at 60 minutes with reactive dye at which bright and even shades were produced. **Sharmila *et al.* (2016)** used 1:30 material liquor ratio for reactive hot brand dye solution using required amount of dye stuff.

5.4 Measurement of Total Dissolved Solids (TDS): After dyeing, electrolytes are neither exhausted nor destroyed and only 60–65% dye utilization is attainable. The residual dyes and electrolytes have caused severe environmental problems and disorders in living organisms so it has become necessary to test the dyeing process on environmental parameter also.

In natural dye, the TDS value was higher (1260 ppm) in the dye liquor left after dyeing of alum treated fabric as compared to the dye liquor left after dyeing of chitosan treated which exhibitedpresence of only 600 ppm total dissolved solids. The results of the

study were found in line with findings of **Sayed and Sharma (2016)** who stated that slight modification of the cellulose polymer either by cationizing or by treatment with chitosan led to environmental friendly process by decreasing the amount of dye in the waste water.

The assessment of synthetic dye liquor revealed that the TDS value was lower in the dye liquor left after dyeing of chitosan treated fabric that showed presence of only 1019 ppm total dissolved solids which were quite less than in the liquor in which alkali treated sample dyed with reactive red dye (1830 ppm). **Ibrahim and Reda (2015)** highlighted that it was necessary to enhance fabric-dye affinity for improving utilization of the reactive dyes and eliminating or reducing the electrolyte. Introducing cationic groups, via carboxymethyl chitosan, into cotton fabrics could enhance interactions between cotton and reactive dyes. **Karthikeyan and Ramachandran (2015)** found that the chitosan treated reactive dyed fabric showed less TDS value as compared to alkali treated reactive dye sample.

5.5 Fourier Transformation Infrared Spectroscopy (FTIR) Analysis

i. FTIR analysis of chitosan powder represented the presence of hydroxyl group (H-bonded–OH- stretch), alkanes, O-H stretching - alkanes, carboxylic acids, -C-double bond-C stretch, amide, aromatic ring stretch, secondary amine, -NH-bend, -OH- bend, secondary amine –CN- stretch (tertiary alcohol, C-O stretch), -C-C- stretch, primary amine, CN stretch and aliphatic bromo compounds. The different groups were available in chitosan structure were responsible for its unique properties. The presence of amine group (NH_2) in its structure made it cationic in nature which showed the antibacterial property and provided active sites for many chemical reactions, including the reaction with cellulose. The results of the study are supported by **Rabea *et al.* (2003) and Jia *et al.* (2001)** that the antimicrobial activity of chitosan was due to its cationic nature. The electrostatic interaction between positively charged R-N $(CH_3)_3^+$ sites and negatively charged microbial cell membranes was predicted to be responsible for cellular lysis and assumed as the main antimicrobial mechanism. Charged chitosan could also interact with essential nutrients therefore interfering on microbial growth. Consequently it was expected that polymers with higher charge densities resulted in improved antimicrobial activity.

ii. FTIR analysis of onion skin dye powder revealed the presence of different functional groups viz. hydroxyl group (H-bonded–OH- stretch), methylene–CH- stretch, carbonyl group (C=O) and aldehyde group, C=C stretch, quinone or conjugated ketone and organic sulphates, OH – bend which showed water absorption characteristics. The presence of quinone was responsible for antibacterial property of onion skin dye whereas presence of >C=O< carbonyl and >C=C< (-C- double bond –C stretch) in onion skin dye powder acted as a chromophore, which were responsible for the colouring of substrate. The hydroxyl (-OH) groups were also present in onion skin dye which acted as auxochromes

and were responsible for deepening of colour. The results of study are supported by **Vankar (2000)** stated that colour of dyed fabrics depend on the nature of the chromophores as well as the substituent functional groups, the auxochromes, of the dye molecular species**.** The skin of onions was inedible however it contains a dyestuff called "Pelargonidin" (3, 5, 7, 4 tetrahydroxy antocyanidol) reported by **Zubairu and Mshelia (2015).** The antimicrobial activities of some dyes were reported as potent owing to the existence of phenol, tannin and quinone in their extracts **(Kanchana *et al.*, 2013). Gawish *et al.* (2017)** found that curcumin dye possessed the best antimicrobial activity against bacteria and fungi as a result of methoxy and hydroxyl groups existence, which was believed to improve the antimicrobial activity of curcumin extract.

iii. Fourier transfer infrared spectroscopy (FTIR) analysis of reactive red dye powder depicted O-H stretching and H- bonded band structure, phenol, alchohols, aromatic ring (-C-H-stretch), -S-H- stretch (thiols), –OH- bend, aromatic primary amine –CN- stretch and –C-C- stretch, cyclo-hexane ring vibrations. The IR absorption of the dye showed the presence of chromophore and auxochromes such as –OH, N-H in the spectra region of 3900-3200 cm^{-1} strong to medium bands. This might be due to the presence of alcohols, phenols, amines and amides. The thiol chromophore present in reactive red dye was responsible for the colouring of the substrate. The presence of hydroxyl group (OH) acted as auxochromes were present in the reactive red dye.

iv. FTIR analysis of chitosan treated fabric demonstrated the presence of functional groups i.e. hydroxyl group (H-bonded–OH- stretch) alcohol, C-H stretching, O-H stretching, alkanes, carboxylic acids, cyano compounds, disubstituted alkynes, -OH bend , tertiary amine –CN- stretch, secondary amine –CN- stretch, C-O stretching - alcohol, carboxylic acids, esters, ethers. According to **Hollen and Saddler (1979)** chemical reactivity of cellulose is related to three hydroxyl groups (OH groups) of the glucose unit. These groups readily react with moisture, dyes, and many finishes. FTIR analysis of chitosan treated cotton fabric indicated the presence of amine groups (NH_2) which are the active sites for many chemical reactions. It revealed that the chitosan imparted its cationic character to the cotton fabric and provided more cationic sites for the attachment of anionic dye. Due to the presence of amino groups the chitosan treated cotton fabric showed bacterial resistance against *E.coli* and *S. aureus* bacteria. The chitosan treatment imparted the secondary amine and tertiary amine characteristics to cotton fabric which provided maximum dye exhaustion because in the acidic condition the secondary and tertiary groups got more protonated form and attracted more anionic dye.

v. FTIR analysis of chitosan treated onion skin dyed fabric illustrated the presence of different functional groups such as hydroxyl group (H-bonded–OH- stretch) alcohol, C-H stretching, O-H stretching, cyano compounds, C-triple bond-C-stretch and functional

group C=O , -C-double bond-C stretch respectively. It confirmed the existence of different functional groups viz. -OH bend and aromatic amino stretch, tertiary amine and, secondary amine, -C-C- stretch. The presence of multiple hydroxyl groups and cyano compounds confirmed the presence of pelargonidin (3, 5, 7, 4 tetrahydroxy antocyanidol), dyestuff of onion skin contained the hydroxyl groups on chitosan treated onion skin dyed fabric. FTIR analysis of chitosan treated onion skin dyed fabric confirmed the presence of tertiary and secondary amine which helped in attachment of anionic dye molecules of onion skin dye with chitosan treated cotton fabric.

vi. FTIR spectrum of chitosan treated cotton fabric dyed with reactive red dye depicted different functional groups namely hydroxyl group (H-bonded–OH- stretch), alkanes and cyano compounds, distributed alkynes, C-triple bond-C-stretch, -C-double bond-C stretch, primary amine and N-H bend, -OH bend (aromatic primary amine stretch), The tertiary amine, –CN- stretch and secondary amine, –CN- stretch. The presence of tertiary and secondary amine was due to the chitosan treatment of fabric was done before dyeing with reactive red dye which helped in the attachment of anionic dye molecules of reactive red dye with cotton fabric and enhanced the dyeability without alkali and salt treatment. The result of the study supported by **Chattopadhyay (2001)** revealed that pretreatment of cotton with polyamide epichlorohydrin (PAE) polymer resulted excellent exhaustion of reactive dye from dye bath in absence of salts but the exhaustion and fixation reached the maximum at 2.0 % (owf). The dye exhaustion found more in acidic condition. The improvement in dye might be attributed to the presence of secondary and tertiary amino groups of polyamide epichlorohydrin (PAE) polymer which got protonated in acidic conditions and produced positively charged cotton surface which attracted more dye anions.

5.6 Assessment of Colour Properties of Dyed Fabrics

5.6.1 Assessment of colour properties of onion skin dyed cotton fabric

i. **Dye absorption and colour strength:** Chitosan treated fabric showed 66.17 percent dye absorption which was higher as compared to alum treated fabric (55.98%). The lower L* value (54.49) of chitosan treated sample indicated its darker colour than the alum treated sample when dyed with onion skin dye. The a* and b* values were found positive for both the treated samples and the hue angle (H*) was below 90^0 which depicted brown and yellowish khaki colour of sample. The chitosan treated and dyed sample was brighter than alum treated sample as indicated by higher chroma (C*) value. The colour strength value of chitosan treated was also higher (16.52) in comparison to alum treated sample (12.21). The results of the study are supported by **Khattak *et al.* (2014)** stated that cross-linking did better job in enhancing the colour fastness of cotton fabric dyed with natural dye from marigold flower. It was also reported that the crosslinker (dicrylan) improved the colour

fastness of cotton sample dyed with marigold flower. The current results confirmed the opinion of **Mughal *et al*. (2007)** who stated that cationization before dyeing could prove more beneficial method for improving the affinity of dye to the fibre.

ii. **Evaluation of colour fastness properties:** Colour fastness of textile material is of considerable importance to consumers. The fastness depends not only upon the nature and depth of shade of the dye stuff used but also upon the nature of fibre and treatment given prior to dyeing.

The onion skin dyed samples pretreated with chitosan had very good wash fastness rating (4/5) for colour change and colour staining where as wash fastness rating was good (4) in terms of colour change and colour staining for the dyed sample pretreated with alum.

Light fastness of dyed samples pretreated with chitosan was higher (4/5) for first two days in comparison to alum pretreated sample, afterwards it remained same (4) for tested samples. However alum treated dyed sample showed good light fastness for each successive day till 7^{th} day. Perspiration fastness was found good (4) for both the treated (alum and chitosan) fabrics dyed with onion skin dye. The rubbing fastness rating was also noticed good (4) for dry and wet samples of chitosan and alum treated dyed with onion skin dye. This was due to the formation of complex with chitosan which protected the chromatophore from photolytic degradation and trap the dye molecules through ionic interaction firmly which provided very good fastness property to chitosan treated onion skin dyed fabric. The flavonoids were found in onion skin dyes which were considered very useful substances during the dyeing process because of their ability to fix dyes within fabrics **(Hussein and Elhassaneen, 2013).** The findings of the study are supported by **Salama *et al.* (2015)** found that the presence of citric acid as a cross linking agent, hydroxyl groups of chitosan and cellulose could form covalent bonds with carboxyl groups of polycarboxylic acid in an esterification reaction, thus led to formation of crosslinks between chitosan and cellulose, which greatly improved durability and wash resistance.

5.6.2 Assessment of colour properties of reactive red dyed cotton fabric

i. **Dye absorption and colour strength:** The dye absorption (78.90 %), colour strength value (18.72) and wash fastness rating (4/5) were higher for the chitosan treated fabric dyed with reactive red dye than alkali treated dyed fabric (68.36 %), k/s value (13.03) and wash fastness rating (4). Lower L* value (36.48) depicted that the chitosan treated reactive dyed fabric was darker in colour than alkali treated dyed fabric for which the L* value was higher (53.76). The chroma (C*) value was higher (44.42) for the reactive red dyed sample pretreated with chitosan which indicated its brightness than alkali treated dyed sample. The hue angle (H*) remained between 270^0 to 360^0 having positive a* and negative b* values for both the treated and dyed cotton fabrics which depicted that the colour of samples was reddish blue (magenta). The results of the study are in line with

findings of **Bhuiyan *et al.* (2014)** revealed that the chitosan present in the cotton fabric enhanced the dye sites causing deeper shade. **Singha *et al*. (2012),** treated cotton with chitosan and found that it enhanced the possibility of dyeing cotton with various commercial reactive dyes and fastness properties were also found adequate and quite comparable with conventionally dyed samples. The dyeing of cotton with reactive dyes using chitosan with cross-linker in the dye bath improved the dyeability of cellulosic fabrics with reactive dye in absence of salt.

ii. **Evaluation of colour fastness properties:** The reactive red dyed sample pretreated with chitosan showed very good (4/5) wash fastness rating for colour change (CC) and colour staining (CS) than dyed sample pretreated with alkali. Light fastness rating was found very good (4/5) for reactive dyed samples pretreated with alkali and chitosan separately for first four days followed by good (4) till 7^{th} day. The perspiration fastness and rubbing fastness were found good (4) and very good (4/5) for both the chitosan and alkali treated dyed samples repectively. The findings are found in line with **Karthikeyan and Ramachandran (2015)** reported that colourfastness properties to wash and wet crocking of the treated cotton samples with chitosan treatment improved.

5.7 Testing of Physical and Functional Properties of Dyed Fabrics

5.7.1 Measurement of physical properties of onion skin dyed cotton fabric

i. **Fabric count:** When the alum and chitosan treatment was given to scoured cotton fabric the increase was noticed in fabric count. The fabric count further increased after the dyeing of alum and chitosan treated fabrics with onion skin dye. The chitosan treated dyed fabric showed more increase in fabric count than alum treated dyed fabric. This might be due to that in chitosan treatment, citric acid was used as a cross-linking agent and the process of cross-linking bonds brought the molecules closer together which resisted the movement as a result yarns came closer to each other. The other reason might be that the chitosan treatment provided more cationic nature to cotton fabric which attracted more anionic dye molecules which got entrapped inside fibre structure giving compactness to the fabric structure. Thus the yarns count increased after chitosan and dyeing treatment.

ii. **Weight and thickness:** The weight and thickness of the cotton fabric increased after alum and chitosan treatment. Additionally the increase in weight and thickness was noticed after dyeing with onion skin dye after alum and chitosan treatment. The increase in weight and thickness was found higher for chitosan treated dyed fabric than that of alum treated dyed fabric. This might be due to the fact that the application of chitosan formed cationic site on the surface of cotton fibre which increased the weight and thickness of the fabric due to the more attachment of dye molecules with chitosan treated cotton fabric increased the weight and thickness. The other reason might be that during

the chitosan treatment, chitosan got attached by citric acid and sodium hypophosphite inside the fibre structure as a result the fibres swell up and it fixed within the fibre and yarns became thicker, thus the weight and thickness increased. The results of the study are supported by finding of **Chattopadhyay *et al.* (2001)** that the weight gain increased with increase in citric acid concentration in presence of catalyst. **Mulasavalagi (2005)** used the citric acid and silicon softener for imparting crease resistant finish to cotton fabric and found increase in thickness after application of finish.

iii. **Bending length and flexural rigidity:** The bending length was found higher for the chitosan treated and chitosan treated onion skin dyed fabric as compared to the alum treated and alum treated dyed fabric. This might be attributed to the cross-linking, because the chitosan was attached to the cotton fabric through process of cross-linking by citric acid in presence of sodium hypophosphite (catalyst). The cross-linking restricted the movement of cellulose molecules within the fibre structure which increased the stiffness of the fabric as a result bending length increased. **Saravanan *et al.* (2013) and Nasir *et al.* (2015)** reported that the chitosan treatment made the fabric stiffer and found that the bending length and flexural rigidity of the cotton fabric increased after chitosan treatment. **Pereira *et al.* (2006)** noticed increase in stiffness for cotton fabric treated with nano silver particles.

iv. **Crease recovery angle:** As the chitosan treatment was given to the cotton fabric, it increased the crease recovery angle remarkably than that alum treated. Likewise the chitosan treated onion skin dyed fabric showed noticeable increase in crease recovery angle than the alum treated dyed fabric. It might be due to that the cross-linking of chitosan with citric acid caused remarkable improvement in crease recovery angle of treated cotton fabric. Cross-linked cotton fabric resisted deformation due to external force and demonstrated crease resistance. Even if, wrinkles were formed due to excessive force, cross-linking made the cotton fabric able to gradually release wrinkles and recovered their smooth appearance after the withdrawal of the external force. The results of the study are supported by the finding of **Montazer *et al.* (2007)** revealed that the cotton fabric treated with chitosan and citric acid showed the excellently improved wrinkle recovery angle and durable antimicrobial activity. **El-Nagar *et al.* (2005)** found that dyeing with natural dyes have a higher crease recovery angle than that of undyed and reactive red dyed samples.

v. **Tensile strength and elongation:** The tensile strength loss was found slightly higher for chitosan treated and chitosan treated onion skin dyed fabrics as compared to the alum treated and alum treated dyed fabrics. The decrease in tensile strength might be due to the cross-linking that resisted the relative movement of chains which did not allow the equal distribution of stress on the neighbouring chains resulting in loss in tensile strength. The elongation of alum and chitosan treated dyed fabric decreased but the percent change was

found higher for chitosan treated dyed fabric because the cross-linking restricted the movement of cellulose molecules as a result elongation decreased. The results of the study are supported by the **Schramm *et al.* (2002)** that the exposure or curing of cotton treated with polycarboxylic acid at higher temperature reduced the tensile strength of the fabric. The cross-linking of the cellulosic fibres by polycarboxylic acid caused reversible loss in tensile strength. **Joshi *et al.* (2013)** reported that cross linking between the molecules stiffen the macro-molecular network and caused fibre embrittlement, which reduced the tensile strength of herbal treated fabrics. **Ramadan *et al.* (2012)** found the decrease in elongation of chitosan treated samples.

vi. **Moisture regain:** When the alum and chitosan treatment was given to the cotton fabric the decrease was noticed in moisture regain. The moisture regain further decreased in alum and chitosan treated onion skin dyed fabrics. The findings of study are supported by **Waly *et al.* (2016)** revealed that cationic agent block the negative cites on cotton fibers during the pretreatment process resulting in diminishing their capability to absorb moisture.

vii. **Air-permeability:** Air permeability of the chitosan treated dyed fabric was found slightly lower than the alum treated onion skin dyed fabric. This might be due to the reason that the chitosan finish got entrapped between the interstices of fabric which blocked the passage of air resulting in decreased air permeability. **Karolia and Mendapara (2007)** reported that air permeability of the treated samples decreased after chitosan applications because chitosan molecules deposited on the fiber surface to block pores through which air could pass rather than penetrate into the fiber. **Uttam and Sethi (2006)** found that with the rise in fabric weight, air permeability value gradually decreased which might be due to the reduction in inter-yarn space and pore size of the fabric. **Rathinamoorthy and Thilagavathi (2013)** reported that an increase in plant extract concentration decreased the air permeability of the fabric which might be due to the filling up of the inter-fibre voids and pores of the fabric by plant extracts.

5.7.2 Evaluation of functional properties of onion skin dyed cotton fabric

i. **Antibacterial property:** Cotton fabric is susceptible to mildew, fungus and bacterial attack in damp, dark and warm surroundings and bacteria also degrade cotton.

Chitosan treated dyed fabric provided more resistant against the growth of *E.coli* and *S.aureus* bacteria than alum treated dyed fabric. This might be due to the polycationic nature of chitosan responsible for its antifungal and antimicrobial properties. It could easily bind with negatively charged residues of macromolecules at the cell surface of bacteria and subsequently inhibited the growth of bacteria. The onion dye extract contain the tannins and quinone which also provided the bacterial resistant. Thus when the chitosan treated fabric was dyed with onion skin dye extract more antimicrobial property

was provided to the cotton fabric. The results of the study are supported by findings of **Gupta and Haile (2007),** that the chitosan had shown enormous potential as therapeutic material due to its interesting features, such as antimicrobial nature and biocompatibility. **Giri *et al.* (2009)** studied the dyeing and antimicrobial characteristics of chitosan treated wool fabrics with heena dye and supported that microbial reduction percentage values were found better for chitosan treated samples against both bacteria *E.coli* and *S. aureus.* The fabric dyed with heena dye alone without chitosan also exhibited significant antimicrobial activity but the combined antimicrobial effect of chitosan and heena dye was found very good and could be used to develop clothes for protection against common infection. **Chattopadhyay and Inamdar (2013)** reviewed that chitosan could be used as dye fixing agent for shade, nap coverage and to improve the fastness properties of dyed fabrics. By virtue of its bacteria impeding property, chitosan could prevent garments to develop bad odour.

ii. **Ultra-violet protection factor:** Alum and chitosan treatment did not show any noticeable increase in the UPF value of the scoured cotton fabric. But when alum and chitosan treated fabrics were dyed with onion skin dye, it showed the UPF value 66.7 and 84.8 respectively i.e. excellent protection category. The chitosan treated dyed fabric showed higher UPF value and this might be due to the reason that chitosan treatment increased the percent dye absorption of cotton fabric due to its polycationic nature. The treatment of cotton fabric with chitosan followed by the dyeing with onion skin dye created the synergetic effect in increasing the dye absorption. The fabric became darker due the more absorption of dye than alum treated dyed fabric and the darker shades have higher UPF values. **Kim (2006)** studied the dyeing characteristics and UV protection property of green tea dyed cotton fabric using chitosan mordanting conditions. The results showed that chitosan mordanted green tea dyed cotton fabric exhibited increased UV protection property against UV-A and UV-B radations whereas chitosan mordanted cotton fabric did not show an increase in UV protection property. **Sarkar and Seal (2003)** evaluated the UV protection property of cotton fabrics dyed with madder, cochineal and indigo and manifested that dyeing of cotton fabrics with natural colourants increased the ultraviolet protective abilities of the fabrics and could be considered as an effective protection imparted medium against ultraviolet rays. **Mongkholrattanasit *et al.* (2011)** stated that the natural dye not only provided colour but also other functional finishes such as UV protection, antibacterial and deodorizing properties. It was also found that the dyeing the fabrics with natural dyes in deeper colour shades could reduce exposure to UV radiation more efficiently.

5.7.3 Measurement of physical and functional properties of reactive red dyed cotton fabric

i. **Fabric count:** The alkali and chitosan treatment was given to scoured fabric and the increase in fabric count was noticed and further increase was also assessed in fabric count after dyeing of both the treated fabrics with reactive red dye. The increase in percent change was found higher for chitosan treated dyed fabric.

ii. **Weight and thickness:** The scoured fabric exhibited the increase in weight and thickness after both the treatments (alkali and chitosan). Howeover more increase was noticed in weight and thickness after dyeing of treated fabrics. The chitosan treated dyed fabric showed the higher percent change i.e. 2.17 percent and 18.81 percent increase in weight and thickness respectively. This might be due to the deposition of finish and dye molecules within the fabric structure. The deposition of chitosan was more on the cotton fabric due to the cross-linking with citric acid and attracted more dye anions as results showed maximum increase in weight after chitosan and dyeing treatment.

iii. **Bending length and flexural rigidity:** After alkali and chitosan treatments, bending length and flexural rigidity of cotton fabric increased which further slightly increased after dyeing with reactive red dye. The increase in percent increase was noticed slightly higher for chitosan treated dyed fabric as compared to alkali treated dyed fabric. The reason might be that cross-linking increased the bending length and further deposition of dye molecules imparted some stiffness.

iv. **Crease recovery angle:** The chitosan treated and the chitosan treated dyed fabrics showed higher crease recovery angle than the alkali treated and alkali treated dyed fabric. **Yang *et al.* (1997)** reported that cross-linking with polycarboxylic acids (PCAs) also caused significant improvement in crease recovery behaviour of treated cotton fabrics. Crosslinked cotton fabric resisted deformation**. Sunder and Nalankilli (2012)** revealed that cross-links hindered the molecular and fibrillar slippage and stabilized the structure with increase in crease recovery angle.

v. **Tensile strength and elongation:** Elongation of the scoured fabric decreased after alkali and chitosan treatments, it further showed the decrease in elongation after dyeing of alkali and chitosan treated fabric with reactive red dye. **Karthikeyan and Ramachandran (2015)** reported tensile strength of the chitosan treated reactive dyed fabric decreased due to the oxidation and stiffening of the molecular backbone after cross-link formation.

vi. **Moisture regain:** The moisture regain of the scoured fabric decreased after chitosan and alkali treatments. The chitosan treated dyed fabric showed less decrease in moisture regain as compared to alkali treated dyed fabric. **Shahidullah *et al.* (2007)** reported that the moisture regain of fabric decreased after dyeing.

vii. Air-permeability: The air permeability of the scoured fabric decreased with alkali and chitosan treatment. The chitosan treated dyed fabric had slight more decrease in air permeability than the alkali treated dyed fabric. The findings of the study are supported by **Karthikeyan and Ramachandran (2015)** stated that the fabric thickness had significant effect on air permeability values of the fabric, as the air permeability tend to decrease with increased thickness. It was revealed that the air-permeability of the chitosan treated dyed fabric decreased as a result of increase in thickness in comparison to untreated one.

5.7.4 Evaluation of functional properties of reactive red dyed cotton fabric

i. Antibacterial property: The chitosan treatment provided 84.14 and 84.16 percent reduction in the growth of *E. coli* and *S. aureus* bacteria alone which was quite higher than the alkali treatment. The alkali treated dyed fabric showed 26.80 and 25.58 percent against *E. coli* and *S. aureus* bacteria respectively whereas the chitosan treated dyed fabric provided the much better protection against the growth of *E. coli* and *S. aureus* bacteria which was 85.50 and 84.28 percent respectively. The results of the study supported by **Malik and Kumar (2005)** developed antibacterial cotton textile by coating it with chitosan 3-amino-1,2,4-triazolehybrid at different concentrations. The antibacterial activities of the treated cotton materials displayed excellent antibacterial effects against gram-positive bacteria, *S. aureus* and gram-negative *E. coli*. **Chung *et al.* (1998)** used citric acid and chitosan in imparting durable press and antimicrobial finish to cotton.

ii. Ultra-violet protection factor: The ultra violet protection value was found higher for the chitosan treated reactive red dyed fabric as compared to alkali treated dyed fabric. The chitosan treated dyed fabric showed maximum protection against UV-A and UV-B radiation. Because of increased thickness and weight, UPF value increased due to the blockage of pores between the interstices. The chitosan treated reactive red dyed samples attained higher UPF value due to more dye absorption which increased the darkness of hue. **Sarkar and Seal (2003)** revealed that fabric construction parameters of weight and thickness showed a positive correlation with UPF values. Higher the weight and thickness of the fabric, higher was the degree of protection afforded by the fabric.

5.8 Retention of Functional Properties of Dyed Fabrics after Washing

i. Retention of functional properties of onion skin dyed fabric

Though with the increase in washing cycles the performance of alum and chitosan treated dyed cotton fabric against *E. coli* and *S. aureus* bacteria decreased. But the chitosan treated onion skin dyed fabric showed effective control even after 20 washing cycles i.e. 80.74 percent and 80.14 percent reduction in the growth of *E. coli* and *S. aureus* bacteria. It was observed that chitosan treated onion skin dyed cotton fabric demonstrated higher percent reduction in growth of *S. aureus* and *E. coli* bacteria in comparison to alum treated dyed

fabric after 20 washing cycles. The findings of the study are found in line with the results of study carried out by **Thilagavathi and Rajenderan (2005)** that antimicrobial activity of neem, pricky chaff flower and pomegranate treated cotton fabric diminished gradually as the number of washing frequencies increased. **Orhan *et al.* (2007)** checked the antibacterial efficacy of triclosan treated cotton fabrics and observed that washing cycles decreased the efficacy of the treatments.

It was inferred that the UPF value of the alum and chitosan treated onion skin dyed fabric decreased with the increase in washing cycles. It was found that the chitosan treated dyed cotton fabric retained its ultra-violet protection property more than alum treated dyed fabric after 20 washing cycles. The reason might be that due to rubbing and friction movements during washing, fabric structure or weave became loose, space formed between interstices which allowed the transmission of UV radiations which decreased the UV protection properties of the fabrics. It might be due to the fact that with decrease in weight and thickness, UPF value decreased. The fabric count, weight and thickness was higher for the chitosan treated dyed fabric after 20 washing cycles than alum treated dyed fabric that is why the UPF value was higher for the chitosan treated dyed fabric after 20 washing cycles.

ii. Retention of functional properties of reactive red dyed fabric

The results of study depicted that the chitosan treated reactive red dyed cotton fabric provided greater resistance in the growth of *E.coli* and *S.aureus* bacteria after 20 washing cycles but the alkali treated dyed fabric did not show any considerable decrease in the growth of *S. aureus* and *E. coli* bacteria. The reason was that the chitosan treatment remarkably enhanced the antibacterial property but without any significant role of reactive red dye.

It was observed that UPF value of the alkali and chitosan treated reactive red dyed fabric decreased with the increase in washing cycles. It was found that the chitosan treated dyed cotton fabric retained ultra-violet protection property better than alkali treated dyed fabric after 20 washing cycles. The reason might be that with the repetitive washing cycles fabrics structure became loose and formed small pores between yarns resulting in decreased UPF value.

5.9 Comparative Analysis of Functional Properties of Fabrics Dyed with Natural and Synthetic Dyes

It was found that onion skin dye enhanced the antibacterial property of the chitosan treated fabric by creating synergetic effect and also provided antibacterial property to the alum treated dyed fabric against *E. coli* and *S. aureus* bacteria more than reactive red dyed fabric. The reason might be that the natural dye containing various antibacterial compounds in its structure such as tannins, quinone which enhanced the antibacterial and antioxidant property of dye whereas these were not found in reactive red dye but presence of thiol groups

in reactive red dye gave some antibacterial effect but did not possesses any significant bacterial resistance property.

It was concluded that the onion skin dye played a significant role in increasing the UPF value of the alum and chitosan treated fabric than reactive red dye. The reason might be that the dark hue provided more UPF protection by absorbing more UV radiations. The findings of the study are supported by **Mongkholrattanasit *et al.* (2011)** who confirmed that dyeing the fabrics with natural dyes in deeper colour shades reduced exposure to UV radiation more efficiently than paler ones.

CHAPTER -VI

SUMMARY AND CONCLUSION

Dyeing is an application which imparts the beauty and aesthetic look to the textiles through different colours and their tints or shades. Various natural and synthetic dyes are colour compounds of great interest since they play an important role in everyday life. The broad variety of technical and industrial applications required in dyeing of textiles and other consumer goods has produced a great deal of researches in this field. The main driving force is the constant demand for improved dyeing efficiency and fastness properties. The present study on 'Effect of biopolymer treatment on dyeing efficiency of cotton fabric' was carried out to see the effect of biopolymer on dyeing of cotton fabric through following objectives:

- To optimize the process of biopolymer treatment for application on cotton fabric.
- To standardize the dyeing process for biopolymer treated fabrics and to assess the colour fastness properties.
- To analyze the effect of treatment on physical and functional properties of treated fabrics.

To achieve the proposed objectives, pure cotton fabric was procured. Enzymatic desizing and scouring treatment was done to prepare fabric. One biopolymer, cross-linking agent, catalyst, natural dye and synthetic dye were selected on the basis of colour properties i.e. dye absorption, colour strength and wash fastness of dyed fabrics. Aqueous medium of extraction for natural dye was selected on the basis of cost effectiveness and phytochemical presence. The standardization of biopolymer treatment and dyeing process for different variables was done for onion skin and reactive red dye on the basis of colour properties. The biopolymer treatment was given using optimized concentrations and conditions for natural and synthetic dye by pad dry-cure method and the natural and synthetic dye application was given by exhaust method. The TDS values were measured of the left over dye liquors. The dye absorption, colour coordinates, colour strength and wash, light, perspiration, rubbing fastness of different treated dyed samples were assessed and compared. The FTIR analysis of chitosan, dye powders and chitosan treated dyed samples were analyzed. The physical and functional properties were tested and their retention after different washing cycles was also assessed in terms of mechanical, performance and functional properties. The comparative analysis was made between onion skin and reactive red dye on the basis of their functional properties.

The important findings of the study are summarized as follows:

Selection of biopolymer, natural and synthetic dye, cross-linking agent and catalyst

- Among the different biopolymers, chitosan showed the maximum percent dye absorption, colour strength value and wash fastness with all the eight natural dyes and fourteen synthetic dyes of three different classes. Thus the chitosan was selected as biopolymer for the natural and synthetic dye.

- Among all the eight natural dyes, onion skin dye exhibited the highest dye absorption (66.60 %) and colour strength (15.37) having very good wash fastness grade (4/5) with chitosan hence selected.
- Among the fourteen synthetic dyes, the reactive red dye was selected as it showed the highest dye absorption (83.84 %), colour strength (14.56) and very good (4/5) wash fastness grade with chitosan treated fabric.

Phytochemical analysis of natural dye

The aqueous extraction of onion skin dye showed the comparable results as in ethanol and methanol extraction hence aqueous extraction method was selected for dye extraction. It showed the presence of anthraquinone, cardiacgycocids, flavonoids, reducing sugar and tannins.

Standardized biopolymer treatment for onion skin dye

The 4 % of chitosan, 6 % of citric acid and 5 % of sodium hypophosphite were found optimum concentrations for biopolymer treatment on cotton fabric along with pH 5.0 using 1:30 M:L Ratio. The biopolymer application was given to scoured fabric by pad dry cure method using 90^0C treatment temperature for 45 minutes. The 100^0C temperature for 5 minutes was found optimum drying temperature and time for chitosan treated fabric. For the fixation of chitosan on cotton fabric the curing was done at optimized temperature (140^0C) and time (4 minutes). It was noticed that at all optimized concentrations and conditions the biopolymer treatment depicted the higher dye absorption, colour strength and wash fastness grade for natural dye.

Standardized dyeing process for onion skin dye

Dyeing of biopolymer treated fabric was done using the optimized concentration and conditions for onion skin dye viz. 6 % dye maintaining the 5.5 pH at 90^0C for 75 minutes using the 1:30 M:L ratio which showed maximum increase in percent dye absorption, colour strength and wash fastness grade.

Standardized biopolymer treatment for reactive red dye

The chitosan treatment was given on scoured fabric using optimized parameters i.e. 6.0 % chitosan, 4 % citric acid, 5 % sodium hypophosphite at 90^0C of treatment temperature for 60 minutes keeping M:L ratio 1:30 maintaining 5.0 pH and chitosan treated fabric was dried at 100^0C for 7 minute and cured at 150^0C for 3 minutes which depicted the higher percent dye absorption, colour strength value and wash fastness rating.

Standardized dyeing process for reactive red dye

Reactive red dye showed the maximum percent dye absorption, colour strength value and wash fastness rating at optimized dye concentration and dyeing conditions of cotton fabric i.e. 2.5 % reactive red dye, 5.0 pH and 1:30 M:L Ratio at 80^0C for 45 minutes.

TDS values for different treated fabrics dyed with onion skin and reactive red dye

In case of natural dye, the TDS value was higher (1260 ppm) in the dye liquor left after dyeing of alum treated fabric as compared to the dye liquor left after dyeing of chitosan treated dyed fabric (618 ppm).

The TDS value was lower in the dye liquor left after dyeing of chitosan treated fabric with reactive red dye (1019 ppm) than alkali treated sample was dyed with reactive red dye (1830 ppm) in liquor.

Colour properties of onion skin dyed fabrics

The chitosan treated dyed fabric showed higher percent dye absorption as compared to alum treated dyed fabric. The colour strength value of chitosan treated was also higher (16.52) in comparison to alum treated sample (12.21) with very good (4/5) wash fastness rating than alum treated dyed sample. The light fastness was found very good (4/5) for first two days for chitosan treated onion skin dyed fabric and remained good (4) till 7^{th} day where as the alum treated onion skin dyed fabric showed good rating (4) for all the seven days. The good grade (4) was noticed for perspiration and rubbing fastness for both the alum and chitosan treated onion skin dyed fabrics.

Colour properties of reactive red dyed fabrics

The percent dye absorption (78.90%), colour strength (18.72) and wash fastness rating (4/5) was higher for the chitosan treated dyed fabric than alkali treated dyed fabric (68.36%). The wash fastness rating was also higher 4/5 (very good) for chitosan treated reactive dyed fabric. Light fastness rating was found very good (4/5) for both treated dyed fabrics for first four days followed by good (4) till (7^{th}) day. The perspiration fastness was good (4) for both chitosan and alkali treated dyed samples. The rubbing fastness was found very good (4/5) for both (alkali and chitosan) treated dyed fabric.

FTIR analysis of chitosan, dyes, treated and dyed fabrics

FTIR analysis of chitosan powder showed the presence of primary, secondary, tertiary amine groups which were responsible for increasing the dyeing efficiency and providing the antibacterial property and hydroxyl groups helped in reacting with cotton fabric with increased the absorbency. FTIR analysis of onion skin dye and reactive red dye showed the presence of chromophore and auxochromes which were responsible for the colour and deepening of shade.

FTIR analysis of chitosan treated cotton fabric depicted that it imparted its cationic characteristic to cotton fabric. FTIR analysis of chitosan treated onion skin dyed fabric and reactive red dyed fabric confirmed the presence of different functional groups responsible for increasing the dyeing efficiency of cotton fabric.

Physical and functional properties of onion skin dyed fabrics

The fabric count, weight and thickness of the chitosan treated onion skin dyed fabric was found higher than alum treated dyed fabric. The bending length, flexural rigidity was found slightly higher for chitosan treated onion skin dyed fabric whereas the tensile strength was observed almost similar for both treated (alum and chitosan) onion skin dyed fabrics. Elongation was found higher for alum treated dyed fabric than chitosan treated dyed fabric. The crease recovery angle (103.2 degree) and moisture regain was found higher for chitosan treated onion skin dyed fabric than alum treated dyed fabric whereas the air permeability was

found slightly higher for the alum treated onion skin dyed fabric (80.16 m^3/m^2/minute) than chitosan treated dyed fabric. The chitosan treated onion skin dyed fabric showed more percent reduction in the growth of *E. coli* (97.20%) and *S. aureus* (98.03%) bacteria than alum treated onion skin dyed fabric. The UPF value was found higher for the chitosan treated onion skin dyed fabric (84.8) than alum treated onion skin dyed fabric.

Physical and functional properties of reactive red dyed fabrics

The chitosan treated reactive red dyed cotton fabric showed maximum increase in fabric count, weight and thickness than alkali treated dyed fabric. The chitosan treated dyed sample showed slight increase in bending length and flexural rigidity than alkali treated dyed sample. Tensile strength loss was found higher for alkali treated dyed fabric than chitosan treated dyed fabric. The chitosan treated reactive dyed sample showed higher crease recovery angle than alkali treated dyed sample. The decrease in moisture regain was found higher for alkali treated dyed fabric. The chitosan treated reactive red dyed fabric showed higher reduction in the growth of *E. coli* (85.50 %) and *S. aureus* (84.28 %) bacteria than alkali treated dyed fabric. UPF value was found higher for chitosan treated reactive red dyed fabric (32.1) than alkali treated dyed fabric (27.4).

Thus it is concluded that the combination of dyes with biopolymer is the promising approach to fulfill the requirement of the consumers for safe and eco-friendly products. This approach enhanced dyeing efficiency of cotton fabric without using salts and alkalis and also improved other properties such as ultra-violet protection, antibacterial and crease recovery ever demanded by consumers.

Recommendations

- Optimized chitosan treatment and dyeing process of natural and synthetic dye enhanced the dyeing efficiency and provided very good wash fastness to cotton fabric without any salts or electrolyte. Thus it makes the dyeing process more eco-friendly, safe and it will also reduce the cost of production and waste generation.
- The chitosan treatment along with dyes not only enhanced the UPF value but also provide resistance against creases and bacteria. The chitosan treated onion skin dyed fabric showed higher antibacterial property against *S. aureus* and *E.coli* bacteria and UPF values than chitosan treated reactive red dyed fabric. This approach will increase the consumption of onion skin dye which is discarded as waste. This will also help in manufacturing of UV protective, antibacterial and easy care textile required in medical and sports textile which ever demanded by consumers.
- The study will increase income of the farmers who are engaged in production of cotton, dyers and manufacturers occupied in business and trade of natural dyes in small scale industry and will also generate employment.

BIBLIOGRAPHY

Agrawal PB, Ali K and Warmoeskerken MMCG. 2008. Inkjetable β-cyclodextrin based release system for cotton textiles paper presented in Autex World Textile Conference. Vilnus, Lithuania on 28 August.

Alam S, Khan GM and Razzaque SM. 2008. Dyeing of cotton fabrics with reactive dyes and their physico-chemical properties. *Indian Journal of Fibre and Textile Research*, **33**(1):5 8-65.

Allam OG, El-Sayed H, Kantouch A and Haggag K. 2009. Use of sericin in feltproofing of wool. *Journal of Natural Fibers*, **6**(1):14-26.

Aly SA, Hashem and Hussein SS. 2004. Utilization of chitosan citrate as crease resistant and antimicrobial finishing agent for cotton fabric.*Indian Journal of Fibre and Textile Research*, **29(3)**: 218-222.

Angela C, Guguianu E, Muresan EI, Horhogea C, Rimbu C and Borhan O. 2015. Antimicrobial controlled release systems for the knitted cotton fabrics based on natural substances. *Fibers and Polymers*, **16**(8): 1688-1695.

Annapoorani G and Sundarraj D. 2014. Dyeing of cotton and wool fabric using Mirabilis Jalapa Flower. *International Journal of Science and Research*, **3**(7): 1126-1129.

Bahrum AMK. 2012. Comparison of effectiveness between conventional scouring & bio-scouring on cotton fabrics. *International Journal of Scientific and Engineering Research*, **3**(8): 2229-5518

Bashar MM and Khan MA. 2013. An overview on surface modification of cotton fiber for apparel use. *Journal of Polymers and the Environment*, **21**(1): 181-190.

Bhandari B. 2014. Effect of sericin treatment on dyeability of cotton fabric using natural dye. Master's Thesis, CCS Haryana Agricultural University, Hisar.

Bhuiyan MR, Shaid A, and Khan M. 2014. Cationization of cotton fiber by chitosan and its dyeing with reactive dye without salt. *Chemical and Materials Engineering*, **2**(4): 96-100.

Bhuyan S, Gogoi N and Kalita BB. 2016. Natural dyes and its antimicrobial effect. *International Journal of Engineering Trends and Technology*, **42**(3): 102-105.

Borland VS. 2010. King cotton: here today and here tomorrow-from fiber to fashion, cotton weaves its way through the supply chain. *Textile World*, **160**(3):1-6

Broadbent. 2001. Basic principles of textile coloration. *Society of Dyers and Colorists.* West Yorkshire, England p-207.

Chattopadhyay DP and Inamdar MS. 2010. Aqueous behaviour of chitosan. *International Journal of Polymer Science*, **15**(12): 1-7.

Chattopadhyay DP and Inamdar MS .2013. Improvement in the properties of cotton fabric through synthesized nano chitosan application. *Indian Journal of Fibre and Textile Research*, **38**(3): 14-21

Chattopadhyay DP. 2001.Cationization of cotton for low-salt or salt-free dyeing. *Indian Journal of Fibre and Textile Research*, **26**(2): 108-115.

Chung YS, Lee KK and Kim JW. 1998. Durable press and antimicrobial finishing of cotton fabrics with citric acid and chitosan treatment. *Textile Research Journal*, **68**(10): 722-755.

Cireli A and Yurdakul B .2006. Application of cyclodextrin to the textile dyeing and washing processes, *Journal of Applied Polymer Science*, **100**(1): 208-218.

Das D, Datta DB and Bhattacharya P. 2015. Concurrent dyeing and finishing of cotton fabric with natural color and maleic anhydride. *International Journal of Recent Research in Physics and Chemical Sciences*, **1**(2):13-23.

Davarpanah S, Mahmoodi NM, Arami M, Bahrami H and Mazaheri F. 2009. Environmentally friendly surface modification of silk fiber: chitosan grafting and dyeing. *Applied Surface Science*, **255**(1): 4171–4176.

Edeogal HO, Okwude and Mbaebie BO .2005. Phytochemical constituents of some Nigerian medicinal plants. *African Journal of Biotechnology*, **4**(7): 685- 688.

El-Nagar K, Sanad SH, Mohamed AS and Ramadan A .2005. Mechanical properties and stability to light exposure for dyed Egyptian cotton fabric with natural and synthetic dyes. *Polymer-plastics Technology and Engineering*, **44**(7): 1269-1279.

El-Tahlawy K, Gaffar MA and El-Rafie S. 2006. Novel method for preparation of β-cyclodextrin/grafted chitosan and its application. *Carbohydrate Polymers*, **63**(3): 385-392.

Etters JN, Husain PA and Lange NK. 1999. Alkaline pectinase: an ecofriendly approach to cotton preparation. *Textile Asia*, **5**(5): 83–85.

Furter R, Ghorashi H and Schleth A. 2007. The role of cotton classification in the textile industry. *Asian Textile Journal*, **16**(5): 67.

Gawish SM, Mashaly HM, Helmy HM, Ramadan AM and Farouk R. 2017. Effect of mordant on U-V protection and antimicrobial activity of cotton, wool, silk and nylon fabrics dyed with some natural dyes. *Journal of Nanomedicine and Nanotechnology*, **8**(1): 421.

Gillingham E, Lewis D and Voncina B. 1999. An FTIR study of anhydride formation on heating butane tetracarboxylic acid in the presence of various catalysts. *Textile Research Journal*, **69**(12): 949-955.

Giri D, Venugopal J, Sudha S and Ramakrishna S. 2009. Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. *Carbohydrate Polymers*, **75**(4): 646–650.

Grifoni D, Bacci L, Zipoli G, Albanese A and Sabatini F. 2011. The role of natural dyes in the UV protection of fabrics made of vegetable fibres. *Dyes and Pigments*, **91**(3): 279-285.

Gupta D and Haile A. 2007. Multifunctional properties of cotton fabric treated with chitosan and carboxymethyl chitosan, *Carbohydrate Polymers*, **69**(1): 164–171.

Haggag K, El-Molla and Mahmoued ZM. 2014. Dyeing of cotton fabric using reactive dyes by microwave irradiation technique. *Indian Journal of Fibre and Textile Research*, **39**(12): 406-410.

Hebeish A. and El-Hilw ZH. 2001. Chemical finishing of cotton using reactive cyclodextrin. *Coloration Technology*, **117**(2): 104-110.

Hollen NR and Saddler J. 1979. *Textiles*. Macmillan:New York Publications. New York, USA.p-132.

Houshyar, S and Amirshahi SH. 2002. Treatment of cotton with chitosan and its effect on dyeability with reactive dyes. *Iranian Polymer Journal*, **11**(5): 295-302.

Hussein I and Elhassaneen Y. 2013. Protection of humans from ultraviolet radiation (uvr) through the use of cotton clothes dyed with aqueous extracts of onion skin as the natural colorant. *Journal of American Sciences*, **9**(8): 16-24.

Ibrahim HMP and Reda MM. 2015. Multi-function Modification of cotton fabrics for improving utilization of reactive dye. *International Journal of Innovative Science, Engineering and Technology*, **2**(7): 11.

Ibrahim NA, Allam EA, El-Hossamy MB and El-Zairy WM. 2007. UV-protective finishing of cellulose/wool blended fabrics, polymer-plastics. *Technology and Engineering*, **46**(9): 905-911.

Islam SM and Shahid FM. 2013. Perspectives for natural product based agents derived from industrial plants in textile applications-a review. *Journal of Cleaner Production*, **57**(7): 218.

Jia ZS, Shen DF, and Xu WL. 2001. Synthesis antibacterial activities of quaternary ammonium salt of chitosan. *Carbohydrate Resrearch*, **33**(1): 1-6.

Joshi A, Bhobe M and Saatarkar A. 2013. Phytochemical investigation of the roots of *Grewia microcos* Linn. *Journal of Chemistry and Pharmaseutical Research*, **5**(2): 80-87

Jothi D. 2008. Extraction of natural dyes from African marigold flowers (*Tagetes ereectal*) for textile coloration. *Autex Research Journal*, **8**(2): 49.

Kanchana R, Fernandes A, Bhat B, Budkule S, Dessai S and Mohan R.2013. Dyeing of textiles with natural dyes - an eco-friendly approach. *International Journal of Chemical Technology Research*, **5**(5): 2102-2109

Karolia A and Mendapara S. 2007. Imparting antimicrobial and fragrance finish on cotton fabric using chitosan with silicon softener. *Indian Journal of Fibre and Textile Research*, **32**(3): 99- 104.

Karthikeyan K and Ramachandran T. 2015. Salt free cotton reactive dyeing by plasma-nano chitosan treatment. *International Journal of Applied Research on Textile*, **3**(2): 15-25.

Katewaraphorn J and Kongdee AA. 2016. A study of microcapsules containing psidium guajava leaf extract for antibacterial agent on cotton fabric. *International Journal of Chemical Engineering and Applications*, **7**(1): 27-31.

Kavitha T, Padmashwini R, Swarna A, Giridev VR. and Neelakandan R. 2007. Effect of chitosan treatment on the properties of turmeric dyed cotton yarn. *Indian Journal of Fibre and Textile Research*, **32**(3): 53-56.

Khatri A. 2015. A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *Journal of Cleaner Production*, **87**(1): 50-57.

Khattak SP, Rafique S, Hussain T and Ahmad B. 2014. Optimization of fastness and tensile properties of cotton fabric dyed with natural extracts of marigold flower (*Tagetes erecta*) by pad-steam method. *Life Science Journal*, **11**(7): 52-60.

Kim S. 2006. Dyeing characteristics and UV protection property of green tea dyed cotton fabrics: focusing on the effect of chitosan mordanting condition. *Fibers and Polymers*, **7**(3): 255-261.

Kittinaovarat S. 2004. Using chitosan for improving the dyeability of cotton fabrics with mangosteen rind dye, *Journal of science Researches*, **29**(2): 155-164.

Kondgee A and Chintrawan N. 2007. Modification of cotton fibers with sericin using non-formaldehyde released crosslinking agents. *Journal of the Textile Association*, **11**(3): 18- 26.

Kurioka F and Shiozaki H. 2011. Hydrophilic and thermal characteristics of cotton fabric treated with sericin and citric acid. Retrieved from https://www.jstage.jst.go.jp/article/silk/18/0/18063 on 8.03.2015.

Lee LH, Hwang EH and Kim. 2009. Colorimetric assay and antimicrobial activity of cotton, silk and fabrics dyed with peony, clove, coptis chinensis and gallnut. *Materials*, **2**(1): 10- 21.

Lokesh P and Kumara-Swamy M. 2013. Extraction of natural dyes from Spathodea campanulata and its application on silk fabrics and cotton. *Pelagia Research Library*, **4**(1): 111-115

Lu Y and Yang C Q.1999.Fabric yellowing caused by citric acid as a cross linking agent for cotton. *Textile Research Journal*, **69**(9): 685–690.

Mailoa MN, Mahendradatta M, Laga A and Djide N. 2014.Antimicrobial activities of tannins extract from guava leaves (*Psidium guajava* L.) on pathogens microbial. *International Journal of Science and Technology*, **44**(1): 3-5.

Malik S and Kumar S. 2005. Simultaneous dyeing and finishing of cotton fabric using reactive dyes and citric acid. *Indian Journal of Fibre and Textile Research*, **30**(4): 444-450.

Massibo M and He Q. 2008. Major mango polyphenols and their potential significance to human health. *Comprehensive Reviews in Food Science and Food Safety*.**7**(5): 309–319.

Menezes E. 2011. Novel feature of nano-titanium dioxide on textiles: anti-felting and antibacterial wool. *Journal of Applied Polymer Science*, **121**(6): 3407–3413.

Mohanraj S, Vanathi P, Sowbarniga N and Sararanan D. 2012. Antimicrobial effectiveness of vitex negundo leaf extract. *Indian Journal of Fibre and Textile Research*, **37**(12): 389-392.

Mojsov K. 2012. Enzymatic scouring of cotton. *International Journal of Marketing, and Technology*, **2**(9): 256-275.

Mongkholrattanasit R, Krystufek J, Wiener J and Vikova M. 2011. Dyeing, fastness and UV properties of silk and wool fabrics dyed with eucalyptus leaf extract by the exhaustion process. *Fibres and Textiles in Eastern Europe*, **19**(3): 94-99.

Montazer M, Malek RMA and Rahimi A. 2007. Salt free reactive dyeing of cationized cotton. *Fibers and Polymers*, **8**(6): 608-612.

Moses JJ and Radhika R. 2012.Study of antimicrobial effect on modal fabric and its cotton counterpart dyed with some natural dyes and synthetic dyes.*International journal of Textile and Fashion Technology*, **2**(1): 1-15.

Mughal MJ, Naeem A, Aleem A, Saeed R and Ahmed K. 2007. Effect of a cationising agent on the conventional reactive dyeing of cotton. *Coloration Technology*, **78**(12): 1478-1480.

Mulasavalagi SH. 2005. Special finishes to improve resiliency and hand-feel of the naturally coloured cotton khadi fabric. Master's Thesis, University of Agricultural Sciences, Dharwad.

Munna KH, Chinyerenwa AC, Kamruzzaman, Hossain A, Ahamed K and Wahab A. 2017. Effect of Gamma Radiation on Cotton Fabric with Chitosan to Improve the Mechanical Properties. *International Journal of Textile Science*, **6**(1):1-6.

Naikwade PV, Salavi G, Dalavi S and Jadhav K. 2014. Evaluation of antibacterial properties of Musa *paradisiaca* L. leaves. *Bioscience Discovery*, **6**(3): 80-84.

Nasir E, Tulos N, Ashikin S and Zamri M. 2015. Gluta aptera dyeing on surface treated knit cotton structure. *ARPN Journal of Engineering and Applied Sciences*, **10**(15): 6305- 6308.

Needles HL. 1986. *Textile Fibres, Dyes, Finishes, and Processes: A Concise Guide*. Noyes Publications. New Jersey. USA.p-36-39.

Neorati. 2008. Multifunctional properties of cotton fabric treated with chitosan and carboxymethyl chitosan. *Carbohydrate Polymers*, **69**(6): 164-171.

Orhan M, Kut D and Gunesoglu C. 2007. Use of triclosan as antibacterial agent in textiles. *Indian Journal of Fibre and Textile Research*, **32**(1): 119-121.

Papita S and Siddhartha D. 2008. Dyeing of Textile Fibres using Marigold Flowers. *www.fibrefashion.com*, **55**(5): 52-56.

Parthiban M and Thilagavathi G. 2012. Optimisation of process parameters for coloration and antibacterial finishing of wool fabric using natural fungal extract. *Indian Journal of Fibre and Textile Research*, **37** (9): 257-264.

Pavlidon V. 2005. New Multifunctional Textiles: Antimicrobial Treatments paper presented in Intelligent Textile Structures-Application, Production and Testing International Workshop, Thessaloniki on 23 June.

Pereira JA, Pereira APG and Ferreira ICFR. 2006. Table olives from Portugal: Phenolic compounds, antioxidant potential, and antimicrobial activity, *Journal of Agricultural and Food Chemistry*, **54**(10): 8425–8431.

Rabea EI, Badawy MET, Stevens CV, Smagghe G, Steurbaut W. 2003. Chitosan as antimicrobial agent: applications and mode of action. *Biomacromolecules*, **4**(6): 1457-1465.

Rajendran R, Sundaram K, Radhar R and Rajapriya P. 2011. Bioscouring of cotton fabrics using pectinase enzyme its optimization and comparison with conventional scouring process. *Pakistan Journal of Biological Sciences*, **14**(5): 519-525.

Ramadan NK, Mohamed AO, Shawky SE and Salem MY. 2012. Spectrophotometric determination of triclabendazole by acid-dye complexation method in bulk and pharmaceutical formulation *Journal of Applied Pharmaceutical Science*, **2**(1): 128-133

Rashmi BAU, Agrawal PB. and Warmoeskerken MCG. 2011. Applications of b -cyclodextrins in textiles. *Autex Research Journal*, **11**(4): 94-101.

Raslan W, El-Aref A and Bendak A. 2009. Modification of cellulose acetate fabric with cyclodextrin to improve its dyeability. *Journal of Applied Polymer Science*, **112**(6): 3192-3198.

Rathinamoorthy R and Thilagavathi G. 2013. Optimization of process conditions of cotton fabric treatment with *Terminalia chebula* extract for antibacterial application. *Indian Journal of Fiber and Textile Research*, **38**(7): 293-302.

Rattanaphani S, Chairat M, Bremner J and Rattanaphani V. 2007. An adsorption and thermodynamic study of lac dyeing on cotton pretreated with chitosan, *Dyes and Pigments*, **72**(8): 88-96.

Salama AA, Rehab MK and Rania NS. 2015. Effect of treatment durability and coloration of coated cotton fabrics on antibacterial, UV-blocking, healing and anti-inflammatory properties. *Journal of Chemical and Pharmaceutical Research*, **7**(10): 181-193

Saleh MS1,Yasser AA and Khan EB. 2013. Eco-friendly Dyeing of Cotton Fabric with Natural Colorants Extracted from Banana Leaves. *International Journal of Textile Science*, **2**(2): 21-25.

Samanta AK and Agarwal P. 2009. Application of natural dyes on textiles. *Indian Journal of Fibre and Textile Research*, **34**(12): 384- 399.

Samanta AK. 2009. Application of polyethylene glycol, cetrimide, chitosan and their mixtures on cotton muslin fabric to improve rot resistance, antimicrobial property and its salt-free reactive dyeing. *Journal of the Textile Institute*, **17**(2): 1-20.

Saravanan P, Chandramohan G, Mariajancyrani J and Shanmugasundaram P. 2013. Extraction and application of eco – friendly natural dye obtained from leaves of acalypha indica linn on cotton fabric. *International Research Journal of Environment Sciences*, **2**(12):1-5.

Sarkar AK and Seal CM. 2003. Color strength and colorfastness of flax fabrics dyed with natural colorants. *Clothing and Textiles Research Journal*, **21**(3): 162–166.

Sayed U and Sharma R. 2016. Dyeing and anti-microbial finishing of jute using natural bio-polymer and pharmaceutical drugs. *International Journal of Management and Applied Science*, **4**(3): 221-224

Schramm C, Bischof SV and Katovic D. 2002. Non-formaldehyde durable press finishing of dyed fabrics: evaluation of cotton-bound polycarboxylic acids. *coloration technology*, **5**(3): 118-244.

Selvi AT, Dinesh MG, Satyan RS, Chandrasekaran B and Rose C. 2011. Leaf and seed extracts of *Bixa orellana* L. exert anti-microbial activity against bacterial pathogens. *Journal of Applied Pharmsecutical Science*, **1**(9): 116–120.

Shahidi S, Rashidi A, Ghoranneviss M, Anvari A, Rahimi MK, Moghaddam MB and Wiener J. 2010. Investigation of metal absorption and antibacterial activity on cotton fabric modified by low temperature plasma. *Cellulose*, **17**(3): 627.

Shahidullah M, Rabiul IM and Sayed M. 2007. Improvement of light fastness properties of dyed jute fabrics through pretreatment. *Journal of Applied Science*s, **7**(6): 3791-3795.

Sharmila P, Kotaiah B and Srivastava R. 2016. Decolorization of simulated spent reactive dye batch using solar/TiO_2/H_2O_2. *International Journal of Environment Science and Technology*, **12**(2):245–251.

Singha K, Maity S and Singha M. 2012. The salt-free dyeing on cotton: an approach to effluent free mechanism; can chitosan be a potential option. *International Journal of Textile Science*, **1**(6): 69-77.

Skerget M, Majhenie L and Bezjak M. 2009. Antioxidant, radical scavenging and antimicrobial activities of red onion (allium cepa l) skin and edible part extracts. *Chemistry and Biochemistry Engineering*, **23**(4): 435–444.

Specos MMM, Garcia JJ, Tornesello J, Marinoa P and Vecchia MD. 2010. Microencapsulated citronella oil for mosquito repellent finishing of cotton textiles. *Transactions of the Royal Society of Tropical Medicine Hygiene*, **104**(1): 653-658.

Sricharussin W, Ryo-Aree W, Intasen W and Poungraksakirt S. 2004. Effect of boric acid and BTCA on tensile strength loss of finished cotton fabrics. Textile Research Journal, **74**(6): 475-480.

Sricharussin W, Sopajaree C, Maneerung T and Sangsuriya N. 2009. Modification of cotton fabrics with b-cyclodextrinderivative for aroma finishing. *Journal of Textile Insitute*, **100**(3): 682-687.

Srisuk S and Srikulkit K. 2008. Properties evaluation of some sodium nitrite chitosan-cotton fabric. *Journal of Metals, Materials and Minerals*, **18**(2): 41–45.

Suitcharit C, Awae F, Sengmama WAR and Srikulkit K. 2010. Effect of chitosan's molecular weights on mangosteen dye fixation on cotton fabric. *Journal of Metals, Materials and Minerals*, **20**(1): 27-31.

Sundar S, Kundu Jd, Kundu S. 2010. Biopolymeric nanoparticles. *Science, Technology of Advanced Material*, **11**(3): 13-16.

Sunder AE and Nalankilli G. 2012. Polyfunctional finishes on cotton textiles. Indian *Journal of fibre and Textile Research*, **37**(12):364-371.

Sundrarajan M, Rukmani A, Gandhi RR and Vigneshwaran S. 2012. Eco friendly modification of cotton using enzyme and chitosan for enhanced dyeability of curcuma longa. *Journal of Chemical and Pharmaceutical Research*, **4**(3):1654-1660.

Tamirat I, Butt MT, Khan MN and Ali M. 2015. Effect of electrolyte concentration on dyeing process of cotton.*Pakistan Journal of Scientific and Industrial Research*, **50**(2): 159-164.

Tepparin S, Sae-be P, Suesat J, Chumrum S, and Hongmeng W. 2012. Dyeing of cotton, bombyx mori and eri silk fabrics with the natural dye extracted from tamarind seed. *International Journal of Bioscience, Biochemistry and Bioinformatics*, **2**(3):1-4.

Thilagavathi G and Rajenderan K. 2005. Development of antimicrobial textile finishes from plant species. *Indian Journal of Fiber and Textile Research*, **30**(12): 430.

Uddin MG. 2005. Extraction of eco-friendly natural dyes from mango leaves and their application on silk fabric.*Textiles and Clothing Sustainability*, **14**(6):1-7.

Uttam D and Sethi R. 2006. Impact of repeated washings on dimension stability and fabric physical factors of woven cotton fabric. *International Journal of Multidisciplinary Research*, **30**(2): 13-15.

Vankar PS. 2000. The Chemistry of Natural dyes. *Resonance*, **35**(3): 73-80.

Vigneshwaran C, Ananthasubramanian M, Anbumani N and Kandhavadivu P. 2013. Eco-friendly Approach to improve pectinolytic reaction and process optimization of bioscouring of organic cotton textiles. *Journal of Engineered Fibers and Fabrics*, **8**(2): 121-132.

Voncina B, Vand V and Jausovec D. 2007. Beta-cyclodextrin as a retarding reagent in polyacrylonitrile dyeing. *Dyes and Pigments*, **74**(3): 642-646.

Vukusic BS, Katovic D and Soljacic I. 1999. Polycarboxylic acid in crease-proof finishing, *Tekstil*, **48**(11): 549-561.

Waly AI , Marie MM, El-Zairy WMR and Abo Elela RMH. 2016. Improving dyeing properties of cotton fabrics to natural dyes via cationization and nano chitosan treatments. *IOSR Journal of Polymer and Textile Engineering*, **3**(3):11-20.

Welch CM, Kottes BA and Andrews. 1993. A route to high performance nonformaldehyde finishing of cotton, *Textile Chemist and Colorist*, **21**(2):13-17.

Wu JH, Wang Z and Xu SY. 2007. Preparation and characterization of sericin powder extracted from silk industry wastewater, *Food Chemistry*, **103**(3):1255-1262.

Yang, CQ, Wang X and Kang I. 1997. Ester crosslinking cotton fabric by polymeric carboxylic acids and citric acid, *Textile Research Journal*, **67**(1):334-342.

Yu J, Ahmedna M and Goktepe I. 2010. Potential of peanut skin phenolic extract as antioxidative and antibacterial agent in cooked and raw ground beef. *International Journal of Food Science and Technology*, **45**(7): 1337-1344.

Zhou L, Shao J Z, Chai LQ and Fu GD. 2012. Adsorption behavior of annatto dye on cotton fabrics modified by sericin. *Advanced Materials Research*, **441**(2): 111-115.

Zubairu A and Mshelia YM. 2015. Effects of selected mordants on the application of natural dye. *Science and Technology*, **5**(2): 26-32.

ANNEXURE-1

Table 1: Percent dye absorption of natural dyes on alum and biopolymers treated fabrics

Natural dyes	Alum treated fabric (control)			Biopolymer treated fabrics								
				Beta cyclodextrin			Chitosan			Sericin		
	O.D. before dyeing	O.D. After dyeing	% Dye absorption	O.D. before dyeing	O.D. After dyeing	% Dye absorption	O.D. before dyeing	O.D. After dyeing	% Dye absorption	O.D. before dyeing	O.D. After dyeing	% Dye absorption
Banana leaves	1.16	0.87	25.00	1.16	0.88	24.13	1.16	0.86	25.86	1.16	0.87	25.00
Guava leaves	0.97	0.53	45.36	0.97	0.54	44.32	0.97	0.52	46.39	0.97	0.56	42.26
Mango leaves	1.68	0.95	43.45	1.68	0.99	41.07	1.68	0.94	44.04	1.68	0.97	42.26
Marigold petals	1.93	0.96	50.25	1.93	0.98	49.22	1.93	0.96	50.25	1.03	0.97	49.74
Onion skin	1.65	0.6	63.63	1.65	0.58	64.84	1.65	0.56	66.06	1.65	0.59	64.24
Peanut skin	0.64	0.25	60.93	0.64	0.25	60.93	0.64	0.23	64.06	0.64	0.26	59.37
Pomegranate rind	1.02	0.44	56.86	1.02	0.47	53.92	1.02	0.44	56.86	1.02	0.45	55.88
Teak leaves	1.14	0.44	61.40	1.14	0.46	59.64	1.14	0.43	62.28	1.14	0.49	57.01

Table 2: Percent dye absorption of synthetic dyes on alkali and biopolymers treated fabrics

Synthetic dyes		Alkali treated fabric (Control)			Biopolymer treated fabrics								
					Beta-Cyclodextrin			Chitosan			Sericin		
		O.D. before dyeing	O.D. After dyeing	% Dye absorption	O.D. before dyeing	O.D. After dyeing	% Dye absorption	O.D. before dyeing	O.D. After dyeing	% Dye absorption	O.D. before dyeing	O.D. After dyeing	% Dye absorption
Acid	Red	1.14	0.69	39.47	1.14	0.70	38.59	1.14	0.52	54.38	1.14	0.79	30.70
	Yellow	1.32	0.89	32.57	1.32	1.00	24.24	1.32	0.56	57.57	1.32	0.82	37.87
	Black	1.49	0.83	44.29	1.49	0.85	42.95	1.49	0.62	58.38	1.49	0.72	51.67
Direct	Red	1.28	0.38	70.31	1.28	0.40	68.75	1.28	0.33	74.21	1.28	0.45	64.84
	Brown	1.54	0.43	72.07	1.54	0.36	76.62	1.54	0.32	79.22	1.54	0.49	68.18
	Chlorantine FastYellow5GLL	1.67	0.35	79.04	1.67	0.34	79.64	1.67	0.29	82.63	1.67	0.53	68.26
	Chloragol Orange RS	1.83	0.52	71.58	1.83	0.51	72.13	1.83	0.42	77.04	1.83	0.59	67.75
	Shakuntala Green BD	1.97	0.72	63.45	1.97	0.71	63.95	1.97	0.44	77.66	1.97	0.74	62.43
Reactive (hot)	Red	2.29	0.65	71.61	2.29	0.83	63.75	2.29	0.37	83.84	2.29	0.89	61.13
	Brown H4R	2.32	0.69	70.25	2.32	0.73	68.53	2.32	0.41	82.32	2.32	0.92	60.34
	Turquoise HTG	2.05	0.74	63.90	2.05	0.73	64.39	2.05	0.41	83.44	2.05	0.75	63.41
Reactive (cold)	Red M8B	2.02	1.06	47.52	2.02	1.05	48.01	2.02	0.84	58.41	2.02	1.52	24.75
	Blue MR	1.67	0.96	42.51	1.67	0.94	43.71	1.67	0.73	56.28	1.67	0.82	50.89
	Orange M2R	1.29	0.73	43.41	1.29	0.70	45.73	1.29	0.58	55.03	1.29	0.77	40.31

Table 3: Colour coordinates and colour strength of alum and biopolymers pretreated fabrics dyed with natural dyes

S. No.	Natural dyes	Pretreatments	Colour coordinates					Colour strength (k/s)
			L*	a*	b*	C*	H*	
1.	Banana leaves	Alum	75.73	0.22	1.78	1.79	82.92	4.82
		Beta-cyclodextrin	77.50	1.63	10.02	10.15	80.69	2.61
		Chitosan	75.61	-0.08	0.69	0.70	96.57	6.97
		Sericin	77.33	0.63	8.82	8.85	85.85	2.74
2.	Guava leaves	Alum	73.18	1.98	14.25	14.39	82.03	8.10
		Beta-cyclodextrin	73.19	2.80	14.94	15.20	79.34	7.77
		Chitosan	73.16	2.25	14.42	14.59	81.07	12.86
		Sericin	74.67	0.59	18.12	18.13	88.08	7.00
3.	Mango leaves	Alum	72.40	-1.10	13.85	13.85	94.59	7.38
		Beta-cyclodextrin	72.74	0.87	16.01	16.03	86.83	4.35
		Chitosan	72.33	-0.94	13.70	13.73	93.99	9.05
		Sericin	77.19	-2.13	24.28	24.38	95.04	4.40
4.	Marigold petals	Alum	70.10	-2.22	24.01	24.11	95.31	9.68
		Beta-cyclodextrin	73.16	-3.22	35.41	35.56	95.22	8.84
		Chitosan	68.95	-1.93	21.51	21.60	95.16	10.51
		Sericin	70.48	-3.09	25.01	25.20	97.08	8.87
5.	Onion skin	Alum	64.29	1.93	33.25	33.30	86.64	12.32
		Beta-cyclodextrin	58.86	6.88	18.41	19.66	69.46	14.70
		Chitosan	58.31	10.29	19.06	21.66	61.64	15.37
		Sericin	59.31	7.34	19.81	21.12	69.63	14.53
6.	Peanut skin	Alum	64.19	9.82	17.56	20.12	60.76	13.99
		Beta-cyclodextrin	64.37	10.49	18.13	20.95	59.92	13.25
		Chitosan	64.14	10.13	17.48	20.20	59.88	14.14
		Sericin	64.40	10.59	18.25	21.10	59.84	12.80
7.	Pomegranate rind	Alum	64.81	3.91	22.03	21.13	79.30	12.58
		Beta-cyclodextrin	67.99	3.20	27.60	27.77	83.70	11.20
		Chitosan	64.59	4.98	20.76	21.69	76.67	13.79
		Sericin	65.33	3.83	3.83	22.36	80.09	12.09
8.	Teak leaves	Alum	70.15	1.41	10.15	10.25	80.05	12.95
		Beta-cyclodextrin	71.52	2.72	15.28	15.52	79.85	12.87
		Chitosan	69.99	1.68	9.72	9.87	80.15	14.03
		Sericin	71.57	3.39	15.71	16.07	77.78	12.73

Table 4: Colour coordinates and colour strength of alkali and biopolymers pretreated fabrics dyed with synthetic dyes

S. No.	Synthetic dyes		Pretreatments	Colour coordinates					Colour strength (K/S)
				L*	a*	b*	C*	H*	
1.	Acid	Red	Alkali	58.94	14.14	-5.24	15.24	339.67	2.49
			Beta-cyclodextrin	59.48	11.45	-3.58	12	342.65	2.40
			Chitosan	58.77	10.55	-6.15	12.22	329.77	5.13
			Sericin	61.10	32.79	2.72	32.9	4.75	1.02
		Yellow	Alkali	60.43	2.84	0.24	2.86	4.95	1.06
			Beta-cyclodextrin	73.83	5.61	40.04	40.43	81.97	0.98
			Chitosan	58.46	6.04	-6.82	9.11	311.54	5.46
			Sericin	60.42	3.31	0.22	3.32	3.79	2.60
		Black	Alkali	59.79	-4.05	-7.37	8.41	241.21	3.56
			Beta-cyclodextrin	60.15	-7.95	-11.47	13.96	235.25	3.51
			Chitosan	59.35	-1.57	-7.916	8.07	258.69	5.74
			Sericin	59.52	-1.68	-8.74	8.9	259.04	4.08
2.	Direct	Red	Alkali	48.96	41.00	15.85	43.95	21.13	9.90
			Beta-cyclodextrin	50.00	46.19	16.29	48.98	19.42	9.19
			Chitosan	48.72	36.01	14.49	38.82	21.91	11.62
			Sericin	50.18	41.01	20.84	46.00	26.93	8.79
		Brown	Alkali	43.67	15.04	5.63	16.06	20.51	11.13
			Beta-cyclodextrin	43.46	14.1	4.39	14.77	17.29	11.73
			Chitosan	42.57	11.38	0.44	11.39	2.23	12.13
			Sericin	43.82	16.07	5.72	17.06	19.58	8.94
		Chlorantine FastYellow 5GLL	Alkali	69.63	2.59	61.42	56.09	37.17	12.04
			Beta-cyclodextrin	69.56	2.4	61.52	50.5	39.05	12.67
			Chitosan	64.26	-3.32	50.51	41.33	32.91	12.92
			Sericin	72.68	0.16	65.67	44.95	33.76	9.06
		Chloragol Orange RS	Alkali	56.27	39.21	31.83	50.5	39.05	10.50
			Beta-cyclodextrin	52.51	37.36	24.99	44.95	33.76	11.05
			Chitosan	51.25	34.69	22.46	41.33	32.91	11.86
			Sericin	56.83	44.68	33.91	56.09	37.17	8.82
		Shakuntala Green BD	Alkali	49.71	-32.79	1.67	32.83	177.07	8.52
			Beta-cyclodextrin	49.01	-23.35	12.56	26.51	151.72	8.75
			Chitosan	47.76	-8.27	15.69	17.74	117.83	11.92
			Sericin	49.88	-28.23	11.66	30.55	157.56	8.42
3.	Reactive (hot)	Red	Alkali	55.28	22.55	-17.46	28.52	322.26	10.92
			Beta-cyclodextrin	56.34	31.92	-16.34	35.86	332.89	8.71
			Chitosan	55.17	13.44	-15.87	20.80	310.28	14.56
			Sericin	56.62	33.49	-16.09	37.16	334.35	8.38
		Brown H4R	Alkali	43.62	10.54	-10.67	14.99	314.66	10.02
			Beta-cyclodextrin	43.68	10.33	-10.04	14.41	315.14	9.10
			Chitosan	43.54	9.98	-11.44	15.18	311.14	12.84
			Sericin	43.83	10.97	-8.40	13.82	322.55	8.00
		Turquoise HTG	Alkali	57.04	-31.55	-26.19	41.00	219.68	8.64
			Beta-cyclodextrin	52.41	-21.91	-19.72	29.48	221.97	8.89
			Chitosan	47.27	-6.73	-15.08	15.52	245.93	14.23
			Sericin	52.67	-21.34	-22.21	30.80	226.12	8.79
4.	Reactive (cold)	Red M8B	Alkali	64.38	31.01	-15.43	34.64	333.55	3.98
			Beta-cyclodextrin	64.21	27.78	-15.39	31.76	331.02	5.07
			Chitosan	63.76	20.38	-16.25	26.07	321.44	5.14
			Sericin	64.57	6.34	-12.35	13.89	297.21	1.00
		Blue MR	Alkali	56.58	10.98	-8.39	13.83	322.62	3.01
			Beta-cyclodextrin	43.62	10.09	-10.00	14.21	315.28	4.13
			Chitosan	43.38	10.54	-10.64	14.99	314.66	5.35
			Sericin	49.66	9.17	-10.76	14.14	310.43	4.00
		Orange M2R	Alkali	64.68	22.30	8.53	23.88	20.92	3.12
			Beta-cyclodextrin	61.79	8.90	-3.58	9.60	338.11	5.17
			Chitosan	61.33	8.29	-6.74	10.68	320.90	5.23
			Sericin	67.22	31.10	14.65	34.38	25.21	2.93

ANNEXURE-2

Table 1: Phytochemical analysis of natural dyes

S. No.	Natural dyes	Extraction mediums	Phytochemicals									
			Phenol	Alkaloids	Steroids	Cardiacgycocids	Terenoids	Tannins	Flavonoids	Anthraquinone	Saponins	Reducing Sugar
1.	**Banana leaves**	Aqueous	+	+	-	-	-	+	+	-	-	-
		Ethanol	-	-	+	+	-	-	+	-	-	-
		methanol	-	-	-	-	+	-	-	-	-	-
2.	**Guava leaves**	Aqueous	-	-	+	+	+	+	+	-	-	-
		Ethanol	-	+	+	-	+		-	-	-	-
		methanol	-	-	+	-	+	+	+	+	+	-
3.	**Mango leaves**	Aqueous	-	+	+	-	+	+	-	-	-	-
		Ethanol	-	+	+	+	+	+	+	-	-	-
		methanol	+	+	+	-	+	+	+	-	-	-
4.	**Marigold petals**	Aqueous	-	+	-	-	+		+	-	+	-
		Ethanol	-	+	+	+		+	-	-	+	-
		methanol	-	-	+	-	+	+	-	-		+
5.	**Peanut skin**	Aqueous	-	+	-	+	-	-	-	+	+	+
		Ethanol	-	+	-	+	-	-	-	-	+	+
		methanol	-	+	-	-	+	-	-	+	+	-
6.	**Pomegranate rind**	Aqueous		+	-	-	+	+	+	+	-	-
		Ethanol	+	+	-	+		+	+	+	-	+
		methanol	+	-	-	-	+	+	+	+	-	+
7.	**Teak leaves**	Aqueous	-	+	-	-	+	+	+	-	-	-
		Ethanol	-	-	-	-	+	-	-	-	-	-
		methanol	-	-	+	-	+	-	-	-	+	-

ANNEXURE-3

Table 1: Retention of preliminary properties of onion skin dyed fabric after washing

S. No.	Treated samples	Properties						
		Fabric count (ends and picks/ inch)			Weight per unit area (g/m^2)		Thickness (mm)	
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Percent change	Mean ± S.E.(m)	Percent change	Mean ± S.E.(m)	Percent change
1.	**Scoured fabric (control)**	47 ± 0.37	43 ± 0.49	-	135.0 ± 0.50	-	0.232 ± 0.002	-
2.	**Alum treated dyed**	51 ± 0.70	46 ± 0.63	-	136.6 ± 0.51	-	0.282 ± 0.004	-
Washing cycles	**5**	48 ± 0.70	44 ± 0.73	-6.52	135.7 ± 0.78	-0.66	0.280 ± 0.000	-0.71
	10	46 ± 0.44	42 ± 0.67	-11.36	134.3 ± 0.79	-1.71	0.276 ± 0.001	-2.17
	15	45 ± 0.54	40 ± 0.40	-13.95	132.8 ± 0.52	-2.86	0.271 ± 0.002	-4.06
	20	44 ± 0.83	38 ± 1.20	-19.51	131.6 ± 0.48	-3.79	0.268 ± 0.002	-5.22
3.	**Chitosan treated dyed**	54 ± 0.70	50 ± 0.94	-	140.0 ± 0.63	-	0.296 ± 0.002	-
Washing cycles	**5**	52 ± 0.67	48 ± 0.94	-4.00	139.0 ± 1.00	-0.72	0.290 ± 0.01	-2.07
	10	49 ± 0.58	46 ± 1.04	-8.33	137.4 ± 0.40	-1.89	0.284 ± 0.01	-4.23
	15	47 ± 0.83	44 ± 0.58	-15.55	137.0 ± 0.54	-2.19	0.274 ± 0.01	-8.03
	20	45 ± 0.80	43 ± 1.31	-18.18	136.8 ± 0.58	-2.34	0.270 ± 0.003	-9.63

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean

Table 2: Retention of mechanical properties of onion skin dyed fabric after washing

S. No.	Treated samples	Properties													
		Bending length (cm)				Flexural rigidity (mg-cm)	Percent Change	Tensile strength (kg)				Elongation (%)			
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp+weft)	Percent Change			Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp+weft)	Percent Change	Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp+weft)	Percent Change
1.	**Scoured (control)**	3.04 ± 0.08	2.72 ± 0.03	2.94	-	39.66	-	17.60 ± 0.24	16.18 ± 0.28	16.89	-	13.54 ± 0.27	13.86± 0.20	13.70	-
2.	**Alum treated dyed**	3.20 ± 0.05	2.84 ± 0.12	3.02	-	41.17	-	16.94 ± 0.12	15.7 ± 0.18	16.32	-	13.04 ± 0.08	13.24 ± 0.26	13.14	-
Washing Cycles	**5**	2.85 ± 0.01	2.67 ± 0.04	2.76	-9.22	37.43	-9.99	16.78 ± 0.15	15.62 ± 0.22	16.20	-0.73	13.30 ± 0.05	13.84 ± 0.07	13.57	+3.16
	10	2.65 ± 0.02	2.58 ± 0.03	2.61	-15.26	35.11	-17.26	16.69 ± 0.04	15.44 ± 0.12	16.06	-1.58	13.80 ± 0.13	13.99 ± 0.41	13.89	+5.39
	15	2.34 ± 0.18	2.41 ± 0.05	2.37	-26.99	31.53	-30.57	16.38 ± 0.13	15.05 ± 0.70	15.71	-3.82	14.11 ± 0.05	14.14 ± 0.07	14.12	+6.94
	20	2.11 ± 0.01	2.38 ± 0.01	2.24	-34.16	29.49	-39.60	16.17 ± 0.34	14.70 ± 0.18	15.43	-5.69	14.54 ± 0.13	14.44 ± 0.15	14.49	+9.31
3.	**Chitosan treated dyed**	3.26 ± 0.05	2.92 ±0.03	3.09	-	41.88	-	16.82 ± 0.25	15.80 ± 0.09	16.31	-	12.38 ± 0.19	13.56 ± 0.16	12.97	-
Washing Cycles	**5**	2.88 ± 0.04	2.74 ± 0.02	2.92	-9.96	37.86	-10.61	16.76 ± 0.25	15.64 ± 0.13	16.20	-0.74	13.76 ± 0.65	13.98 ± 0.21	13.87	+6.48
	10	2.68 ± 0.04	2.62 ± 0.02	2.65	-16.60	34.86	-20.13	16.72 ± 0.24	15.56 ± 0.11	16.14	-1.11	13.86 ± 0.11	14.06 ± 0.12	13.96	+7.09
	15	2.38 ± 0.02	2.48 ± 0.02	2.43	-27.16	31.21	-34.18	16.64 ± 0.21	15.44 ± 0.08	16.06	-1.74	13.98 ± 0.10	14.28 ± 0.04	14.13	+8.20
	20	2.16 ± 0.02	2.42 ± 0.02	2.29	-34.93	28.69	-45.97	16.20 ± 0.10	14.98 ± 0.07	15.59	-4.68	14.18 ± 0.16	14.50 ± 0.06	14.34	+9.55

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean

Table 3: Retention of performance properties of onion skin dyed fabric after washing

S. No.	Treated samples	Properties							
		Crease recovery angle (degree)				Moisture regain (%)	Percent change	Air permeability ($m^3/m^2/min$)	Percent change
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp +weft)	Percent Change				
1.	**Scoured fabric (control)**	85.40 ± 0.24	82.60 ± 0.67	84.0	-	6.78	-	82.39	-
2.	**Alum treated dyed**	93.40 ± 1.03	91.20 ± 0.58	92.3	-	6.60	-	80.16	-
Washing cycles	**5**	92.80 ± 0.54	89.36 ± 0.34	91.08	-1.34	6.62	+0.30	81.56	+1.72
	10	91.00 ± 0.33	88.78 ± 0.26	89.89	-2.68	6.65	+0.75	81.97	+2.21
	15	89.56 ± 0.25	86.84 ± 0.90	88.20	-4.64	6.68	+1.19	82.08	+2.34
	20	88.96 ± 0.59	84.54 ± 0.33	86.75	-6.39	6.69	+1.34	82.99	+3.41
3.	**Chitosan treated dyed**	103.8 ± 0.37	102.6 ± 0.68	103.2	-	6.75	-	79.33	-
washing cycles	**5**	102.0 ± 0.31	101.6 ± 0.93	101.4	-1.37	6.76	+0.14	80.29	+1.19
	10	101.4 ± 0.24	100.0 ± 0.84	100.5	-2.48	6.79	+0.58	80.69	+1.68
	15	99.80 ± 0.20	97.20 ± 0.37	98.8	-4.77	6.81	+0.88	81.46	+2.61
	20	97.80 ± 0.20	95.40 ± 0.40	97.1	-6.83	6.83	+1.17	82.19	+3.47

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean

ANNEXURE- 4

Table 1: Retention of preliminary properties of reactive red dyed fabrics after washing

S. No.	Treated samples	Properties							
		Fabric count (yarns per inch)				Weight per unit area (gm/m^2)		Thickness (mm)	
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (warp+weft)	Percent change	Mean ± S.E.(m)	Percent change	Mean ± S.E.(m)	Percent change
1.	**Scoured (control)**	47 ± 0.37	43 ±0.49	45	-	135.0 ± 1.18	-	0.232 ± 0.002	-
2.	**Alkali treated dyed**	52 ± 0.91	47 ± 0.55	50	-	137.8 ± 0.74	-	0.262 ± 0.01	-
Washing cycles	**5**	48 ± 0.49	45 ± 0.51	47	-6.38	135.9 ± 0.74	-1.39	0.256 ± 0.01	-2.34
	10	46 ± 0.45	43 ± 0.73	45	-11.11	133.7 ± 0.48	-3.06	0.249 ± 0.001	-5.22
	15	44 ± 0.73	42 ± 1.03	43	-16.27	132.2 ± 0.51	-4.23	0.240 ± 0.01	-9.16
	20	41 ± 0.60	39 ± 0.51	40	-25.00	130.8 ± 0.62	-5.35	0.230 ± 0.01	-13.91
3.	**Chitosan treated dyed**	53 ± 0.70	49 ± 0.70	51	-	138.0 ± 0.71	-	0.286 ± 0.004	-
Washing cycles	**5**	50 ±1.44	47 ± 0.71	49	-	137.0 ± 0.71	-0.72	0.274 ± 0.01	-4.37
	10	47 ± 0.86	45 ± 0.71	46	-4.08	136.0 ± 0.51	-1.47	0.268 ± 0.004	-6.71
	15	44 ± 0.37	43 ± 0.71	44	-10.86	135.6 ± 0.51	-1.76	0.250 ± 0.01	-14.40
	20	43 ± 0.51	42 ± 0.83	43	-15.90	135.0 ± 0.71	-2.22	0.238 ± 0.004	-20.16

+ = Increase, - = Decrease, **S.E. (m) =** Standard Error of Mean

Table 2: Retention of mechanical properties of reactive red dyed fabrics after washing

S. No.	Treated samples	Properties													
		Bending length (cm)				Flexural rigidity (mg-cm)	Percent Change	Tensile strength (kg)				Elongation (%)			
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp+weft)	Percent Change			Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp+weft)	Percent Change	Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp+weft)	Percent Change
1.	**Scoured (control)**	3.04 ± 0.08	2.72 ± 0.04	2.88	-	38.81	-	17.60 ± 0.24	16.18 ± 0.28	16.89	-	13.54 ± 0.27	13.86 ± 0.20	13.70	-
2.	**Alkali treated and dyed**	3.15 ± 0.01	2.78 ± 0.04	2.96	-	40.83	-	15.96 ± 0.18	15.19 ± 0.18	15.57	-	12.20 ± 0.16	13.21 ± 0.31	12.70	-
Washing cycles	**5**	2.75 ± 0.03	2.48 ± 0.05	2.61	-13.41	35.49	-15.04	15.38 ± 0.18	15.02 ± 0.17	15.20	-2.43	12.94 ± 0.16	13.36 ± 0.07	13.15	+3.42
	10	2.56 ± 0.02	2.37 ± 0.02	2.46	-20.32	32.93	-23.99	15.09 ± 0.26	14.84 ± 0.26	14.96	-4.07	13.19 ± 0.26	13.80 ± 0.14	13.49	+5.85
	15	2.30 ± 0.02	2.21 ± 0.02	2.25	-31.55	29.80	-37.01	14.78 ± 0.24	14.23 ± 0.24	14.50	-7.37	13.86 ± 0.18	13.99 ± 0.13	13.92	+8.76
	20	2.04 ± 0.02	2.11 ± 0.03	2.07	-42.99	27.13	-50.49	14.37 ± 0.18	13.90 ± 0.18	14.13	-10.19	14.04 ± 0.19	14.32 ± 0.07	14.18	+10.43
3.	**Chitosan treated dyed**	3.22 ± 0.04	2.78 ± 0.03	3.00	-	41.28	-	16.90 ± 0.23	16.12 ± 0.12	16.63	-	13.54 ± 0.27	13.74 ± 0.32	13.59	-
Washing cycles	**5**	2.76 ± 0.02	2.58 ± 0.02	2.67	-12.35	36.55	-12.94	16.78 ± 0.23	16.08 ± 0.15	16.43	-1.21	13.66 ± 0.12	13.78 ± 0.17	13.72	+0.94
	10	2.66 ± 0.02	2.42 ± 0.02	2.54	-18.11	34.50	-19.65	16.74 ± 0.19	15.96 ± 0.10	16.35	-1.71	13.74 ± 0.06	13.96 ± 0.11	13.85	+1.87
	15	2.36 ± 0.02	2.20 ± 0.03	2.28	-31.57	30.98	-33.24	16.60 ± 0.24	15.78 ± 0.73	16.19	-2.71	13.89 ± 0.20	14.02 ± 0.17	13.95	+2.58
	20	2.12 ± 0.02	2.10 ± 0.03	2.11	-42.18	28.48	-44.94	16.32 ± 0.28	15.42 ± 0.12	15.87	-4.78	14.12 ± 0.33	14.22 ± 0.17	14.17	+4.09

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean

Table 3: Retention of performance properties of reactive red dyed fabrics after wash

S. No.	Treated samples	Properties							
		Crease recovery angle (degree)			Percent Change	Moisture regain (%)	Percent change	Air permeability ($m^3/m^2/min$)	Percent change
		Warp Mean ± S.E.(m)	Weft Mean ± S.E.(m)	Mean (Warp +weft)					
1.	**Scoured (control)**	85.4 ± 0.25	82.6 ± 0.67	84.00	-	6.78	-	82.39	-
2.	**Alkali treated dyed**	89.4 ± 0.51	86.4 ± 0.51	87.90	-	6.30	-	81.21	-
Wash cycles	**5**	88.4 ± 0.59	84.9 ± 0.70	86.65	-1.44	6.33	+0.47	82.16	+1.15
	10	87.8 ± 0.68	83.3 ± 0.90	85.55	-2.74	6.44	+2.17	82.98	+2.13
	15	86.7 ± 0.56	83.0 ± 0.42	84.85	-3.59	6.48	+2.77	83.10	+2.27
	20	85.1 ± 0.44	82.9 ± 1.05	84.00	-4.64	6.49	+2.92	83.60	+2.85
3.	**Chitosan treated dyed**	100.6 ± 0.93	99.4 ± 0.75	100.0	-	6.39	-	80.04	-
Wash cycles	**5**	99.0 ± 0.32	97.6 ± 0.40	98.30	-1.72	6.40	+0.15	81.69	+2.01
	10	98.2 ± 0.37	96.4 ± 0.51	97.30	-2.77	6.42	+0.46	82.11	+2.52
	15	97.8 ± 0.37	94.2 ± 0.37	96.00	-4.16	6.47	+1.23	82.81	+3.34
	20	96.0 ± 0.54	93.6 ± 0.81	94.80	-5.48	6.50	+1.69	83.16	+3.75

+ = Increase, - = Decrease, S.E. (m) = Standard Error of Mean

ABSTRACT

Tile of thesis	:	**Effect of Biopolymer Treatment on Dyeing Efficiency of Cotton Fabric**
Full name of the degree holder	:	Mona Verma
Admission Number	:	2013HS10D
Title of degree	:	Doctor of Philosophy (Ph.D)
Name and address of Major Advisor	:	Prof. Saroj.S.Jeet Singh Deptt. of Textile and Apparel Designing CCS HAU, Hisar – 125004
Degree awarding university	:	CCS Haryana Agricultural University Hisar
Year of award of degree	:	2017
Major subject	:	Textile and Apparel Designing
Total number of pages in thesis	:	124 + viii + X
Number of words in abstract	:	446

Key words: Cotton, chitosan, dyes, colour properties, ultra-violet protection, antibacterial properties

Textile dyeing and printing industry is one of the most polluting sectors from an ecological point of view. There is need to approach new strategies, methods, material for dyeing treatment of cotton fabric with natural and synthetic dyes using environment benign route. To achieve the objectives of the study, different biopolymer, natural and synthetic dyes were tried and one of each was selected on the basis of colour properties of dyed fabrics. Standardization of chitosan treatment and dyeing process for onion skin and reactive dye was done on the basis of colour properties i.e. dye absorption colour strength and wash fastness for different concentrations and conditions. It was found that the chitosan treated onion skin dyed fabric showed higher dye absorption (66.17%), colour strength (16.52), wash fastness rating than alum treated dyed fabric (55.98%, 12.21 k/s, 4/5) respectively. Similarly the chitosan treated reactive red dyed fabric showed higher dye absorption (78.90%) colour strength (18.72) and wash fastness rating (4/5) than alkali treated dyed fabric (68.36 %, 13.03 k/s, 4) respectively. The less total dissolved solids (TDS) were in the liquor after dyeing chitosan treated fabrics with onion skin dye (618 ppm) and reactive red dye (1019 ppm) than in the dye liquor in which alum treated onion skin dyed fabric (1260 ppm) and alkali treated reactive red dyed fabric (1830 ppm) respectively. The chirosan treated dyed fabric showed higher crease recovery (103.2 degree for onion skin dye and 100 degree for reactive red dye) than alum treated (92.3 degree) and alkali treated dyed (87.90 degree) fabrics. The chitosan treated onion skin dyed fabrics showed increased bacterial resistance against *E. coli* (97.20 %) and *S. aureus* (98.03%) bacteria than alum treated dyed fabric (85.57% and 83.91 %) respectively. Likewise the chitosan treated reactive dyed fabric showed higher reduction against *E. coli* and *S. aureus* bacteria. The onion skin dye showed the higher UPF value for chitosan treated fabric (84.80) than with alum treated (66.70). The reactive red dye also showed higher UPF value with chitosan pretreatment (32.1) than alkali pretreatment (27.4). Chitosan treated onion skin and reactive red dyed fabrics demonstrated better retention of antibacterial and ultra-violet protection property than alum treated and alkali treated dyed fabrics after 20 washing cycles. Thus it is concluded that chitosan treatment enhanced colour properties without using any harsh chemicals and is capable enough to replace the use of salts and alkali in dyeing with natural and synthetic dye. The chitosan treatment along with onion skin dye imparted the multi-functionality to the cotton fabric in terms excellent protection against UV radiations, antibacterial and crease resistant properties effectively with environmental friendly manner, reduced the pollution load on environment and save resources.

MAJOR ADVISOR **DEGREE HOLDER**

HEAD OF THE DEPARTMENT

CURRICULUM VITAE

Name of the Student	:	Mona Verma
Date of Birth	:	28 June, 1990
Place of Birth	:	Pantnagar
Mother's Name	:	Mrs. Phoolwati Verma
Father's Name	:	Mr. Khem Karan Lal Verma
Permanent Address	:	Meerganj, Bareilly
Mobile	:	9729175490
E-mail	:	mona.verma35057@gmail.com
Academic Qualifications	:	

Examination/ Degree	University / Board	Year	Division	G.P.A.	Subject
Ph.D.	CCSHAU, Hisar, Haryana	2017	First	8.65	Major Subject -Textiles And Apparel Designing (TAD)
M.Sc.	CCSHAU, Hisar, Haryana	2013	First	8.55	Major Subject -Textiles And Apparel Designing (TAD)
Graduation	G.B.P.U.A&T, Pantnagar, Uttarakhand	2011	First	7.930	(FN, HDFS, CT, FRM and Extension (Specialization In Clothing and Textiles)

Medals/ Honours Received:

- Recipient of first division with distinction in B.Sc. degree programme
- *ICAR-JRF Fellowship* during M.Sc. degree programme.
- Recipient of *Dr. Saroj Kashyap Gold Medal* for M.Sc. degree programme
- Recipient of *UGC-NET JRF* Fellowship
- Recipient of *DST-INSPIRE* Fellowship
- Recipient of *Best Poster Presentation Award* in the national seminar on Sustainable Agriculture and Food Security: Challenges in Changing Climate-2012 held at CCSHAU, Hisar, and 27-28 march 2012 under the theme 3: Natural Resource Management for Sustainable Productivity.
- Recipient of *Best Poster Presentation Award* (Topic-Wrinkle Resistant Finish on Cotton by Using Biomaterial (Chitosan) in national seminar on the topic Women and Rural Development: Critical Issues on May 2&3, 2012 Ludhiana.
- Recipient of *BEST PAPER AWARD IN JOURNAL* (*International Journal of Textile and Fashion Technology)* for "Effect of Crease Resistant Finish on Crease Recovery Properties of Cotton Fabric" published in (Oct 2013), vol. 3 (4): 9-14.

Paper presented and abstracted in symposium:

- Verma M, Singh Jeet SS for "Improving the dye uptake of cotton fabric by surface modification through biopolymer (chitosan)." 44th Textile Research Symposium. at IIT Delhi on 14-16 December 2016 organised by Deptt. of Textile Technology (IIT Delhi) & The Textile Machinery Society of Japan.

Paper published:

- Verma M, Singh Jeet SS, Rose NM and Singh R. 2017. Ecofriendly dyeing of cotton fabric after biopolymer treatment by using outer skin of onion. *International Journal of Pure and Applied Bioscience.* 5 (1): 552-557. *Naas Rating:* 4.74

UNDERTAKING OF THE COPY RIGHT

I, **Mona Verma,** Adm. No. **2013HS10D** undertake that I give copy right to the CCS HAU, Hisar of my thesis entitled **"Effect of Biopolymer Treatment on Dyeing Efficiency of Cotton Fabric".**

I also undertake that, patent, if any, arising out of the research work conducted during the program shall be filed by me only with due permission of the competent authority of CCS HAU, Hisar.

Signature of student