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ORIGINAL RESEARCH

Sustainable dyeing and functionalization of jute fabric with a Chinese sumac gall-derived gallotannin using eco-friendly mordanting agents

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Abstract Natural fiber-made apparel dyed with natural dyes is drawing consumer attention because of the possible toxic and health hazards associated with fabric dyed with synthetic dyes. However, many textile products dyed with natural dyes available in the market could pose a health risk because of the use of toxic heavy metals as a dye-complexing agent. In this work, jute fabrics were dyed and multi-functionalized with gallotannin (GT), using ferrous sulfate ($FeSO_4$), calcium chloride ($CaCl_2$), and aluminum chloride ($AlCl_3$) as a non-toxic mordanting agent. The shades produced and other physicochemical properties of the GT-dyed jute fabrics were compared with the jute fabric treated with GT using copper sulfate ($CuSO_4$), a common mordanting agent. It was found that the GT with various mordanting agents produced navy blue and brown shades with tonal changes along with quite good colorfastness to washing. The concentration of GT and mordanting agents, types of mordanting agents, and the treatment pH affected the shade produced and physicochemical properties of the treated fabrics. The surface resistivity was reduced from 235×10^{10} Ω/sq for the control to 6.7×10^{10} Ω/sq for the $AlCl_3$ mordanting agent, slightly higher than the surface resistivity exhibited by the $CuSO_4$ mordant. The fabric treated with GT using $FeSO_4$ and $CaCl_2$ mordanting agents showed excellent antioxidant activity, even at the lowest GT dosage applied. Similarly, $FeSO_4$ and $CaCl_2$ also showed excellent UV radiation absorption capability. The developed treatment can be used in the textile industry to make cellulosic textiles multifunctional without using any toxic dyes and chemicals.

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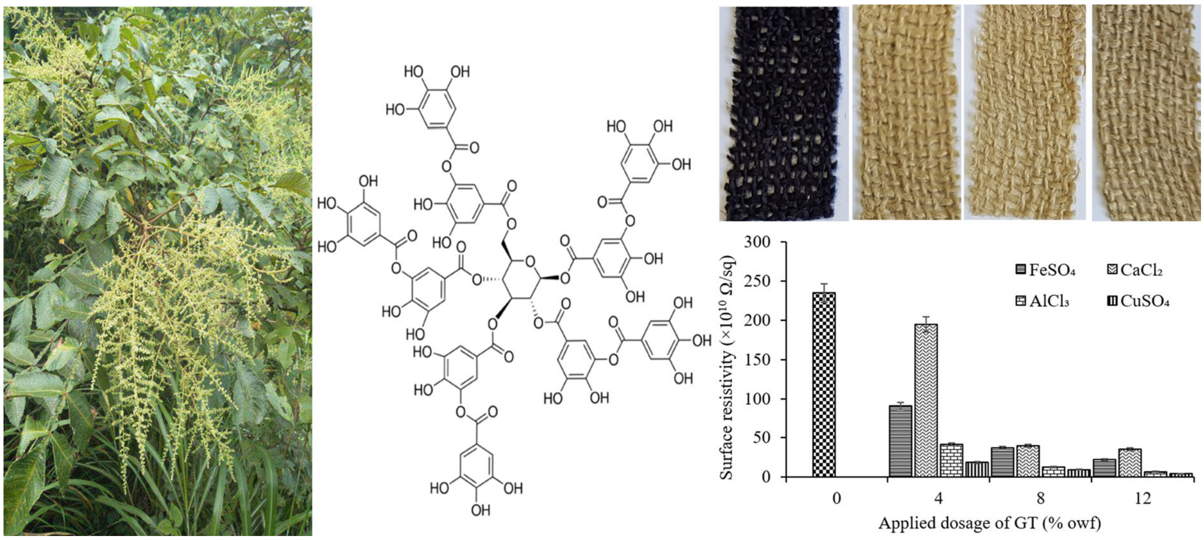
Graphic abstract



Keywords Jute cellulose fabric · Natural polyphenol · Dyeability · Colorfastness to washing · UV transmission

Introduction

Dyeing of textiles is necessary for the successful selling of textile products. However, the textile dyeing industries are considered as one of the key industrial polluters as large amounts of water is consumed in dyeing operations producing a large volume of effluent that needs treatment before discharging it to watercourses (Hassan and Shao 2016). Most of the textiles are dyed with synthetic dyes and the discharged effluents not only contain dyes but also salts, dispersing agents, and other textile auxiliaries. These dyebath additives negatively affect the photosynthesis reaction in water steams causing deficiency of oxygen, which is vital for the survival of aquatic animals, fish, and plants. Many synthetic dyes used in the textile industry are toxic and do not biodegrade in the environment (Lellis et al. 2019). Therefore, it is necessary to develop alternatives to toxic synthetic dyes used in the textile industry. In this context, natural dyes have drawn attention as they are mostly harmless and biodegrade in the environment. They can be extracted from abundantly available biomasses but the fabrics dyed with natural dyes exhibit poor colorfastness to light and washing. Mordanting or dye-complexing agents are used to enhance the colorfastness to washing of the textiles dyed with natural dye by reducing the solubility of the dye.

Jute is a natural cellulosic fiber under the category of bast fibers, where cells of jute fibers are bonded together by lignin. Jute fibers are mainly used in the manufacturing of sacking clothes and coarse cloths, carpets, and carpet backings. A small portion of jute is used in fine fabric manufacturing, in which case it is usually blended with cotton fiber to provide high moisture absorbency to the fabric as jute is one of the highest hygroscopic natural fibers. Jute fibers are naturally light cream in color but for their application in apparel, carpets, and decorative materials, they need to be dyed in various colors to make them attractive to the consumers. Generally, jute fibers are dyed with synthetic dyes, such as direct and reactive classes of dyes, but most of them are not environmentally friendly. Because of recent awareness of possible toxic and health hazard effects of synthetic dyes, the application of natural dyes in textile fiber dyeing is increasing. Natural dye effluent is generally treated as safe as they have relatively low toxicity and allergic effect compared to synthetic dyes (Kumar and Bharti 1998). Although natural dye-producing plants are abundantly available in the world, standardization of natural dye is a difficult task as color strength may vary from season to season and plant to plant. The color strength depends on the maturity of plants, soil quality, and other environmental factors; some of which are beyond human control.

The dyeing of jute with natural dyes recently has drawn attention as it is now possible to make fine fabrics from jute for apparel applications. Deo and Desai investigated the application of tea extract for the dyeing of cotton and jute fabrics without using any metallic salt (Deo and Desai 1999). The color strength of jute fabric dyed with the tea extract produced almost double the color strength produced by the cotton fabric with the same dye. Pan et al. investigated the extracts of deodara leaf (*Cedrus deodara L.*), jackfruit leaf (*Artocarpus integrifolia L.*), and eucalyptus leaf (*Eucalyptus globulus* L.) for the dyeing of jute using ferrous sulfate as a mordanting agent that produced deep shades with good washing fastness (Pan et al. 2003). It was also reported that pre-mordanting of jute fabric with ferrous sulfate showed increased dye uptake in the case of dyeing of jute fabrics with the extract of marigold flower (Pan et al. 2004). Chattopadhyay et al. investigated the extract of natural annatto dye for the dyeing of jute fabrics using myrobolan, pomegranate, ferrous sulfate, and potash alum as mordants (Chattopadhyay et al. 2014). Double mordanting using myrobolan and ferrous sulfate produced optimal color yield but the post-mordanting with chemical mordants produced higher color yield and fastness properties. Jute fabric pre–mordanted with hydrated ferrous sulfate dyed with natural dyes extracted from manjistha, annatto, ratanjot, and babool provided moderate to good colorfastness to light, and good colorfastness to washing and rubbing (Chattopadhyay et al. 2015).

Natural dyes are not only derived from plants but also insects but most of the natural dyes are sourced from roots, barks, leaves, and stems of plants. Before the advent of synthetic dyes, natural dyes, such as turmeric, madder, cochineal, henna, indigo, and saffron have been used in the dyeing of textiles since thousands of years ago. Natural dyes have been extensively investigated for the dyeing of cellulosic fibers and also to introduce new functionalities, such as antibacterial properties and UV radiation resistance (Ibrahim et al. 2010). One of the most abundant dye-producing components is tannin available in various plants, which produces mostly brown shades. However, they can be used for producing other shades by using an appropriate mordanting agent. Mordants produce a coordination complex that increases the molecular weight of the dye resulting in decreased water-solubility of the dye, thereby increasing the colorfastness to washing of dyed fabrics. Salts of various heavy metals, such as copper, chromium, and nickel, are a polar mordanting agent that forms a stable coordination complex with the chelating sites of natural dyes so that they become insoluble in water (Ibrahim et al. 2010; Chakraborty 2014). However, many mordanting agents that are used in the textile industry to improve the poor wash fastness of dyed fabrics, such as chromium, copper, and nickel, are not ecofriendly. Some of them, such as copper sulfate and stannous chloride are highly toxic and potassium dichromate, which liberates hexavalent chromium, is a recognized carcinogen, and a genotoxin (Flora 2000; Proctor et al. 2002). Tannic acid has been extensively investigated as mordant for the dyeing of cellulosic and protein fabrics with various natural dyes (Togo et al. 2010; Ali et al. 2010; Burkinshaw and Kumar 2009; Kim and Park 2007), and also to enhance fire retardancy (Nam et al. 2017). It is also necessary to develop a non-toxic mordant for the dyeing of jute with natural dyes. However, the composition of polyphenols varies from plant to plant affecting the physicochemical characteristics of the dyed fabrics. Gallotannin extracted from galls (*Galla chinensis*) of the Chinese sumac is used as traditional Chinese medicine for various diseases (Huang et al. 2012; Djakpo and Yao 2010). However, published literature shows that gallotannin from galls was hardly considered for the dying of jute fiber. The effects of this gallotannin treatment on the antistatic, UV radiation absorption, and antioxidant activity of jute fabrics have been rarely considered. The effect of treatment conditions, such as treatment pH, mordanting agent concentrations, and the effect of ecofriendly mordanting agents on the various properties of the dyed fabrics have been scarcely reported.

In this work, jute fabrics were treated with gallotannin (GT) using various environmentally friendly mordanting agents, such as calcium chloride, ferric sulfate, aluminum chloride, and compared the results with the fabric dyed with tannic acid using copper sulfate as a mordanting agent. Traditionally, dyeing with natural dyes is carried out in two steps but in this work dyeing and mordanting both were carried out in a single bath. The effect of the treatments on the color of shades, color strength, UV transmission through the fabric, antioxidant activity, and colorfastness to washing have been evaluated.

Experimental section

Materials

A plain-woven 320 g/m^2 hessian fabric having 6 ends/cm and 5 picks/cm was used in this work, which was supplied by Latif Bawani Jute Mills Ltd (Dhaka, Bangladesh). Chinese gallotannin (molecular weight = 1701.2) extracted from galls of Chinese sumac was supplied by Xi'an Quanao Biotech Co., Ltd. (China), and its chemical structure is shown in Fig. 1. Acetic acid, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid, phosphate buffer (pH 7.4), sodium acetate, hydrogen peroxide (H_2O_2, 50% w/w), $AlCl_3$, $FeSO_4$, $CuSO_4$, $CaCl_2$, sodium carbonate (Na_2CO_3), sodium silicate (Na_2SiO_3) and Antimussol SI (defoaming agent) were purchased from Sigma-Aldrich Limited (USA). Sandozin MRN (a non-ionic wetting agent) and Sandoclean PC (a detergent) were purchased from Clariant Chemicals (Singapore) Ltd.

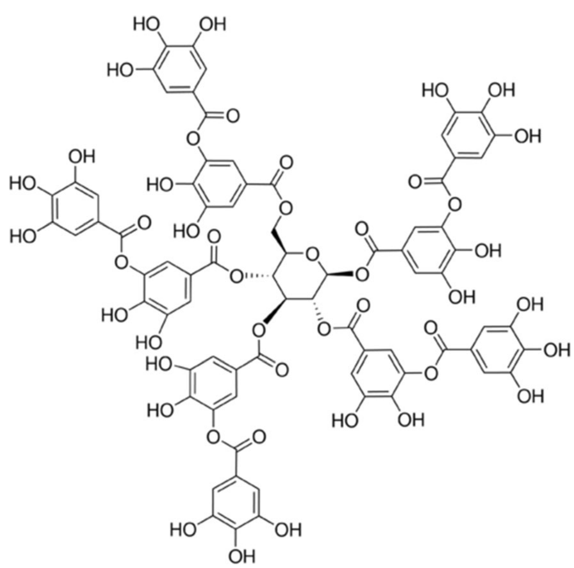


Fig. 1 Chemical structure of Chinese gallotannin

Pre-treatment of jute fabric

The jute fabric was scoured by treating it in a cocktail of 4 g/L sodium hydroxide, 2 g/L Sandoclean PC, 1 g/L ethylenediaminetetraacetic acid, and 0.2 g/L Sandozin MRN at 80 °C for 30 min. After the scouring, the fabric was washed several times in hot water and cold water. It was then bleached at 60 °C for 60 min using 8 g/L H_2O_2, 2 g/L Na_2CO_3, 1 g/L Sandoclean PC, 3 g/L Na_2SiO_3, and 0.25 g/L Sandozin MRN. The fabric was then washed at 60 °C for 15 min for once and then washed again several times with cold water. After washing, the fabric was hydro-extracted and dried.

Evaluation of whiteness and yellowness indices

The CIE *L*, a*, b** values of the grey and bleached jute fabrics were measured by a hand-held X-Rite spectrophotometer (X-Rite International, USA). The assessment of whiteness was then deduced by the following equation (Gooch 2011):

$$\text{Whiteness index} = 100 - \left[(100 - L^*)^2 + (a^*)^2 + (b^*)^2\right]^{0.5} \quad (1)$$

The yellowness index was also measured by the same instrument according to the ASTM test Method D1925: *Standard Test Method for Yellowness Index of Plastics*.

Dyeing of jute fabric with GT

The combined dyeing and mordanting method were used for the dyeing of jute fabric with GT using $CaCl_2$, $AlCl_3$, $FeSO_4$, and $CuSO_4$ as a mordanting agent. All dyeings were carried out in a Mathis laboratory dyeing machine (Model: Labomat BFA-24, Werner Mathis A.G., Switzerland) using tap water and materials to liquor ratio of 1:30. The dyeing pot was filled with sufficient water, pre-dissolved tannic acid, 5 g/L sodium sulfate (as a leveling agent), and 0.5 g/L Antimussol SI. The pH of the bath was set at 5.0 with sodium acetate and acetic acid. The temperature was then raised to 95 °C at 2 °C/min and held for 60 min. A pre-determined quantity of mordanting agent dissolved in 20 ml water was added to the bath and held for another 30 min. The dye bath was then cooled to 45 °C and the liquor was drained, and the dyed fabric was rinsed with cold water. The fabric samples were then hot washed with 1 ml/L Sandoclean PC at 60 °C for 15 min and again cold washed several times. The samples were then dried at 60 °C for 30 min.

Evaluation of fabric properties

Color measurement

The color strength (at the appropriate wavelength of maximum absorption for each dyeing) of the dyed samples was measured using a Datacolor Spectraflash 600 reflectance spectrophotometer, interfaced with a personal computer (Hassan and Hawkyard 2002). Samples were measured under illuminant D65, using a 10° standard observer with UV components excluded and specular included. For each sample, the measurements were made at 4 positions of the fabric and the average value is reported.

UV Absorption and colorfastness to washing

A Varian UV–VIS Spectrophotometer (Model: CARY 3E, Varian Inc., Palo Alto, USA) with Cary 1/3E Diffuse Reflectance Measurement attachment was used to assess the percent transmission at wavelength intervals up to 2 nm in the 220–400 nm spectral span. The colorfastness to the washing of the treated fabrics was measured according to the ISO Test Method 105-C03 2013: *Textiles – Tests for colorfastness – Part C03: Colorfastness to washing: Test 3* by washing in a Gyrowash (Model 415/8) using the phosphate-free standard detergent. In both cases, fastness grades were assessed by using the Datacolor Spectraflash 600 spectrophotometer (Datacolor International, Switzerland).

Surface resistivity

The antistatic properties of untreated jute fabric and also jute fabric treated with GT using various mordanting agents were assessed by measuring their surface resistivity. The untreated and various treated jute fabrics were preconditioned at the standard atmospheric conditions (20 ± 2 °C and 50 ± 2% relative humidity) for 48 h and the surface resistance measurement was then carried out at those conditions by a surface/volume resistance meter with a concentric ring probe (Model 152-1, Trek, Inc., Lockport, USA) at an applied voltage of 100 V. Samples were placed on an insulative plate over an earthed stainless steel conductive plate and the concentric ring probe was placed on the fabric samples. The surface resistivities (Ω/sq) were obtained by multiplying the measured surface resistance by a factor of 10 (geometry coefficient). At least 10 measurements were taken for each treatment at various positions of the face and back surfaces of the fabrics and the averages are reported here.

Surface morphologies

The surface morphologies of the jute fabrics dyed with GT using various mordanting agents were investigated by using the field emission scanning electron microscopy (SEM) technique. The treated fabric surfaces were scanned using a JOEL FESEM (Model: JSM-7000f, JEOL Ltd., Tokyo, Japan) at an accelerated voltage of 15 kV without any conductive coating. The elemental analysis of Ca, Cu, Fe, and Al in the dyed fabrics was carried out by an energy dispersive X-ray (EDX) attached to the SEM.

Antioxidant activity

The antioxidant activity of jute fabrics was measured by measuring the scavenging activity against 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) radicals according to the method mentioned in a published literature (Zhou and Tang 2017). The ABTS radical was prepared by reacting ABTS with potassium persulfate (PPS). ABTS and PPS solution were separately prepared and then mixed at the ratio of 2.86:1 and stored in dark for 16 h. Then it was diluted with phosphate buffer solution until the absorbance became 0.7. Then 10 mg/mL of various treated jute fibers were mixed with 10 ml ABTS solution and the absorbance was spectrometrically measured at 734 nm. The scavenging activity was measured according to the following formula:

$$\textit{Antioxidant activity}(\%) = \frac{(\textit{Absorbance of control} - \textit{Absorbance of sample})}{\textit{Absorbance of control}} \times 100$$

Fourier transform infrared spectroscopy (FTIR)

The surface of jute fabrics treated with GT in a combination with various mordanting agents was characterized by using a Shimadzu FTIR (Model Prestige 21, Shimadzu Corporation, Japan) with an attenuated total reflectance (ATR) attachment at a resolution of 4 cm^{-1} in the range from 650 to 4000 cm^{-1}. The diamond crystal was used to record the ATR-FTIR spectra and 64 scans were signal-averaged.

Results and discussion

Whiteness and yellowness of jute fabric

Table 1 shows the CIE L*a*b* values of the jute fabric before and after the scouring and bleaching operation. The lightness of the jute fabric increased and the yellowness and redness decreased by the scouring and bleaching treatments. The whiteness and yellowness indices of grey and scoured/bleached jute fabric are presented in Table 1. The higher the whiteness index the better the whiteness but the lower the yellowness index the better. The untreated jute fabric had a quite low whiteness index (54.06) and a high yellowness index (56.46 in the D1925 method). The bleaching treatment increased the whiteness index of the fabric to 76.34 and the yellowness index was reduced to 29.04.

Effect of dyeing parameters on color strength and colorfastness washing

The color strength and color produced in the jute fabric treated with GT using various metal-based mordants varied depending on the mordanting agents used, pH of the dyebath, GT concentration as well as mordanting agent concentration. Except for $FeSO_4$, which produced a deep navy blue shade, all other mordanting agents produced various shades of brown color with some tonal changes.

Effect of pH

The effect of treatment pH on the shade of the jute fabric treated with GT using various metal-based mordanting agents is shown in Fig. 2. For all the mordanting agents used, the fabrics treated at pH 9 produced the deepest shade except for the $FeSO_4$ mordant, which produced the deepest shade at pH 3. The jute fabric samples treated with $FeSO_4$ mordant produced a dark navy blue color and the depth of the shade decreased with an increase in the pH of the dyebath. On the other hand, the fabric treated with GT using $CaCl_2$ and $AlCl_3$ produced a greenish grey shade at pH 3 but with an increase in the pH the color of the fabric turned to brown. The jute fabrics treated with GT using $CuSO_4$ produced only brown shade at pH 3 and the depth of shade increased with an increase in the pH. At pH 9, the shade produced by $CuSO_4$ was similar to the color of unbleached jute fiber.

Figure 2 shows the color strength (K/S) of jute fabrics treated with GT using $FeSO_4$, $CaCl_2$, $AlCl_3$, and $CuSO_4$ over various wavelengths. All the mordanting agents produced the highest color strength at the wavelength of 400 nm except for $FeSO_4$, which produced the highest color strength at the wavelength of 580 nm. In the case of $FeSO_4$, the color strength gradually increased to 540 nm and then very slowly increased to the highest at 580 nm and from 580 again gradually decreased. In the case of all other mordanting agents, the color strength rapidly decreased from 400 to 460 nm and then slowly decreased up to 700 nm for all pHs. The color strength produced by the jute fabric sample using $FeSO_4$ mordant dyed at pH 3 was the highest, which was 18.5 and the color produced was quite bright. The color changed to dull bluish-black with an increase in the

Table 1 Whiteness and yellowness indices of untreated and bleached jute fabric

Treatment ID	CIE			Whiteness index	Yellowness index (D1925)	Yellowness index (E313)
	*L**	*a**	*b**			
Grey fabric	59.53 ± 0.19	6.34 ± 0.21	20.80 ± 0.39	54.06 ± 0.02	56.46 ± 0.02	41.45 ± 0.04
Bleached fabric	85.28 ± 0.23	0.71 ± 0.18	18.51 ± 0.13	76.34 ± 0.04	35.42 ± 0.02	29.04 ± 0.03

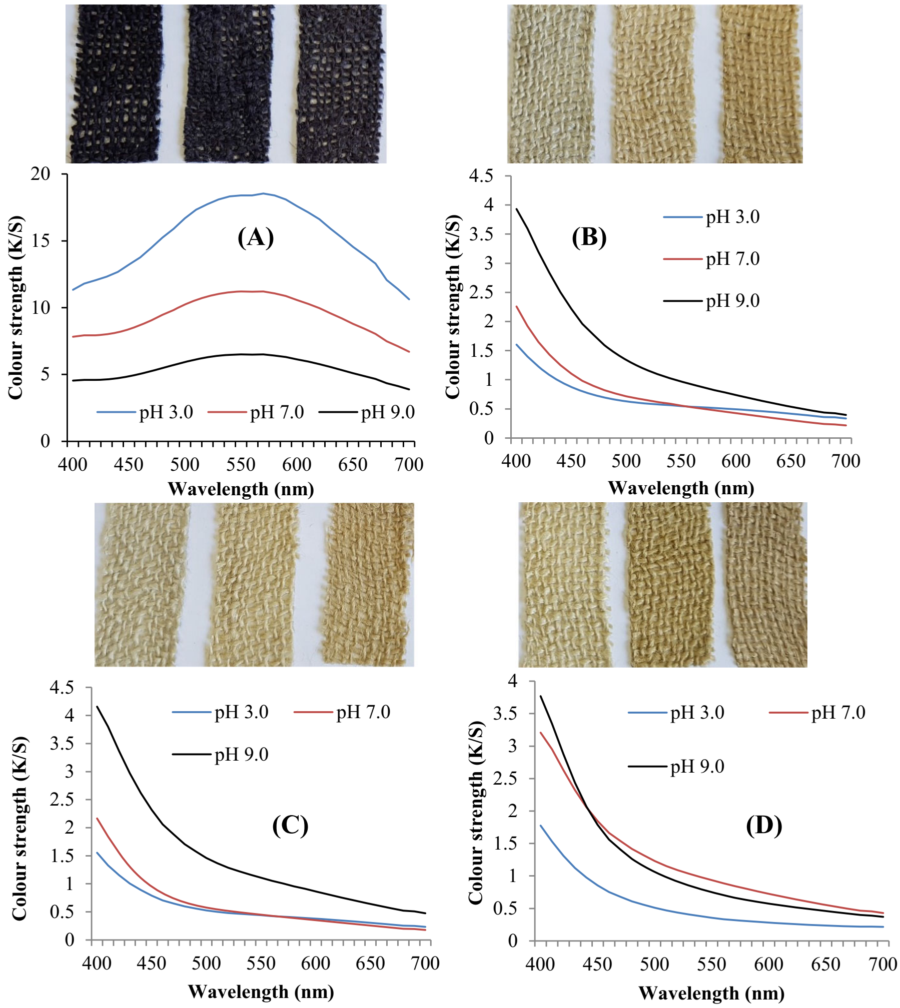


Fig. 2 Effect of pH on the color strength and the shades produced of GT-treated jute fabrics using $FeSO_4$ (A), $CaCl_2$ (B), $AlCl_3$ (C), and $CuSO_4$ (D) as a mordanting agent

pH. Conversely, $CaCl_2$ produced dull and greenish-brown at pH 3, which turned to yellowish–brown with an increase in pH to 8.0. Similarly, $AlCl_3$ and $CuSO_4$ also produced dull brown color at pH 3, which turned to dark brown with an increase in pH to 8.0.

The second highest color strength was produced by $CuSO_4$ at pH 8.0 but it was less than one-third of the color strength of the fabric treated with $FeSO_4$ mordant at pH 3.0. Fig. S1 (Supplementary Material) shows the optical images of left-over effluent after the dyeing with GT using various mordanting agents. It can be seen that the best adsorption of GT was achieved for the $FeSO_4$ mordanting agent at pH 3 as the effluent was almost colorless but for other mordants, the leftover effluents were moderately colored at the highest applied dosage of GT.

Table S1 (Supplementary Materials) shows the effect of pH on the lightness values (L^*) of jute fabrics treated with GT using various mordanting agents. For all mordanting agents, the value of L^* decreased with an increase in the pH, i.e. the color became lighter with an increase in the treatment pH. For the $FeSO_4$ mordanting agent, the reddish tone of the color decreased and the bluish tone increased with an increase in pH. Conversely, for all mordanting agents except $FeSO_4$ and $CuSO_4$, the redness increased and the yellowish tone increased with an increase in pH as the values a^* and b^* increased. Table S1 also shows the effect of pH on the colorfastness of the wool fabrics treated with GT. The pH had a little effect on the fabric's colorfastness to washing as all fabrics treated at different pHs showed quite a good colorfastness to washing as the change of color grades were 4 and above.

In the case of $FeSO_4$, the increase in the pH slowly decreased the color strength of dyed fabrics up to pH 8 but for $AlCl_3$, $CuSO_4$, and $CaCl_2$, the color strength slowly increased with an increase in the pH. Jute fiber and GT both are weakly anionic and therefore the adsorption of GT into jute fiber is not electrostatically controlled. The zeta potential measurement of jute fiber surface showed that the isoelectric point of jute fiber surface is between 5 and 8, i.e. at these pHs, the surface charge of jute fiber is neutral and below 5 or over 8 jute fiber surface becomes negative (Bismark et al. 2000). Therefore, better adsorption of GT should occur at these pHs than pHs lower than 5 or higher than 8 but for all mordanting agents except $FeSO_4$, the highest color strength was produced at pH 9. Therefore, the color strength increased with an increase in pH (especially at alkaline conditions) is not related to the increased adsorption of GT but due to the oxidation of GT at alkaline conditions, which produced deeper color with an increase in pH. The GT chelating ability of mordanting agents should be the highest at pH 3 but except for $FeSO_4$, other mordanting agents showed quite poor GT chelating ability as the produced color strength was the poorest at that pH as most of the absorbed GT was removed during washing after the dyeing process. On the other hand, $FeSO_4$ exhibited excellent GT chelating ability at pH 3 and therefore the jute fabric treated at pH 3 produced the highest color strength. As the chelating ability of $FeSO_4$ decreased with an increase in pH, the color strength decreased with an increase in pH, i.e. the color became lighter.

Effect of GT concentration

The effect of GT dosage on the color strength of the jute fabric treated with GT using various metal-based mordanting agents over various wavelengths is shown in Fig. 3. The color strength of jute fabrics over various wavelengths increased with an increase in the concentration of GT. For all mordanting agents, the highest color strength was shown by the fabric sample treated with 12.0% owf GT and the lowest by the fabric treated with 4.0% GT. The jute fabrics treated with GT using $CaCl_2$, $AlCl_3$, and $CuSO_4$ produced the highest color strength at the wavelength of 400 nm except for $FeSO_4$, which produced the highest color strength at the wavelength of 580 nm. In the case of Fe mordant, the color strength gradually increased to 540 nm and then very slowly increased to the highest at 570 nm, and from 580 nm gradually decreased. In the case of $FeSO_4$, the color strength of the fabric increased from 11.16 to 25.46 when the applied dosage of GT was increased from 4% owf to 12% owf respectively, which produced very deep shade fabric. Similarly, the samples became darker with the increased concentration of GT as the lightness value decreased from 27.10 for the 4% GT to 17.22 for the 12% applied dosage of GT. The fabric treated with GT using other mordanting agents also showed a trend similar to the trend observed for the $FeSO_4$ but the color strength produced by all other mordanting agents was very low compared to the color strength shown by the fabric treated with GT using $FeSO_4$ mordanting agent. For all the mordanting agents, the lightness of the fabric (L^*) decreased with an increase in the concentration of GT (Table S2 in Supplementary Material). In the case of $FeSO_4$, the redness and the blueness of the fabric decreased with an increase in the GT concentration for other mordanting agents the redness and yellowness increased with an increase in the GT concentration.

The fabric treated with 4% owf GT showed excellent colorfastness to washing as the change in color grade was 4–5 (Table S2), but the increase in the concentration of GT slightly reduced the colorfastness to washing. The increase in the concentration of GT increased its saturation inside fibers and therefore some GT molecules were near to the surface of the fibers and possibly they were removed during the washing test, resulting in a slight decrease in colorfastness.

Effect of mordanting agent concentration

The effect of mordanting agent concentration on the color strength of the jute fabric treated with GT using various metal-based mordanting agents over various wavelengths is shown in Fig. 4. For all the mordanting agents the fabric treated with GT using 50% mordanting agents on the weight of GT produced deeper color compared to the fabric treated with 25% mordanting agents on the weight of GT. The effect on color strength was not very high as the increase in color strength was approximately 2 only. The fabric became darker with an increase in the mordanting agent

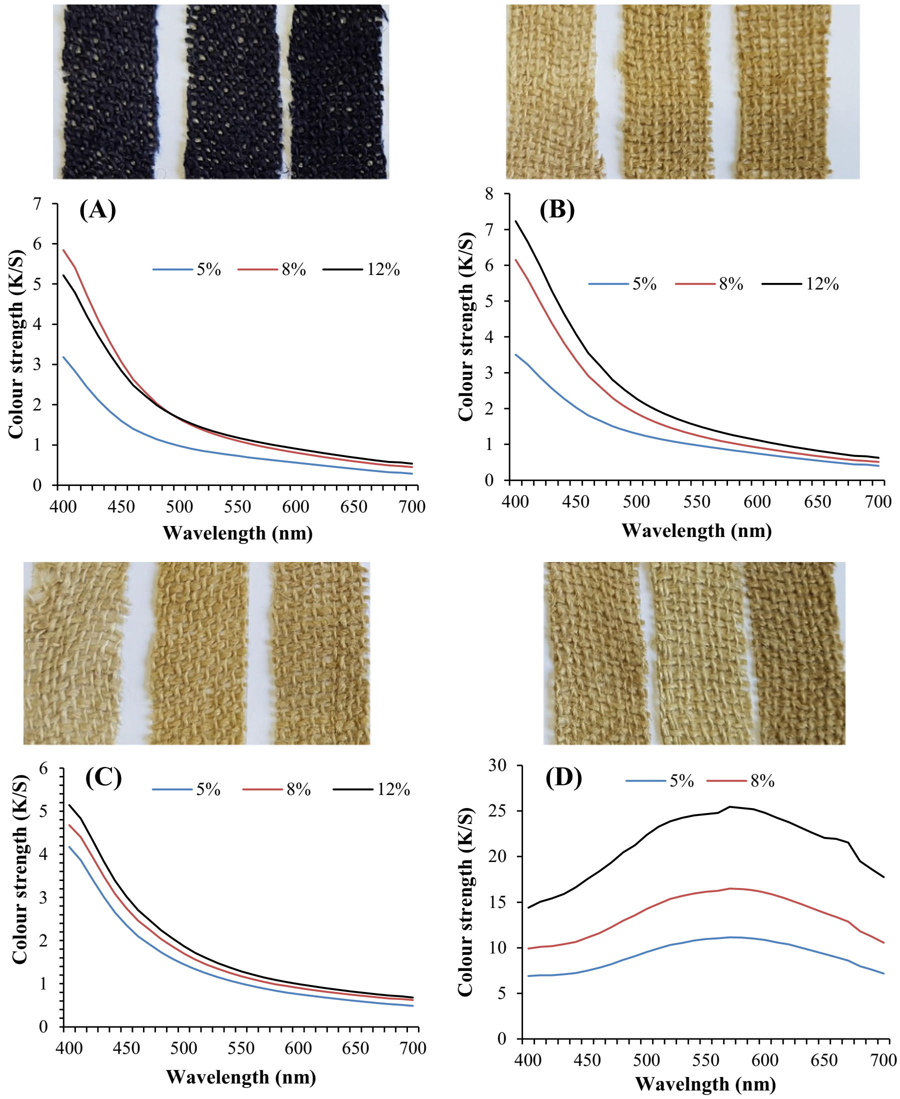


Fig. 3 Effect of GT concentration on the color and color strength of jute fabrics treated at pH 9 (in the case of $FeSO_4$ at pH 3) using $FeSO_4$ (A), $CaCl_2$ (B), $AlCl_3$ (C), and $CuSO_4$ (D) mordants

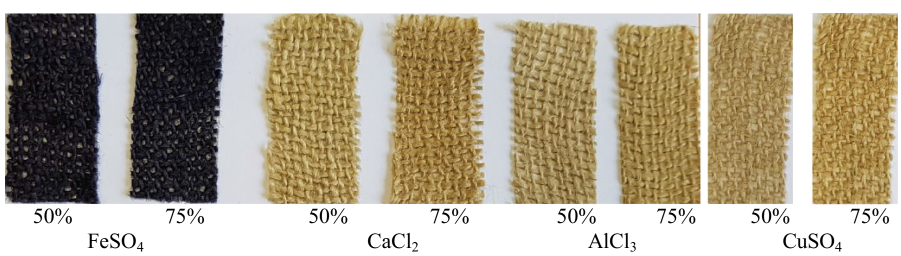


Fig. 4 Effect of mordanting agent concentration (% on the weight of GT) on the color and color strength of jute fabrics dyed with 4% GT at pH 9 (in the case of $FeSO_4$, at pH 3) using $FeSO_4$, $CaCl_2$, $AlCl_3$ and $CuSO_4$ mordanting agents

concentration but for $FeSO_4$ the redness and blueness increased and for other mordanting agents redness and yellowness increased with the increase in mordanting agent concentration (Table S3 in Supplementary Material). A great effect was observed on the lightness value in the case of $FeSO_4$ but for other mordanting agents the effect observed was less as $FeSO_4$ produced considerably higher color strength compared to the color strength produced by other mordanting agents.

The surface resistivity of untreated and various treated fabrics measured at the applied voltage of 100 V is presented in Fig. 5. The lower the surface resistivity the better the antistatic properties. The untreated fabric exhibited very poor antistatic properties although the jute fibers have many hydrophilic hydroxyl groups. The surface resistivity of the control fabric was very high, 235×10^{10} Ω/sq, but still was better compared to fabrics made with synthetic fibers, such as polyester. All the treated fabrics showed considerably lower surface resistivity compared to the surface resistivity exhibited by the control fabric suggesting that the surface resistivity is related to the hydrophilicity of the fabric, not to the mordanting agents used. The surface resistivity decreased with an increase in the concentration of GT. The mordanting agents applied affected the surface resistivity of the fabric. Of the mordanting agents used, $CuSO_4$ showed the best effect in decreasing the surface resistivity. At 4% owf GT concentration, the surface resistivity of the fabric treated with $FeSO_4$, $CaCl_2$, $AlCl_3$, $CuSO_4$ were 90.4×10^{10}, 195×10^{10}, 41.7×10^{10}, and 18.3×10^{10} Ω/sq, respectively, which decreased to 22×10^{10}, 35.8×10^{10}, 6.7×10^{10}, 4.7×10^{10} Ω/sq respectively, when the concentration of GT was increased to 12% owf.

Jute fibers have some level of antistatic properties because of a large number of hydrophilic hydroxyl groups in cellulose and lignin of jute fibers but for certain applications, such as at low humidity or application in electronic industries, jute fibers need to have better antistatic properties. The untreated jute fabrics exhibited surface resistivity 2.35×10^{12} Ω/sq, which falls under the class of insulative materials. Generally, antistatic fabrics have surface resistivity between 1×10^9 and 1×10^{12} Ω/sq, the lower the surface resistivity the better the antistatic property of the material. In this work, the jute fabric treated with GT using $CuSO_4$ as a mordanting agent exhibited surface resistivity 4.7×10^{10} Ω/sq, which shows its strong antistatic properties. GT has many hydrophilic carboxyl and hydroxyl groups and therefore the treatment of jute fabrics with GT enhanced the antistatic properties due to the increased hydrophilicity.

Antioxidant activity

The antioxidant activity of jute fabrics treated with 3% owf GT using various mordanting agents is shown in Fig. 6. The control jute fabric showed some level of antioxidant activity but was much lower compared to the antioxidant activity exhibited by the jute fabrics treated with GT using various mordanting agents. It is reported that lignin extracted from various plants and jute fibers shows moderate levels of antioxidant activity (Jiang et al. 2018; Del Río et al. 2009). Therefore, it is not unexpected that in this work the control untreated fabric showed some level of

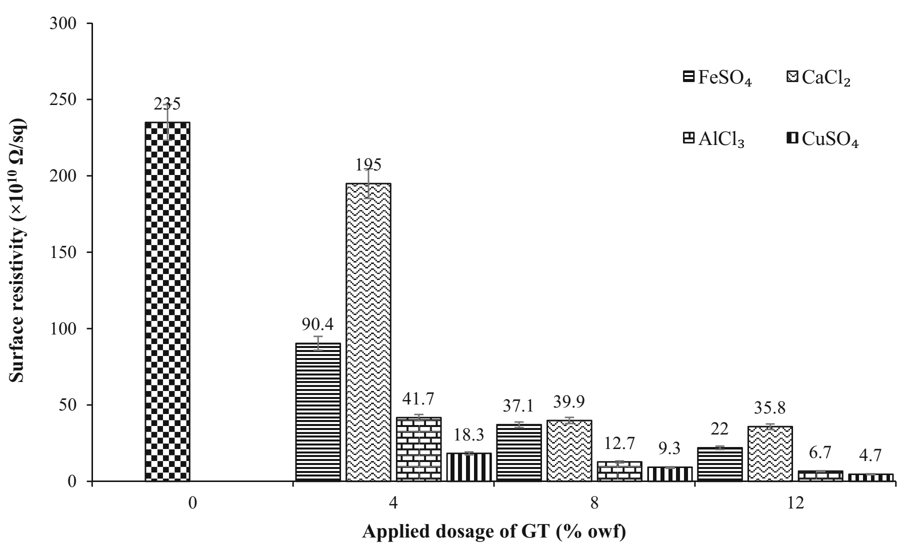


Fig. 5 Effect of GT dosage on the antistatic properties of wool fabric treated with GT using various mordanting agents

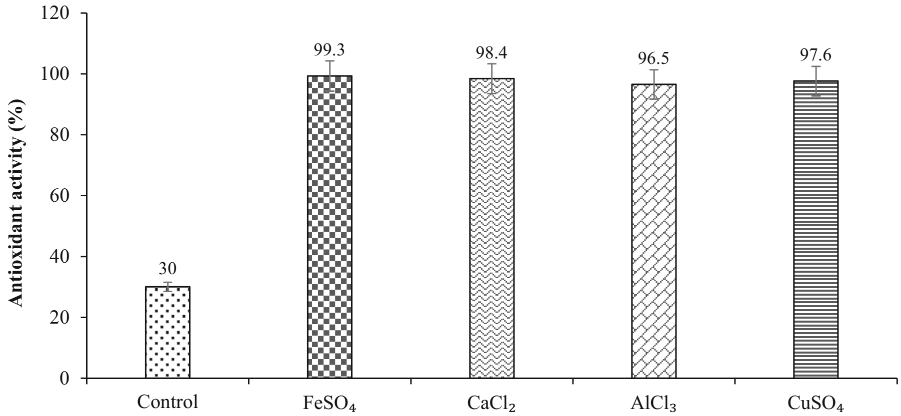


Fig. 6 Antioxidant activity of jute fabrics treated with 3% owf GT using various mordanting agents

antioxidant activity as jute fibers contain a small quantity of lignin even after scouring and bleaching. Jute fabrics treated with GT using various mordanting agents showed quite similar antioxidant activity. The jute fabric treated with GT at the lowest concentration also showed excellent antioxidant activity. The control fabric showed very weak antioxidant activity, only 30% as most of the lignin was removed by the pre-treatments. Conversely, the lowest antioxidant activity shown by the jute fabric treated with GT using $AlCl_3$ mordanting agent was also 96.5%. The highest antioxidant activity (99.3%) was provided by the $FeSO_4$ mordanting agent. The fabric treated with other mordanting agents also showed very similar antioxidant activity. Zhao et al. investigated the antioxidant properties of two GTs isolated from the leaves of *Pistacia weinmannifolia* and found that the antioxidant activity is dependent on the number of galloyl moieties in the GT (Zhao et al. 2005). It was reported that gallotannin of Chinese sumac galls is consists of mainly 3–14 galloylglucopyronse (Huang et al. 2012), which is responsible for the high antioxidant activity exhibited by GT-treated fabrics.

UV light transmission through the fabrics

Fig. S2 (Supplementary Material) shows the UV radiation absorption capability of untreated and GT-treated jute fabrics with various mordanting agents. The fabric's ability to block UV-A and UV-B is the determining factor in deciding the UV protection capability of the fabric. The UV radiation transmission below 2% is treated as a good UV protective fabric (Saravanan 2007; Hassan 2020). Jute fibers are known to have some levels of UV radiation absorption capability because of the presence of lignin in jute fiber as lignin is known to have UV radiation absorption capability (Zhang et al. 2019), but that level of absorption may not be enough to provide long term protection against solar irradiation. The results achieved represent it, as the control fabric showed pretty low UV radiation transmission through it. The UV light transmission through the untreated jute fabric at 290 and 340 nm was 2.40% and 3.55% respectively, slightly higher than ideal. In the case of $CaCl_2$ mordant, the UV transmission through the jute fabric reduced to 0.28% and 0.60% at 290 and 340 nm respectively, which made the fabric highly UV protective. Several other researchers also reported that cellulosic and protein fabrics treated with polyphenolic extracts of Mediterranean flora (Grifoni et al. 2014), *Xylocarpus granatum* bark extract (Pisitsak et al. 2016), and flavonoids (Zhou and Tang 2017) also provided excellent UV protection ability. Gallotannins are known to have excellent UV radiation absorption capability, especially at 276 nm wavelength (Romani et al. 2012). The second best UV protective performance was provided by fabric GT-treated with $FeSO_4$ mordanting agent. The other two mordanting agents also considerably reduced the level of UV radiation transmission through the fabric. Of the mordanting agents studied, $CaCl_2$ treated fabric offered the best UV protection performance. Phenolic groups of gallic acid components of gallotannin are responsible for high UV radiation absorption (Ghigo et al. 2018). It looks like trivalent Al^{3+} ions blocked more phenolic groups compared to other mordanting agents used in this work, resulting in lower UV radiation absorption in the case of GT-treated fabric mordanted with $AlCl_3$ compared to other divalent mordanting agents.

Elemental analysis of dyed jute fabrics

An EDX analysis was carried out on the surface of jute fabric treated with GT using various mordanting agents. The chemical composition of C, O, and metallic elements of jute fabric dyed with GT using various mordanting agents are presented in Fig. 7. The presence of C and O content arises not only from cellulose but also from lignin (also GT in the case of treated fabrics) present in the fabrics. The elemental Fe, Cu, Ca and Al arise from various mordanting agents used. The elemental composition of C and O in control untreated jute fabric was 50.33 and 49.67% respectively. In the case of GT-treated fabrics, the C and O contents either increased or decreased. The elemental compositions showed that the absorption of Ca, Cu, and Fe ions in the case of $CaCl_2$ and $FeSO_4$ mordants were greater than the Al content of the fabric treated using $AlCl_3$ mordanting agent. It is quite interesting to see that the adsorption of divalent ions (Cu, Fe, Ca) was higher compared to the trivalent Al ions. As the jute fibers are only weakly anionic, the valency of the metals did not play a great role in metal ions or GT adsorption. The elemental mapping of C, Cu, Fe, Ca, and Al was performed to see the local distribution of these elements on the surface of treated fabrics. The elemental mapping shows that the elements are evenly distributed on the surface of jute fabrics suggesting uniform treatment took place for all the mordanting agents (Fig. S3 in Supplementary Material).

ATR-FTIR

Fig. S4 (top) (Supplementary Material) shows the FTIR spectrum of GT, which shows typical GT associated IR bands at 760, 870, 1040, 1153, 1210, 1324, 1450, 1538, 1614, 1715 cm^{-1}, and also a broad band at 3340 cm^{-1} (Falcão et al. 2014)). The IR bands at 760 and 1208 cm^{-1} are associated with –C–C– and –C–O groups respectively. The band at 1715 cm^{-1} could be assigned to the carbonyl groups (–C = O) of GT. The broad band at 3340 cm^{-1} is associated with the hydroxyl groups.

Fig. S4 (bottom) (Supplementary Material) shows the ATR-FTIR spectra of control jute and also jute fibers treated with GT using different mordanting agents. The ATR-FTIR spectrum of control jute shows IR bands at 1029, 1248, 1424, 1595, 1733, 2900, and 3300 cm^{-1}. The broad band at 3300 cm^{-1} could be attributed to the hydroxyl groups of lignin, hemicellulose, and cellulose (Hassan and Saifullah 2019). The IR band at 2900 cm^{-1} is associated with the –C–H stretching vibrations of cellulose. The FTIR spectrum of jute fiber shows a very small IR band at 1733 cm^{-1}, which could be associated with the carbonyl groups of lignin, but its low intensity suggests that the lignin content of the control jute fiber was quite low, which shows the reason why the control jute fabric show poor antioxidant activity. The IR spectra of GT-treated jute fabrics do not show any new band but the intensity of various bands such as the hydroxyl band increased due to the presence of GT. Some of the GT peaks were overlapped with various IR bands of lignin. In the case of $FeSO_4$, the carbonyl band intensity increased but for other mordanting agents, the carbonyl band is absent. The noticeable effect of GT treatment of jute fabrics using various mordanting agents can be seen for the hydroxyl group band at 3300 cm^{-1}. The untreated control fabric showed the lowest intensity, i.e. the control fabric was the least hydrophilic and therefore showed a quite poor antistatic property. On the other hand, the intensity of the hydroxyl band at 3300 cm^{-1} was the highest for the fabric treated with GT using $CuSO_4$ as a mordanting agent, i.e. this fabric showed the highest hydrophilicity and antistatic property. Of the jute fabrics treated with GT using various mordanting agents, the fabric treated with GT using $CaCl_2$ showed the lowest hydroxyl band intensity. As the surface resistivity is related to the surface hydrophilicity and therefore the lowest antistatic property. The antistatic property observed for jute fabrics treated with various mordanting agents shown in Fig. 5 is consistent with the intensity of the hydroxyl band observed at 3300 cm^{-1}.

Surface morphology

The surface features of jute fabrics treated with GT using various mordanting agents were studied by SEM and the micrographs are shown in Fig. 8. SEM

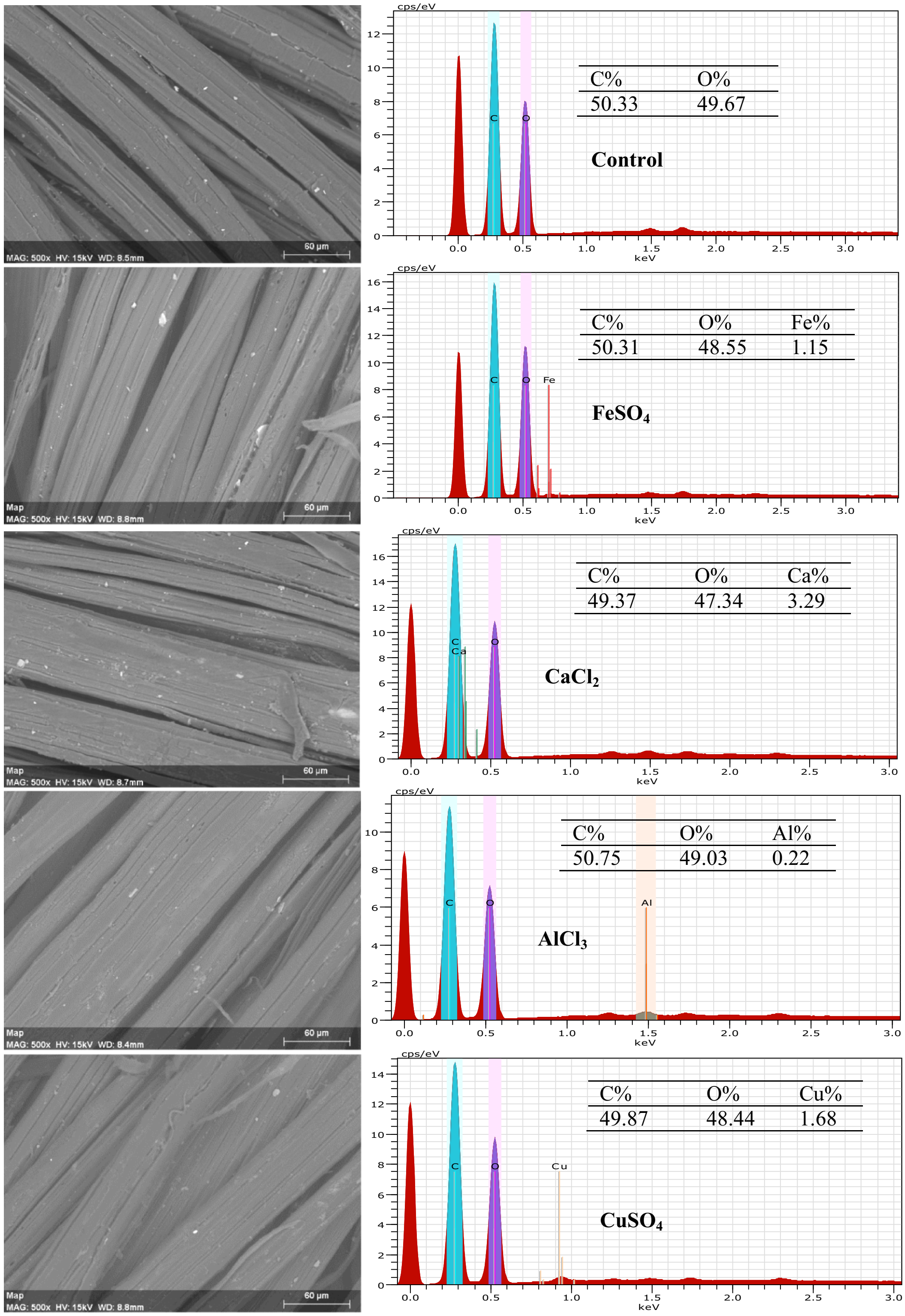
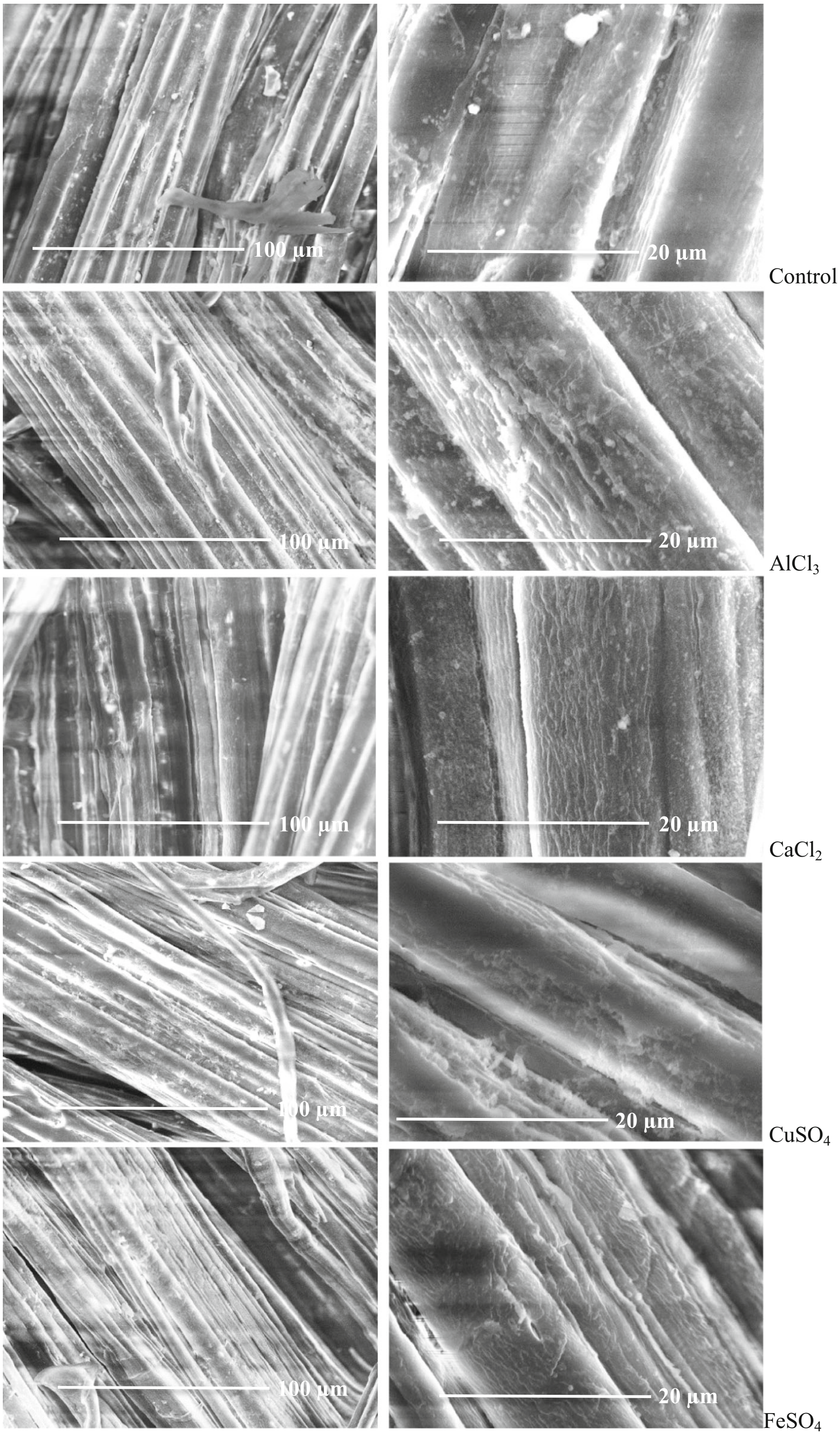


Fig. 7 EDX spectra of wool fabrics treated with GT using various mordanting agents

Fig. 8 SEM micrographs of the surface of wool fabrics treated with GT (12% owf) using $AlCl_3$, $CaCl_2$, $CuSO_4$, and $FeSO_4$ mordanting agents



micrographs reveal the fibrillar arrangement in different layers of the fiber. The pre-treatment made the fiber surface relatively clean but still, some defibrillation and debris of hard lignin are visible on the fiber surface. The surface of undyed fibers is relatively smooth but after treatment with GT the fiber surface became slightly rough due to further removal of impurities as the treatment with GT was carried out at highly alkaline conditions. The surface of GT-treated fabric using $CaCl_2$ is very clean and does not show any deposition of GT on the fiber surface and therefore showed the highest surface resistivity of the GT-treated fabrics. The fabric surface treated with GT using $FeSO_4$ as a mordanting agent also showed almost no surface deposition of GT. On the other hand, the fabric samples treated with GT using $CuSO_4$ and $AlCl_3$ show some deposition of GT/metal ion complexes on the fiber surface. The presence of GT on the fiber surface increased the hydrophilicity of the fiber surface resulting in a decrease in surface resistivity. No visibility of deposition of GT/mordanting agent complex on fiber surfaces (except for $AlCl_3$ and $CuSO_4$) suggests that GT was absorbed into the fiber providing high colorfastness to washing, especially for the fabric treated with GT using $FeSO_4$ as a mordanting agent.

Conclusion

This work demonstrated that GT can be used not only for the sustainable dyeing of jute fabrics but also to make the fabric multifunctional. The application of various mordants made jute fabric multicolored and also enhanced UV radiation adsorption, antioxidant activity, and antistatic properties of the treated jute fabrics. The treatment conditions, such as types and concentration of metallic salts, GT concentration, and treatment pH had effects on the shade produced, color strength, antistatic property, UV radiation absorption, and antioxidant activity of the treated fabrics. The application of $FeSO_4$ mordant produced a very deep navy blue color but other mordants produced brown color with tonal changes. For all metallic salt mordants, the greatest color strength was achieved when the GT absorption and mordanting treatment was carried out at pH 9, but for $FeSO_4$ the highest color strength was achieved at pH 3. The GT-treated fabrics using various mordants, especially $CaCl_2$, exhibited excellent UV protection capability but $FeSO_4$ provided the best antioxidant activity. Conversely, $CuSO_4$ mordant provided the lowest surface resistivity. GT can be used in the textile industry as a sustainable alternative to currently used harmful synthetic dyes, antistatic agents, and UV absorbents.

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Declarations

Conflicts of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

Human or animal rights The work described in this article did not involve human participants and or animals.

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