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Additive effects on cotton dyeing with dye extract from achiote seeds

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Cotton yarns have been pretreated with the additives, such as chitosan, microcrystalline chitosan, quaternized chitosan & aqueous extract from the fruit of *Diospyros mollis* Griff, as well as with the commercial formaldehyde-free cationic fixing agent (Sera® Fast C-NC) & alum (post-mordanting), and their dyeing fastness properties are studied. These treated cotton yarns are then dyed with the annatto dye extract from *Bixa orellana* L. (Achiote) seeds and tested for different properties including *K/S* value, light fastness, and wash fastness. Pre-treatment of cotton yarn with chitosan or microcrystalline chitosan solution (together with glyoxal cross-linking) or quaternized chitosan, or Sera® Fast C-NC before dyeing, shows a better color depth (*K/S*) and improved wash fastness properties in comparison to yarn with alum post-mordanting and the untreated cotton yarn. Improved light fastness is also obtained on inclusion of the anti-oxidant ascorbic acid in the post-treatment protocol. These additive treatments thus offer considerable potential for the improved annatto dyeing of cotton.

Keywords: Annatto, *Bixa orellana* L, Chitosan, Cotton, *Diospyros mollis*, Dyeing, Light fastness, Wash fastness

1 Introduction

The use of natural dyes to color textiles has been revived in recent times due to the strict environmental standards imposed by many countries in response to the toxic and allergic reactions associated with synthetic dyes. In Thailand, particularly in the north and the northeast of the country, generations of villagers have used natural dyes to color cotton and silk fibres as an extra family economic support. The natural dye sources include the secretion of the insect *Laccifer lacca* Kerr (lac dye), Eucalyptus leaves, jackfruit wood, indigo, safflower, and red soil amongst others[1].

Achiote or annatto tree (*Bixa orellana* L.), known as 'kam tai' or 'kam sêt' in Thailand, provides another source of dye. The orange-yellow dye is extracted from the outer coating of the seeds of this tree, a tropical shrub native to the Central and South American rain forests. It is now widely cultivated in tropical or sub-tropical regions of the world, including Thailand. The orange-red pulp that covers achiote seed is used to produce a yellow to orange commercial food colorant. In addition, this colorant is used for textiles, cosmetics, home improvement products, and traditional medicines[2]. Annatto seeds contain a number of carotenoids and terpenoids[3-5], but the major colorant from the pericarp of the seeds is the apocarotenoid *cis*-bixin (9'*Z*) together with a minor amount of *cis*-norbixin. The natural achiote dye extract has been used in the dyeing of cotton[6,7], as well as in the dyeing of wool and silk, with greater dye uptake being observed with wool[8]. With iron (II) sulfate as a mordant, a significant improvement was observed in dye uptake as well as in color fastness properties with both wool and silk[8]. Pre-mordanting of wool yarns with tin (II) chloride and then dyeing with annatto dye and ammonia post-treatment was also shown to improve wash and light fastness properties in the dyed wool[9]. Various metal ion mordants have also been shown to generally improve fastness properties in annatto-dyed cotton[10,11], including sunlight fastness properties when post-dyeing treatments, for example with ammonia, were incorporated[12].

Instead of using metal ion – based mordants, our research has focused more on the use of potentially more environmentally compatible bio-mordants or

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derivatives in order to realize better dye-fibre binding. A variety of agents or extracts have been used as bio-mordants. For example, the concentrated aqueous extract of banana flower petaloids has been used as an effective natural mordant in the dyeing of wool[13]; while chitosan, a low cost, partially deacetylated derivative of the natural polymer chitin, can improve lac dye adsorption on cotton[14,15]. Villagers in the north of Thailand also use the extracted aqueous solution from the fruit of *Diospyros mollis* Griff as a natural mordant solution for the dyeing of cotton with natural dyes, and the dyed cotton shows good light and wash fastness properties. The use of natural mordants such as tannic acid together with enzymes[16], tannic acid alone or the tannins (mainly the hydrolysable tannin chebulinic acid) in myrobolan (*Terminalia chebula*)[11] have also been applied in the annatto dyeing of cotton. In an interesting variation of this theme, cotton fabric dyed with annatto microencapsulated in natural acacia gum which provided cross linking to the cotton, showed decreased water absorbency of the fabric compared to normal dyed material and presumably improved wash fastness[17].

Light fastness of dyed fibres is influenced by a range of physical and chemical factors[18] and can be an issue for a number of natural dyes[19]. Possible approaches to combatting this issue include post-dyeing treatment with UV absorbers or anti-oxidants. For example, the natural anti-oxidant ascorbic acid was found effective in improving the light fastness of some natural dyes on cotton yarn, and was more effective than benzophenone–based UV absorbers[18]. Carotenoid dyes have very poor fastness properties due to the extended conjugated polyene moieties present, making them susceptible to photo-oxidation[20], and anti-oxidants are a possible option for hindering this process[21].

Apart from a recent report[22] on dyeing of cotton fabrics involving chitosan application, there have not been any detailed studies reported, to the best of our knowledge. The dyeing of cotton yarn with aqueous annatto seed extract utilizing mordants (based on chitosan or its derivatives) can potentially further improve dye adsorption characteristics and dyed yarn fastness properties. The present study was therefore undertaken to investigate the dyeing with annatto seed extract of the cotton yarn pretreated with the additives, such as chitosan, microcrystalline chitosan, quaternized chitosan, and the aqueous extract from the fruit of *Diospyros mollis* Griff as compared to commercial formaldehyde-free cationic fixing agent (Sera® Fast C-NC) and alum. The effectiveness of the natural anti-oxidants salicylic acid and ascorbic acid has also been studied for improving the light fastness of the annatto dyed cotton. Potentially, these additives act as mordants as well as anti-oxidants, and hence this proposed dual function role is also assessed.

2 Materials and Methods

2.1 Materials

The cotton yarn (double yarns, 100% combed yarn, model CM/20/2, code 0058/1282; Union Star Co., Ltd.) used was purchased from villagers living in Cheanyai District, Nakhon Si Thammarat, Thailand. Wax and impurities were removed from the cotton yarn as previously described[15]. Annatto seeds were obtained from annatto trees available in the Thasala district, Nakhon Si Thammarat, Thailand.

Chitosan from crab shells (medium molecular weight, 75-85% deacetylation, 200.000 Cp viscosity, CAS 9012-76-4, FW 161) and glycidyltrimethylammonium chloride (GTMAC) were purchased from the Sigma-Aldrich Chemical Company. Alum, $KAl(SO_4)_2{\cdot}12H_2O$ (Merck, Germany), ascorbic acid, $C_6H_8O_6$ (Fluka, Switzerland), salicylic acid, $C_7H_6O_3$ (Ajax Finechem, Australia), and sodium hydroxide, NaOH (Merck, Germany) used in this study were of analytical grade. An aqueous solution of glyoxal (40% v/v) was employed without purification as a crosslinking reagent. This solution was supplied by VPC Group Co., Ltd, Thailand. Formaldehyde-free cationic fixing agent (Sera® Fast C-NC) was supplied by Sumeth Labtest Ltd., Part, Thailand. Thin layer chromatography (TLC) was undertaken on Merck Silica gel 60 F_{254} with a thickness of 0.2 mm on aluminium sheet, and gravity column chromatography was performed using Merck silica gel 60 (230-400 mesh).

2.2 Instruments

A thermostatted shaker bath (SWB 5050 Shaking Water Bath, Labnet National Company, Type SBD50 Labnet), operated at 150 strokes/min was used for all experiments. A colorimetric LabScan XE 0/45 spectrophotometer was used to measure the reflectance of dyed yarn and color coordinate CIE $L^*a^*b^*$ values. A *p*H meter (Orion 420, USA) was employed to measure the *p*H values of the solutions. ATR-FTIR spectra were obtained using an FTIR spectrometer (Bruker/Tensor27, USA). A sonicator (Type T 660/H, HF-Frequency 35 kHz, Elma, Germany) was used to assist the dye extraction from annatto seeds. A Unicam 310 UV-visible

spectrophotometer was employed for the UV-Visible spectra and absorbance measurements using quartz cells of path length 1 cm. A Bruker AVANCE 300 FT-NMR spectrometer was used to record NMR spectra, where proton (^{1}H) spectra were obtained at 300 MHz. Spectra were recorded in $CDCl_3$ and then referenced to the residual non-deuterated solvent signal. A Finnigan LC-Q mass spectrometer was used to record negative-mode ESIMS. The melting point (mp) determination was recorded on a Stuart Scientific SMP11 Analog Melting Point Apparatus and is reported uncorrected.

2.3 Methods

2.3.1 Extraction of Bixa orellana L. Components for Spectroscopic Analysis

Dried annatto seeds (10 g; herbarium specimen number WU 01457, Walailak Botanic Garden, Walailak University) were sonicated with aqueous 0.10 M NaOH (50 mL) for 30 min and then filtered to remove the seed residue. The filtrate was acidified with 0.27 M hydrochloric acid to *p*H 1.50 to give a red precipitate. The precipitate was centrifuged, filtered and then dried to give a crude dye solid (0.408 g).

2.3.2 Dye Extraction from Bixa orellana L. Seeds for Dyeing

Annatto seeds (60 g) were added to a flask with aqueous 0.10 M NaOH (200 mL) and then sonicated at room temperature for 30 min. The solution obtained contained the sodium salts of bixin and norbixin. This solution was filtered to give a dark red solution. Initial dye concentration in the obtained dye solution was determined by UV/VIS measurements at λ_{max} 454 nm and then it is compared with a standard curve (based on standard solutions of precipitated dye redissolved in 0.10 M NaOH; $y = 0.0483x$; $R^2 = 0.9947$). An initial dye concentration of 400 mg/L was employed to dye the untreated and treated cotton yarns in the subsequent experiments.

2.3.3 Determination of Optimal Initial Concentrations and Contact Time of Dye on Dye Adsorption onto Cotton Yarn

Experiments were performed in a conical flask (125 mL) with the dye solutions (50 mL) containing cotton yarn (1 g) in a thermostatted shaker bath operated at 150 strokes/min. The effect on dye adsorption was assessed initially with respect to contact time (5-90 min) and initial dye concentrations (200-1000 mg/L) and a solution *p*H of 11.55. Initial dye concentration was determined by UV/VIS measurements at λ_{max} 454 nm and compared with a standard curve ($y = 0.0483x$; $R^2 = 0.9947$). All subsequent experiments were performed for 60 min at 60 ^oC which are allowed for equilibrium conditions to be reached. After 60 min of contact time, the cotton samples were then rapidly withdrawn. The cotton samples were squeezed, washed several times with tap water, and then air-dried at room temperature.

2.3.4 Pretreatment and Dyeing of Untreated and Treated Cotton Yarn

(i) Chitosan or Chitosan-glyoxal Pretreatment

Cotton yarn was immersed directly in a 2.4% w/v aqueous solution of chitosan (dissolved in 5 % v/v aqueous acetic acid) at 28 ^oC for 12 h. After this, the yarn was removed, and either squeezed and air-dried at 28 ^oC or immersed in a 4% v/v aqueous solution of glyoxal at *p*H 4 and 40 ^oC for 60 min. After the crosslinking reaction, the sample yarn was removed, squeezed, washed several times with tap water and then dried in an oven at 50 ^oC for 16 h before further use.

(ii) Microcrystalline Chitosan-glyoxal Pretreatment

Microcrystalline chitosan (MCCh) in the form of powder was prepared by dissolving native chitosan in aqueous acetic acid solution. The degradation was carried out at 70 °C for 3 h. Then the solution was immediately cooled. The preparation of MCCh hydrogel via aggregation of glucosamine macromolecules was accomplished by introducing an aqueous NaOH solution until *p*H 8.0 of the medium was obtained. Then the precipitated product was washed with distilled water until the conductivity of the filtrate becomes the same as that of the water used. Finally, dry powder MCCh (89±2% deacetylation) was obtained by lyophilization. Weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (PDI) of the dry powder MCCh were found to be 51.04 kDa, 9.44 kDa and 5.40 respectively.

Cotton yarn was immersed directly in a 1.0% w/v aqueous solution of the obtained microcrystalline chitosan (dissolved in 1.0% v/v aqueous acetic acid) at 28 ^oC for 12 h. After this time, the yarn was removed, and either squeezed and air-dried at room temperature or was immersed in a 4% v/v aqueous solution of glyoxal at *p*H 4 and 40 ^oC for 60 min. After the crosslinking reaction, the sample yarn was removed, squeezed, washed several times with tap water and then dried in an oven at 50 ^oC for 16 h before further use.

(iii) Quaternized Chitosan–preparation and Pretreatment

Quaternized chitosan [*N*-(2-hydroxypropyl) trimethylammonium chitosan chloride] was prepared

by reacting chitosan with glycidyltrimethylammonium chloride (GTMAC) under mild acidic conditions. Briefly, chitosan (5 g) was dissolved in 1% (v/v) acetic acid (400 mL) and then GTMAC (30 g) was added. The mixture was stirred at 52 °C for 6 h. The clear solution was dialyzed with deionized water for 3 days and then freeze-dried to give a cotton-like powder of quaternized chitosan. The degree of quaternization (DQ) was found to be 36% by using potentiometric titration with silver nitrate ($AgNO_3$) solution[23]; the titration curve was recorded on a T50 Titrator using a DM141-SC sensor (Mettler Toledo, USA).

The quaternized chitosan was then used to coat the cotton yarn in our study. A 2.0% w/v aqueous solution of quaternized chitosan was prepared by dissolving the required amount of this material in 5% v/v aqueous acetic acid solution. The cotton yarn (10 g), prepared as noted above, was then immersed directly in a 2 % w/v aqueous solution of quaternized chitosan (500 mL) at 60 °C for 24 h. After this, the yarn was removed, squeezed and then oven-dried at 120 °C for 5 min before further use.

(iv) Bio-mordant Pretreatment

The fresh fruits of *Diospyros mollis* Griff were collected in the grounds of Walailak University, Thailand. The fruit (20 g) was ground and then deionized water (200 mL) was added to the ground fruit material. After soaking for 15 min, the mixture was filtered and the untreated cotton yarn (4 g) was immersed in this filtrate. After 30 min, the yarn was removed, washed with tap water and then air-dried before further dyeing.

(v) Cotton Pretreatment with Formaldehyde-free Cationic Fixing Agent

Cotton yarn (10 g) was immersed directly in a 3.0% v/v aqueous solution of cationic fixing agent (Sera® Fast C-NC) at 40 °C (*p*H 6.0) for 30 min in a thermostatted shaker bath operated at 150 strokes/min. After this, the yarn was removed, squeezed and then dried in an oven at 120 °C for 5 min.

(vi) Dyeing of Cotton Yarns

Dyeing of the pretreated cotton yarns and the untreated cotton yarn (control) was carried out by shaking the untreated or treated cotton yarn with the dye solution at an initial dye concentration of 400 mg/L in a conical flask at 60 °C (the optimal temperature) for 60 min using a thermostatted shaker bath operated at 150 strokes/min, keeping the material-to-liquor ratio at 1:50 and the *p*H at 11.55. After dyeing, the dyed cotton yarn was removed, washed with tap water to remove the unfixed dye and then air dried.

(vii) Alum Post-mordanting

Dyed untreated cotton yarn (10 g) was immersed directly in an aqueous solution of alum (15% owf; *p*H 3.51; 500 mL) at room temperature for 30 min. The yarn was then removed, washed with tap water to remove the unfixed dye, and then air dried.

2.4 Treatment with Salicylic Acid or Ascorbic Acid

Dyed untreated cotton yarn (2 g) was placed in a solution (100 mL) of salicylic acid (5 g/L) at 70 °C and the bath mixture was then stirred for 30 min at this temperature. After treatment, the dyed sample was removed, washed with water and then air dried.

Ascorbic acid was prepared in a water/ethanol mixture (9/1 v/v). The dyed untreated cotton (2 g) was then added to this aqueous ethanolic solution of ascorbic acid (5 g/L; 100 mL) at 70 °C and the bath mixture was stirred at this temperature for 30 min. After treatment, the dyed sample was removed, washed with water and then air dried.

The quaternized chitosan-pretreated cotton yarn (5 g) or microcrystalline chitosan-pretreated cotton yarn (5 g) were placed in the dye solution (initial concentration 400 mg/L; 250 mL) to which ascorbic acid (1.25 g) was added. The bath mixture was shaken using a thermostatted shaker bath operated at 150 strokes/min, keeping the material-to-liquor ratio at 1:50, at *p*H 4.22 and 60 °C for 30 min. After this, the dyed samples (Bixa/QCS/ascorbic acid) or (Bixa/MCCh/ascorbic acid) were collected, washed with tap water and then air dried.

2.5 ATR-FTIR Analysis

A ZnSe-equipped FTIR spectrometer was used for the ATR-FTIR measurements to qualitatively assess any changes in the characteristic group absorption bands of cotton yarn, chitosan, crosslinked chitosan-dyed cotton yarn, quaternized chitosan, and quaternized chitosan-dyed cotton yarn. The spectra were obtained using a single reflection horizontal ATR accessory and were measured at a spectrum resolution of 4 cm^{-1}, with 16 scans, over the range of 400-4000 cm^{-1}

2.6 Color Measurement and Fastness Testing

Each dyed cotton yarn sample was wound around the skein holder twice in taut layers and for each measurement an average of three readings was taken. The reflectance of dyed yarn and color coordinate CIE $L^*a^*b^*$ values were measured using illuminant D65 and 10° standard observer. The tristimulus values

(*X*, *Y*, and *Z***)** under illuminant were converted to CIE $L^*a^*b^*$ coordinates. The relative color strength of the dyed cotton (*K/S* values) was measured by the light reflectance technique using the Kubelka-Munk equation[24].

The dyed yarn was tested for fastness properties following the standard methods: namely color fastness to washing [ISO 105-C10: 2006 (E) Method A(1) (40 °C, 30 min)], and color fastness to light [ISO 105-B02: 2014(E)] using an Atlas Xenon Arc Weather-Ometer Model Ci 3000+.

3 Results and Discussion

3.1 Spectroscopic Analysis of *Bixa orellana* L. Dye Components

The crude dye shows the presence of one major colored compound *cis*-bixin (TLC R_f 0.6, 5% v/v methanol in dichloromethane) and an unidentified minor colored component which could be *cis*-norbixin[25-26] (TLC R_f 0.3).

The crude dye was purified by silica column chromatography with dichlomethane-methanol, using an increasing concentration of methanol to give *cis*-bixin as a dark red solid (0.072 g, 0.72%, 3-4% methanol in dichloromethane; TLC R_f 0.6, 5% v/v methanol in dichloromethane), while the minor product was retained on the column. The presence of major component (*cis*-bixin) has been identified by the following: mp 168-170 °C (lit.[25] mp 186-188 °C); UV/Vis ($CHCl_3$) λ_{max} (ε_{max}): 442 sh., 469 (107, 150), 501 (95, 520) nm (lit.[26] 443, 471, 502): ^{1}H NMR ($CDCl_3$) δ: 1.94 (6H, s, 19-CH_3 and 19'-CH_3), 1.97 (3H, s, 20'-CH_3), 1.99 (3H, s, 20-CH_3), 3.77 (3H, s, 6-OCH_3), 5.86 (1H, d, *J* = 15.6 Hz,7-H), 5.90 (1H, d, *J* = 15.3 Hz, 7'-H), 6.27-6.42 (4H, m, 14-H, 10'-H, 12'-H and 14'-H), 6.45-6.60 (2H, m, 10-H, 12-H), 6.63-6.71 (2H, m, 15-H, 15'-H), 6.85 (1H, dd, *J* = 15.6, 11.2 Hz, 11'-H), 7.44 (1H, d, *J* = 15.6 Hz, 8-H), 7.94 (1H, d, *J* = 15.3 Hz, 8'-H); and ESI-MS (-): *m/z* 393.6 (100) [M-H].

Confirmation of the structure of the major colorant was provided by UV/Vis and NMR spectroscopic analyses and mass spectrometry. The major colorant shows UV/Vis absorption bands at λ_{max} 442 sh., 469 and 501 nm in chloroform consistent with *cis*-bixin[26]. The ^{1}H NMR spectrum in $CDCl_3$ also reveals the characteristic vinylic doublet signal for 8'-H at 7.94 ppm for *cis*-bixin[27], while the ESI-MS (negative ion) spectrum supports the molecular formula of bixin with a major peak at *m/z* 393.6 corresponding to the quasi-molecular ion $[M\text{-}H^+]^-$.

3.2 Effect of Initial Dye Concentration, Temperature, and Contact Time on Adsorption of Dye onto Cotton Yarn

Color strength (*K/S*) values for dyed cotton yarn using different initial dye concentrations are shown in Fig. 1 (a). It is found that the adsorption capacity is concentration dependent and it increases with the increase in initial dye concentration. An increase in the initial dye concentration leads to an increase in the amount of dye adsorbed on cotton yarn, consistent with an increase in the driving force of the dye concentration gradient[28]. However, after one wash, the color strength (*K/S*) of the dyed/washed samples is decreased significantly with only a small dependence

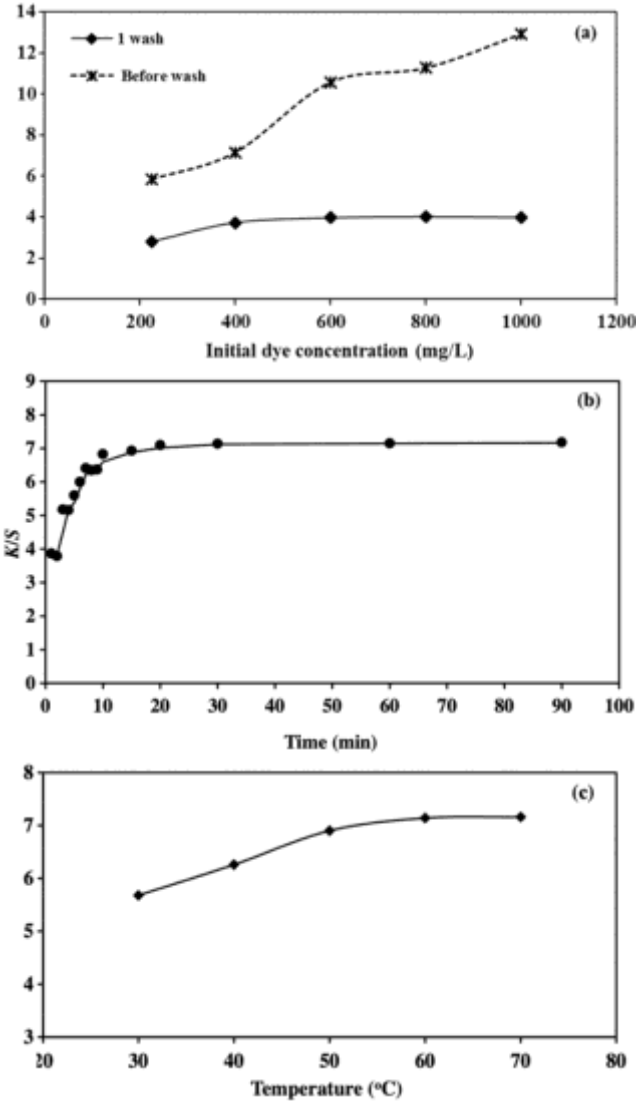

Fig. 1 — Color strength values against (a) initial dye concentrations before and after washing of cotton dyed at *p*H 11.55; (b) contact time for the cotton dyed with an initial dye concentration of 400 mg/L at 60 °C and *p*H 11.55; and (c) temperature for the cotton dyed with an initial dye concentration of 400 mg/L, contact time 60 min and *p*H 11.55

on initial dye concentrations for the dyed yarn. It is thus not necessary to use a high initial dye concentration for the dyeing process because of the ready dye transfer out of the cotton yarn, and a dye concentration of 400 mg/L is thus used in the further studies.

The variation in color strength values with contact time [Fig. 1 (b)] for the cotton dyed with the dye concentration of 400 mg/L at 60 ^{o}C indicates that nearly 30 min is required for the adsorption equilibrium to be reached after a rapid increase in dye adsorption over the first 20 min of contact time. The higher uptake rate of dye during the initial stage of adsorption might be due to the availability of a larger number of vacant surface sites. But then access to the remaining vacant surface sites would be more difficult due to the repulsive forces between the hydrophobic sites of the dye adsorbed on the cotton fibres and the aqueous solution phase. The optimum contact time for the dyeing of cotton yarn with the dye extract from *Bixa orellana* L. seeds has been fixed at 60 min throughout this work.

The effect of temperature on the color strength values of dyed cotton yarn has also been assessed over a temperature range of 30-70 ^{o}C. As shown in Fig. 1 (c), it is clear that the color strength increases with increased dyeing temperature up to 60 ^{o}C, and remains consistent with greater dye uptake with temperature, as a result of greater fibre swelling and hence, the enhanced dye diffusion. Beyond 60 ^{o}C, the *K/S* value is plateaued.

3.3 ATR-FTIR Spectroscopy Analysis

The ATR-FTIR spectra for cotton yarn, chitosan, and crosslinked chitosan-dyed cotton yarn are shown in Fig. 2. The spectrum of chitosan [Fig. 2(b)] shows broad absorption bands at 3357 cm^{-1} and 3296 cm^{-1}, indicating O–H and N–H stretching vibrations, while the weak absorption bands at 2899 cm^{-1} and 2874 cm^{-1} can be assigned to C–H stretching in the chitosan backbone. The characteristic absorption band at 1649 cm^{-1} is consistent with an amide carbonyl group from residual acetamide functionality. The absorption band at 1584 cm^{-1} is assigned to an N–H deformation vibration in the amino groups. The presence of chitosan on the dyed cotton yarn [Fig. 2(c)] is revealed by this typical N-H peak at 1578 cm^{-1}, together with the peak at 1643 cm^{-1} for the amide carbonyl. The regions of these bands are broadened somewhat and probably overlapped the conjugated carboxylate and ester/acid carbonyl groups from the adsorbed dye. In bixin itself in the solid state (KBr disc), IR absorption bands at 1716 cm^{-1} and 1690 cm^{-1} are assigned to the ester and carboxylic acid groups respectively (supplementary material[26]).

The ATR-FTIR spectra for cotton yarn, quaternized chitosan, and quaternized chitosan -dyed cotton yarn are shown in Fig. 2. In the spectrum of quaternized chitosan-dyed cotton yarn [Fig. 2(e)], the peaks at 3298 cm^{-1} and 3357 cm^{-1} which overlapped those from the cellulose are assigned to O–H and N–H stretching vibrations respectively. The peak at 1636 cm^{-1} is rather weak and broad, but is not

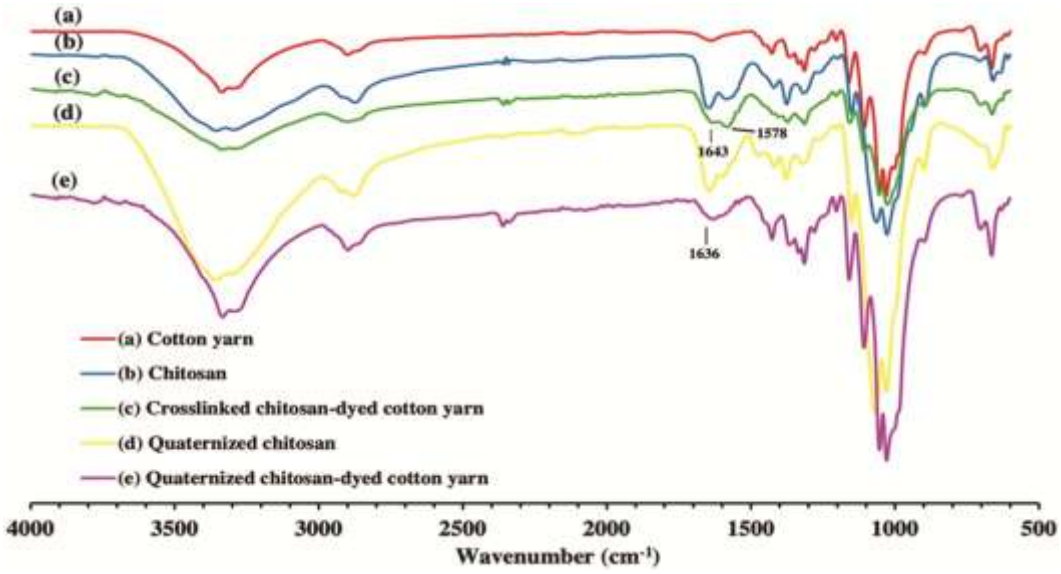

Fig. 2 — ATR-FTIR spectra of (a) cotton yarn, (b) chitosan, (c) crosslinked chitosan-dyed cotton yarn, (d) quaternized chitosan, and (e) quaternized chitosan-dyed cotton yarn

inconsistent with overlapping amide carbonyl and bixin ester/acid carbonyl groups, plus a C–H symmetric bending of the methyl groups on the quaternized chitosan. This absorption band is clear in the spectrum of quaternized chitosan [Fig. 2(d)].

3.4 Color Hue and Fastness Properties

Values of *K/S*, color obtained, and CIE *L*a*b** of the dyed cotton yarn samples are given in Table 1. All samples show an orange shade with different CIE *L*a*b** values, except the black-dyed cotton yarn pretreated with the aqueous *D. mollis* fruit extract, possibly due to the presence of hydroquinone components in the fruit[29]. Cotton yarn pretreated with the combination of chitosan and glyoxal, or microcrystalline chitosan[30] and glyoxal, or pretreated with 3.0% (v/v) aqueous solution of Sera® Fast C-NC, or pretreated with a 2.0% (w/v) aqueous solution of quaternized chitosan provides a better color depth than the untreated cotton yarn. Pre-treatment with the combined glyoxal and chitosan protocol gives the highest b^* value of any of the dyed cotton samples. This is possibly due to some reduction in hydrophilicity of the chitosan on acetal formation with glyoxal[31], thus increasing the interaction with the dye hydrophobic sites. In addition, post-treatment with alum after dyeing gives a higher color depth (orange) than the untreated cotton yarn (control), consistent with Al (III) coordination complexes being formed with the dye carboxylate sites. In other work, it has been reported that alum post-treated annatto dyed cotton gives a 'dark orange shade with a slight reddish tinge' and that this color darkens with increased alum concentration[12].

The fastness properties of dyed cotton with the dye extract solution from *Bixa orellana* L. seeds are summarized in Table 2. Pretreatment of cotton with different mordants, such as the combination of chitosan and glyoxal, the combination of MCCh and glyoxal, the aqueous solution of Sera® Fast C-NC or an aqueous solution of quaternized chitosan before dyeing shows a good wash fastness rating of 4, as compared to the untreated cotton yarn or post-mordanting with alum; similar improvements are also seen in cotton fabric pretreated with a cationic fixing agent on ink jet application of *B. orellana* dye[32] and in cotton fabrics (woven or knitted) pretreated with sodium hydroxide or untreated and then coated by chitosan before dyeing with commercial grade annatto

Table 1 — Color obtained and *K/S* and CIE *L*a*b** values of cotton dyed with dye extract solution from *Bixa orellana* L. seeds

Cotton yarn	Color	*K/S* (λ = 470 nm)	CIE value		
			*L**	*a**	*b**
Untreated (control)	Orange	5.44	61.00	37.98	43.30
Chitosan-glyoxal treated	Deep orange	10.38	57.42	39.01	54.63
Microcrystalline (MCCh)-glyoxal treated	Deep orange	8.29	58.17	35.38	48.77
Sera® Fast C-NC treated	Deep orange	10.10	56.20	35.72	49.20
Quaternized chitosan treated	Deep orange	8.86	56.85	38.65	48.76
Post-mordanting with alum	Orange	6.81	57.85	41.70	44.11
Diospyros mollis Griff extract treated	Black	7.81	45.78	17.87	26.43

*L**–Lightness (0–black, 100–white), *a**–Red-green coordinates (positive values–red, negative values–green), *b**-Yellow–blue coordinates (positive values–yellow, negative values–blue).

Table 2 — Color change and fastness properties of cotton dyed with the aqueous extract of *Bixa orellana* L. seeds

Cotton yarn	Color change	Wash fastness[a] (Staining)						Light fastness[b]
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	
Untreated (control)	2	4	2-3	4	4	4-5	4-5	1
Chitosan-glyoxal treated	4	4-5	3	4-5	4-5	4-5	4-5	3
Microcrystalline (MCCh)-glyoxal treated	4	4-5	3	4-5	4-5	4-5	4-5	3
Sera® Fast C-NC treated	4	4-5	3	4-5	4-5	4-5	4-5	2
Quaternized chitosan treated	4	4-5	3	4-5	4-5	4-5	4-5	2-3
Post-mordanting with alum	3-4	4-5	3	4-5	4-5	4-5	4-5	1-2
Diospyros mollis Griff extract treated	2	4	2-3	4	4	4-5	4-5	1

[a]Evaluated according to ISO 105-C 10: 2006 (E). Rating scale of wash fastness for color change is from 1 (poor) to 5 (excellent).
[b]Rating scale of light fastness is from 1 (poor) to 8 (excellent).

Table 3 — *K/S* and CIE *L*a*b** values and light fastness of cotton dyed with the dye extract solution (Bixa) from *Bixa orellana* L. seeds plus additives

Cotton yarn	*K/S* (λ = 470 nm)	CIE value			Light fastness[a]
		*L**	*a**	*b**	
Untreated cotton yarn (control)	5.44	61.00	37.98	43.30	1
Bixa/ascorbic acid	6.17	57.83	41.40	41.76	2
Bixa/salicylic acid	5.85	57.77	40.03	40.56	2
Bixa/QCS[b]/ascorbic acid	9.53	52.54	33.32	46.84	3
Bixa/MCCh[c]/ascorbic acid	6.94	55.75	32.08	44.89	3

*L**–Lightness (0–black, 100–white), *a**–Red-green coordinates (positive values–red, negative values–green), *b**–Yellow-blue coordinates (positive values–yellow, negative values–blue).
[a]Rating scale of light fastness is from 1 (poor) to 8 (excellent). [b]QCS–quaternized chitosan. [c]MCCh–microcrystalline chitosan.

dye[22]. However, all the dyed samples show very low light fastness because of the conjugated polyene structure in the bixin dye which increases susceptibility to photo-oxidation, except for the cotton yarn pretreated with the combination of microcrystalline chitosan or chitosan and glyoxal; both exhibiting the moderate (rating 3) light fastness. In an attempt to improve this light fastness, post-dyeing treatment with the anti-oxidants salicylic acid and ascorbic acid has been assessed (Table 3). Some improvement in light fastness is seen with both acids, as compared to untreated dyed cotton yarn. Ascorbic acid has a high ability to scavenge reactive oxygen species[18]. However, in an attempt to use ascorbic acid [~ 50% mixture of ascorbate and ascorbic acid (pK_{a1} = 4.17) at *p*H 4.22 in the dye bath] as a potential dual mordant – anti-oxidant by incorporation in the dye bath plus *Bixa* extract and cotton yarn pretreated with quaternized chitosan or microcrystalline chitosan, the resultant dyed cotton shows a good color depth but no improvement in light fastness properties over the equivalent dyed cotton without ascorbic acid in the dye bath. However, cotton pretreated with quaternized chitosan alone or microcrystalline chitosan alone exhibits good wash fastness ratings of 4 (Table 2). Possibly in these cases, the quaternary ammonium ion, or ammonium ion, centers form a stronger electrostatic interaction with the carboxylate oxidation sites on the cellulose, rather than to the delocalized ascorbate anion. Further work would be required to establish this. Low to fair sunlight fastness properties are also seen with alum pre- and post-treated cotton samples with annatto dyeing[12], although better light fastness is observed with simultaneous alum mordanting[6]. Other recent studies have also shown that good light fastness can be obtained with *B. orellana* (seed extract) dyeing of cotton fabric using tannic acid pre-mordanting[33].

4 Conclusion

The dye extract from *Bixa orellana* L. seeds, with the apocarotenoid *cis*-bixin as the major component, has potential for use as a dyestuff in cotton dyeing. Improved dyeing results are obtained on pre-treatment of the cotton yarn with a chitosan solution or a microcrystalline chitosan with a cross-linking glyoxal solution or an aqueous solution of quaternized chitosan. These components, whose presence on the yarn is confirmed by ATR-FTIR analysis, increase the dye binding sites, resulting in better dye adsorption on the cotton yarn in comparison to alum post-mordanting or non-pretreated cotton yarn. However, improvement in the light fastness of the dyed yarn is still required.

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