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Effect of biopolymer treatment on the dyeing of cotton fabric with natural dye (Onion skin)

Mona Verma, Saroj S Jeet Singh and Neelam M Rose

Abstract
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, materials for dyeing treatment of cotton fabric with natural and synthetic dyes using environment benign route. In the present study, biopolymer (chitosan) was taken for the pre-treatment of cotton fabric for improving the dye uptake of natural dyes and comparison was made with aluminium potassium sulphate (alum) on the basis of colour properties of dyed fabrics. Standardization of chitosan treatment and dyeing process for onion skin dye was done. It was found that the chitosan treated onion skin dyed fabric showed higher dye absorption (66.17 %), colour strength (16.52) than alum treated dyed fabric (55.98%, 12.21 k/s) respectively. Thus it is concluded that chitosan treatment enhanced the colour properties of cotton fabric without using any harsh chemicals and capable enough to replace use of salt and alkali used as mordant in dyeing of cotton.

Keywords: chitosan, cotton, natural dyes, colour, dyeing

Introduction

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 dyesfor 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 agentsconsist 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. Biopoloymerscan 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 duringwash 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.

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 (Gupta and Haile, 2007) [4].

Material and Methods

Materials: 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. Chitosan was procured from Indian Sea Food Company Cochin, Kerala**.** Cross-linking agents, catalystsand other chemicals were procured from HIMEDIA Company.

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 air tight containers free from environmental climatic changes, till usage.

Methods

Extraction of dye: Three different mediums (aqueous, methanol and ethanol) 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. Aqueous extraction was selected for extraction of natural dyes. For the aqueous extraction of dye, 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) [7].

Colour Measurement: The methods of measuring colour numerically were established by the Commission International del 'Eclairage (CIE) in 1931 and 1976.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 kubelkamunk theory was used to predict the colour value.

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

Fastness to washing: Wash fastness test was carried out as per recommendation of IS: 3361-1979 method (BIS, 1979). 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 change in colour of dyed samples was assessed with grey scale no.1 as per the recommendation of the ISO 105 method.

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*.

Results and Discussion

1. Selection of biopolymer and natural dye

The scoured cotton fabric was pretreated with biopolymer (chitosan) and dyed with eight natural dyes viz. banana leaves, guava leaves, mango leaves, marigold petals, onion skin, peanut skin, pomegranate rind and teak leaves. The controlled samples were pretreated with aluminium potassium sulphate (alum) and dyed with all the eight natural dyes. Selection between alum and 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 between differently (alum and 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. This might be due to that the amino groups of chitosan were cationic in nature reacted more with dye anions. Kavitha *et al.* (2007) [6] 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) [1] alsofound 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. Results are also supported by the finding of Das *et al.* (2015) [2] thatonion 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 (tetrahydroxyanthocyanidin) as colouring pigment in its structure.

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 whereas alum treated onion skin dyed fabric showed the lowest dye absorption (63.63 %), colour strength (12.32) with comparable wash fastness grade (4).

Table 1: Comparison of alum treated dyed fabric with biopolymer treated dyed fabric with natural dyes on the basis of colour properties

S. No	Natural dyes	Alum treated fabric (control)			Biopolymer treated fabrics Chitosan		
		% Dye absorption	Colour strength (k/s)	Wash fastness grades	% Dye absorption	Colour strength (k/s)	Wash fastness grades
1.	Bananaleaves	25.00	4.82	3	25.86	6.97	3/4
2.	Guavaleaves	45.36	8.10	3/4	46.39	12.86	4
3.	Mangoleaves	43.45	7.38	3/4	44.04	9.05	4
4.	Marigoldpetals	50.25	9.68	4	50.25	10.51	4
5.	Onionskin	63.63	12.32	4	66.06	15.37	4/5
6.	Peanut skin	60.93	13.99	4	64.06	14.14	4/5
7.	Pomegranate rind	56.86	12.58	4	56.86	13.79	4
8.	Teakleaves	61.40	12.95	4	62.28	14.03	4/5

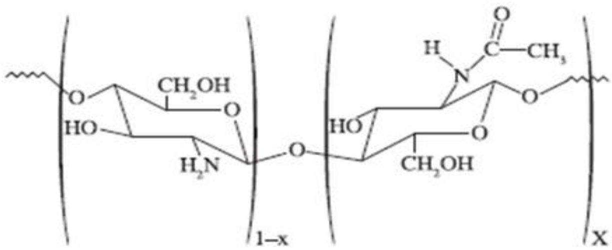
Amongst all the natural dyes, onion skin dye showed the highest dye absorption (66.06 %), colour strength (15.37) and wash fastness grade (4/5) followed by peanut skin (64.06 %, 14.14 k/s value and 4/5), teak leaves (62.28 %, 14.03 k/s value and 4/5), pomegranate rind (56.8 6%, 13.79 k/s value and 4), 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.

2. FTIR analysis of chitosan

The characteristics bands of the chitosan are presented in Table 2. 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.

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.



Structure of chitosan

Table 2: 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

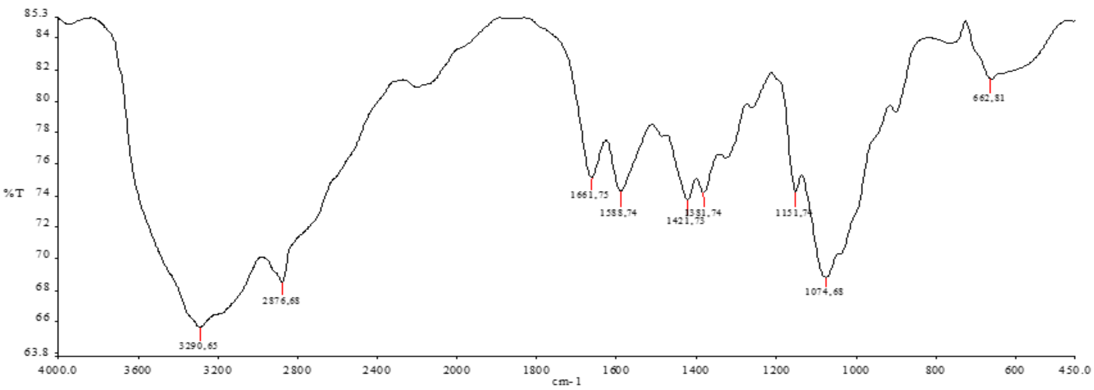


Fig 1: FTIR analysis of chitosan powder

3. FTIR analysis of onion skin dye powder
Table 3 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 3: 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. 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 tetrahydroxyantocyanidol) reported by Zubairu and Mshelia (2015) [8]. 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) [5]. Gawish *et al.* (2017) [3] found thatcurcumin 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.

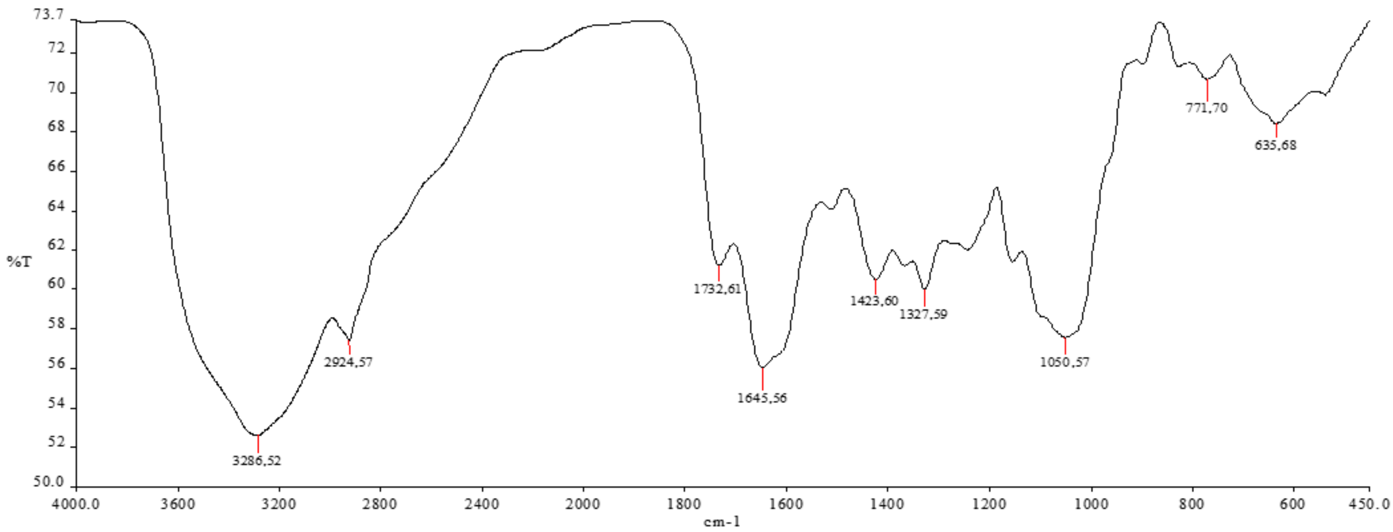
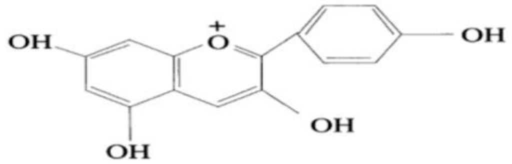


Fig 2: FTIR analysis of onion skin dye powder



Structure of "Pelargonidin" (3, 5, 7, 4 tetrahydroxylantocyanidol - a dye stuff in onion skin

4. 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.

5. 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 Table 4.

Table 4: Optimized concentration/conditions for dyeing process of 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

6. FTIR analysis of chitosan treated onion skin dyed cotton fabric

The data regarding FTIR analysis of chitosan treated onion skin dyed fabric in Table 5 indicated the presence of different functional groups.

The peaks at 3273.69 cm^{-1}, 2895.77 cm^{-1}, 2294.82 cm^{-1}, 2106.81cm^{-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}).

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. 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.

Table 5: 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	Cyanocompounds,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

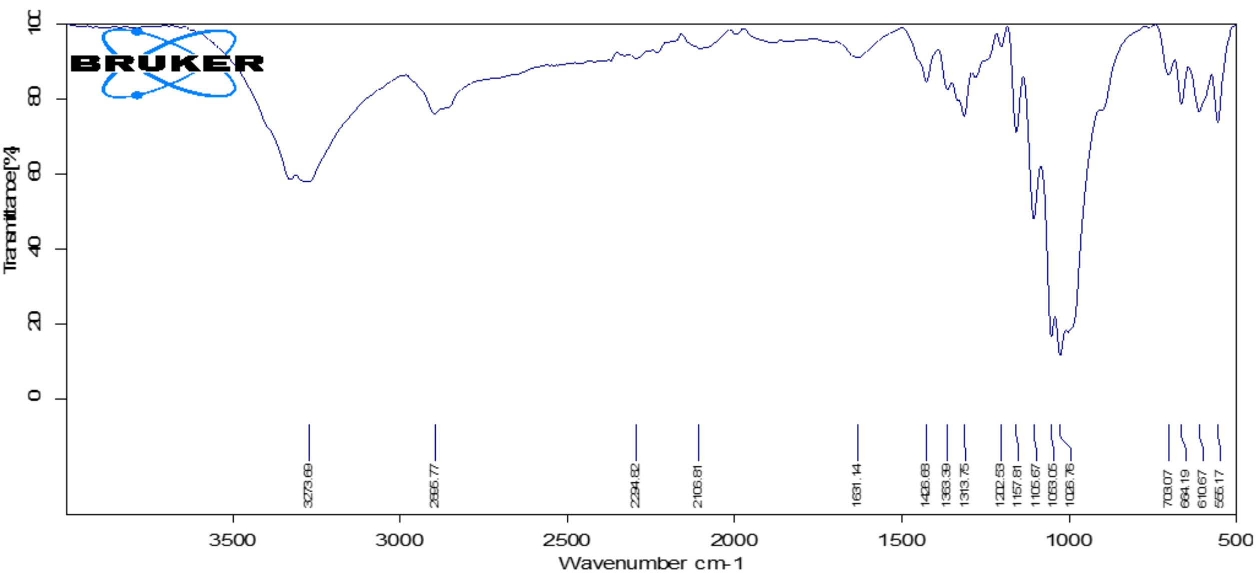


Fig 3: FTIR analysis of chitosan treated onion skin dyed cotton fabric

6. Assessment of dye absorption, colour coordinate and colour strength of dyed fabric

This section comprises the evaluation of colour properties of onion skin dyed cotton fabric which were pretreated with chitosan in terms of percent dye absorption, CIE L*, a*, b*, C*, H* andcolour strength. The results regarding colour properties of dyed fabrics are presented in Table 6**.**

Table 6: 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

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 below90^0, 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).

Conclusion

The dyeing of cotton fabric with natural dyes using biocompatible and biodegradable cationic agent such as chitosan will be cost effective environmental friendly approach in the field of dyeing industry and modification of the fabric is one of the best route to improve affinity between dye and fabric.

References

1. Basher NM, Khan MA. An overview on surface modification of cotton fibre for apparel use. Journal of Polymer and the Environment. 2013; 21(1):181-190.
2. Das D, Datta DB, Bhattacharya P. Concurrent dyeing and finishing of cotton fabric with natural colour and maleic anhydride. International Journal of Recent Research in Physics and Chemical Sciences. 2015; 1(2):13-23.
3. Gawish SM, Mashaly HM, Helmy HM, Ramadan AM, Farouk R. 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. 2017; 8(1):421-430.
4. Gupta D, Haile A. Multifunctional properties of cotton fabric treated with chitosan and carboxymethyl chitosan. Carbohydrate Polymer. 2007; 69(1):164-171.
5. Kanchana R, Fernandes A, Bhat B, Budkule S, Dessai S, Mohan R. Dyeing of textiles with natural dyes- an eco-friendly approach. International Journal of Applied Research on Textile. 2013; 3(2):15-25.
6. Kavitha T, Padmashwini R, Swarna A, Giridev VR, neelakandan R. Effect of chitosan treatment on properties of turmeric dyed cotton yarn. Indian Journal of Fibre and Textile Research. 2007; 32(3):53-56.
7. Lokesh P, kumara-Swamy M. Extraction of natural dyes from spthodea campanulata and its application on silk fabrics and cotton. Pelagia Research Library. 2013; 4(1):111-115.
8. Zubairu A, Mshelia YM. Effect of selected mordants on the application of natural dye. Science and Technology. 2015; 5(2):26-32.