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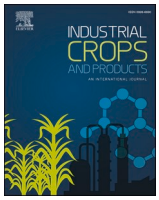

Sustainable dyeing of mulberry silk fabric using extracts of green tea (*Camellia sinensis)*: Extraction, mordanting, dyed silk fabric properties and silk-dye interaction mechanism

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ABSTRACT

Sustainability and environmental awareness had an impulse in increasing the global interest to utilize the industrial crops for producing new colouring shades in place of hazardous synthetic dyes. The present research focuses on extracting functional components from green tea (*Camelia sinensis*) leaves using water and methanol/water solvent systems and their application in the mordant dyeing of mulberry silk fabrics. The effect of pH was studied to maximize the yield of total polyphenols, flavonoids, and antioxidant properties of the solvent extracts. Compared to the unmordanted dyed silk, the mordant dyeing of silk with tea extracts at a temperature of 80 ℃ for 45 min resulted in significant improvements in various color properties. These enhancements include the shade, color strength (K/S), color coordinates, and fastness properties of the dyed silk fabric. Mordant dyeing of silk fabric enhanced UV protection and antimicrobial activities as well. The bonding properties of tea polyphenols on silk was well demonstrated with the help of X-ray photoelectron spectroscopy (XPS). To establish the mechanism of dyeing, catechin was used as a standard and mordant dyeing in silk, resulting in similar golden-yellow coloration. It shows identical properties with the silk dyed with tea extracts resulting in the fact that catechins are the responsible components in silk dyeing while using tea extracts. Theoretical interaction energy ($E_{interaction} = -13.836$ kJ/mol) calculation established good stability of mordanted catechin dyeing on silk, and catechin stability in different solvents were in the order catechin-water > catechin-methanol > catechin-ethanol. This work suggests that the mulberry silk fabrics dyed with green tea extract showed diverse color variations, which is highly promising to be used as a natural dye in the textile industry.

1. Introduction

In the competitive landscape of the manufacturing industry, the global market for the textile industry is flourishing and anticipated to be a 4.4% annual compound increment in the current decade (Panda et al., 2021). Toxic synthetic dyes dominate the textile industry due to their cheaper rate, which damages the environment on a massive scale (Thakker and Sun, 2021). The enhanced awareness towards using natural dyes replacing synthetic dyes in food, textile, medical and agricultural processes to produce materials has been a concern in the industry and academia from the sustainability and eco-safety standpoint in recent decades (Nambela et al., 2020; Shahid-ul-Islam and Sun, 2017). In addition to producing elegant colours, components present in dyes from natural sources like polyphenolics, anthraquinones, flavonoids, anthocyanins can provide several beneficial effects to the coloured fibre like UV protection, antioxidant, antimicrobial and flame retardancy, etc. (Gong et al., 2019).

North-East, especially Assam, is a rich home to tea cultivation and, considered as an Industrial crop, contributes to a major portion of India's total tea production. The tea industries in Assam produces a large amount of tea stem waste which could be valorised for economic benefits (Annual Report, 22, 2021, Tea Board India, Under the Ministry of

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Industries and Commerce, Government of India, https://www.teaboard.gov.in.). Compared to the huge production of tea wastes, the lack of proper disposal of these tea wastes can cause serious pollution and environmental issues. So, the sustainable and potential use of these tea wastes has become a matter of high concern in recent times. We anticipate that green tea extracts may be a choice for dyeing silk to realize the benefits of natural dyes. We understand that silk dyeing with tea extracts from North-East India has hitherto been reported in the literature.

Green tea, a non-fermented tea, is a rich source of catechins. In addition to catechins, other flavanols such as kaempferol, rutin, quercetin, and phenolic acids are in minor amounts. The overall chemical composition of tea is exhibited in Fig. S1 of the supporting information. In general, different organic solvent systems and water have been used for extraction of tea components and the chemical composition in extracts differs depending on the solvent and purification methods used (Bindes et al., 2019). Perva-Uzunalić et al. (2006) reported the effect of solvents like water, acetone, methanol, ethanol etc. on the extraction efficacy of catechins and caffeine from green tea leaves at different temperatures (60–100 °C) and times (5–240 min). Several studies were reported in literature with prime emphasis on the extraction, identification, and purification of polyphenols from tea using solvent extraction (Labbé et al., 2008) and adsorptive separation techniques (Dong et al., 2011). The catechins in green tea possess strong antioxidant properties and show radical scavenging activities towards free radical generators such as DPPH, ABTS and AIBN etc. Moreover, it shows strong antimicrobial activities against bacteria and fungi (Shahid-ul-Islam et al., 2018).

Silk is a fibre and is used as a precious material for the textile industry for its unique advantages, such as soft texture, good air permeability, and hygroscopic properties, along with an elegant lustre. Although silk is known for its promising properties, it has certain drawbacks such as low antioxidant, antimicrobial and UV protection activity, and deterioration which significantly obstruct its practical applications (Zhou and Tang, 2017). Hence, efforts are required to improve the functionalities in silk to overcome these deficiencies. Previously, Shahid-ul-Islam et al. (2018) has reported that green tea extract, known for its high content of polyphenols, is highly effective in enhancing the UV-protection ability, flame retardancy and antimicrobial activity of silk fabrics. The dyed silk exhibited favourable flame retardant, antimicrobial, and antioxidant activities, as highlighted by Cheng et al. (2019). Another study by Saini et al. (2020) proposed a method for functionalizing linen fabric through a layer-by-layer treatment involving chitosan and green tea extract which exhibited good antioxidant, antibacterial, and UV protection properties, contributing to its enhanced functionality. The supporting information includes Table S1, which provides a comprehensive list of previous literature reported on dyeing silk using tea a natural dye source. The stability of colour in dyed silk from natural sources can be enhanced by adding a mordant like alum, zinc chloride, ferrous chloride, ferrous sulphate, stannous chloride, etc. due to the formation of coordination complexes of these mordants and the silk fibre with the natural dye molecules. Textile materials with good colour stability will not show significant colour fading or colour change under various effects such as washing, rubbing and light which could be assessed by the adsorptive interaction between the dye molecules and the fibre (Gong et al., 2019). The color strength of the silk fabric can be significantly altered by dyeing it with the application of different mordants (Uddin et al., 2015). A dyeing mechanism was developed based on oxidative in-situ polymerisation of tea catechins on cellulose fibres which exhibited a good dyeing effect and washing colourfastness to the cotton fabric (Ren et al., 2019).

The main objective of the work is to elucidate the extraction of tea components from tea leaves, an industrial crop, to facilitate the dyeing process of mulberry silk fabric using mordants. Here, we focused on the extraction of tea polyphenols utilizing solvent combinations of water and methanol/water at varying pH levels and characterized to obtain total polyphenolic components, total flavonoids, and antioxidant properties. Subsequently, the dyed silk fabrics were assessed to determine color strength, color fastness, UV protection and antimicrobial properties. In order to gain a deeper understanding of the dyeing process, silk fabrics dyed with both standard catechin and tea extracts undergo characterization techniques such as Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM), respectively to determine the surface functionalities, and surface morphologies. Despite the fact that some researchers have explored the dyeing of silk or cotton using tea extracts, comprehensive mechanistic studies substantiated by both theoretical and experimental evidence have not been documented thus far. The dyeing mechanism was examined by considering catechin as a standard, as it is a major component present in tea extracts. Theoretical interaction energy and ΔG_{solv} calculations were aimed to reveal the stability of catechin in different solvents, using computational techniques. The reported work is expected to provide implications towards the advancement of technology in textile industry resulting in improved quality, aesthetics, comfort, presentability and affordability.

2. Materials and methods

2.1. Materials

The leaves of *Camellia sinensis* used in our study were collected from the local tea garden in Nagaon, Assam, India. The mulberry silk obtained from Nagaon, Assam used in the study was commercially available silk and weighed 41.67 g/m^2. Analytical grade alum, zinc chloride, and sodium carbonate were purchased from Merck Life Sciences Pvt Limited, Mumbai. Laboratory-grade methanol, dichloromethane, hydrogen chloride, aluminium chloride, sodium hydroxide, and sodium nitrite were obtained from Thermo Fischer Scientific India Pvt Limited, Mumbai. The Folin-Ciocalteu reagent (Himedia, India), as well as the catechin and gallic acid (Sigma Aldrich) utilized in the study, were of analytical grade. DPPH was purchased from Sisco Research Laboratories Pvt. Limited Maharashtra, India. Two distinct bacterial strains, viz., Staphylococcus epidermis (MTCC-435) and Escherichia coli (MTCC-443), representing Gram-positive and Gram-negative types, respectively, were obtained from the Institute of Microbial Technology (IMTECH, India).

2.2. Methods

2.2.1. Extraction of tea polyphenols from green tea leaves as colourants

The green tea leaves were subjected to deactivation in water at a temperature of 60 °C for 10 min. Subsequently, they were dried and finely ground into a powder to facilitate the extraction of colorants. About 5 g of the powdered tea leaves were refluxed with 100 ml of dichloromethane for 30 min to remove chlorophyll. The extracted solution was then filtered, and the remaining residue was used for the extraction of dyes using methanol and water solvent systems. In the extraction process, six different solvents, including water and methanol/water combinations, were employed under acidic conditions (5% v/v, HCl) and alkaline conditions (5% w/v, Na_2CO_3). These solvents were utilized to extract colorants from the tea leaf residues after chlorophyll removal. The extraction time was 30 min under reflux at different pH

Table 1
Experimental conditions for extraction of components from tea leaves.

Solvent system	Amount taken (ml)	pH
Methanol/Water	50/50	6
Methanol/Water/HCl	47.5/47.5/5	3
Methanol/Water/Na_2CO_3	47.5/47.5/5	9
water	100	6
water/HCl	95/5	3
water/Na_2CO_3	95/5	9

conditions, as shown in Table 1, and the resulting extracts were subsequently used for dyeing silk fabric. The efficiency of extraction was determined by the amount of total polyphenols and total flavonoids in the tea extracts. The UV-Vis analysis of the dye extracts was performed using Ocean Optics UV-Vis Spectrophotometer (λ_{max} 200–800 nm).

2.2.2. Mordant dyeing of silk fabric using green tea extracts

The silk samples were subjected to dyeing using both a standard catechin solution and tea leaf extracts. Prior to dyeing, the silk fabrics underwent a pre-mordanting process with either alum or zinc chloride at a temperature of 80 °C for 45 min. The mordanting process involved a liquor ratio of 500:1 i.e., using 0.2 g of mordant per 100 ml of water. Following mordanting, the silk fabric was rinsed with tap water and allowed to air dry. The mordanted silk fabric was then immersed in a solution containing 10 mM catechin or a 50 g/L tea extract prepared using the various solvent combinations. The dyeing was performed for a period of 45 min at 80 ^{0}C using a dyeing bath. After cooling, the dyed silk fabric was rinsed with water and allowed to air dry. Fig. 1 depicts the process of dye extraction from tea leaves and subsequent dyeing of the silk fabric.

2.2.3. Determination of total polyphenols, flavonoids, and antioxidant activity

The total polyphenol contents present in green tea extract were estimated using the Folin-Ciocalteu method, which has previously been described by (Rather et al., 2020; Dewanto et al., 2002). Here,1 ml of dye extract was diluted 10–75 times with distilled water with the addition of 1 ml of Folin-Ciocalteu reagent, 2 ml of Na_2CO_3 solution, and 2 ml of distilled water and a change in color could be seen in the solution. The mixture was allowed to be heated at about 60 °C for some time in a water bath. After some time, absorbance values were measured at λ_{max} 725 nm when it cooled down at room temperature. To determine the polyphenol concentration, a calibration curve of gallic acid was drawn and the results were expressed in units of mg/g gallic acid.

For the determination of total flavonoids, about 1 ml of the dye extract from different solvent extracts was mixed with a fixed amount of distilled water with the addition of $NaNO_2$. $AlCl_3$ was added to it after some time, with further addition of NaOH after a few minutes. After stirring for some time, absorbance was recorded at λ_{max} 510 nm. A calibration curve of catechin was drawn at 510 nm, and the results were expressed in terms of catechin equivalents (Rather et al., 2020; Sultana et al., 2007).

The antioxidant activity of the green tea extract was carried out by the DPPH radical scavenging assay. Natural phenolics and flavonoids possess the potential to catch free radicals with the help of an electron donation mechanism. DPPH is a stable radical with maximum absorption at 515 nm. DPPH goes to the reduced form on mixing it with the tea extract that can donate hydrogen atoms resulting in the loss of violet colour (Contreras-Guzmán and Strong, 1982., Kedare and Singh, 2011). The dye extract was first diluted with distilled water. 2 ml of each diluted sample was mixed with 2 ml of a 0.1 mmol DPPH solution in methanol. The mixture was stirred and allowed to remain for 60 min in the dark at room temperature. The reduction in absorbance by DPPH was recorded at 517 nm using a UV- Visible Spectrophotometer, and % of DPPH inhibition activity can be calculated as given in Eq. 1 (Liu et al., 2009; Senapitakkul et al., 2020).

$$\text{DPPH inhibition activity } (\%) = (A_0 - A_1)/A_0 \times 100 \quad (1)$$

where, A_1 is the mixture of sample extract and DPPH solution and A_0 is the mixture of methanol and DPPH solution.

2.2.4. Statistical analyses

Data generated in the study were entered and arranged for analysis using Microsoft Excel 2016 version. Prior to analysis, Kolmogorov-

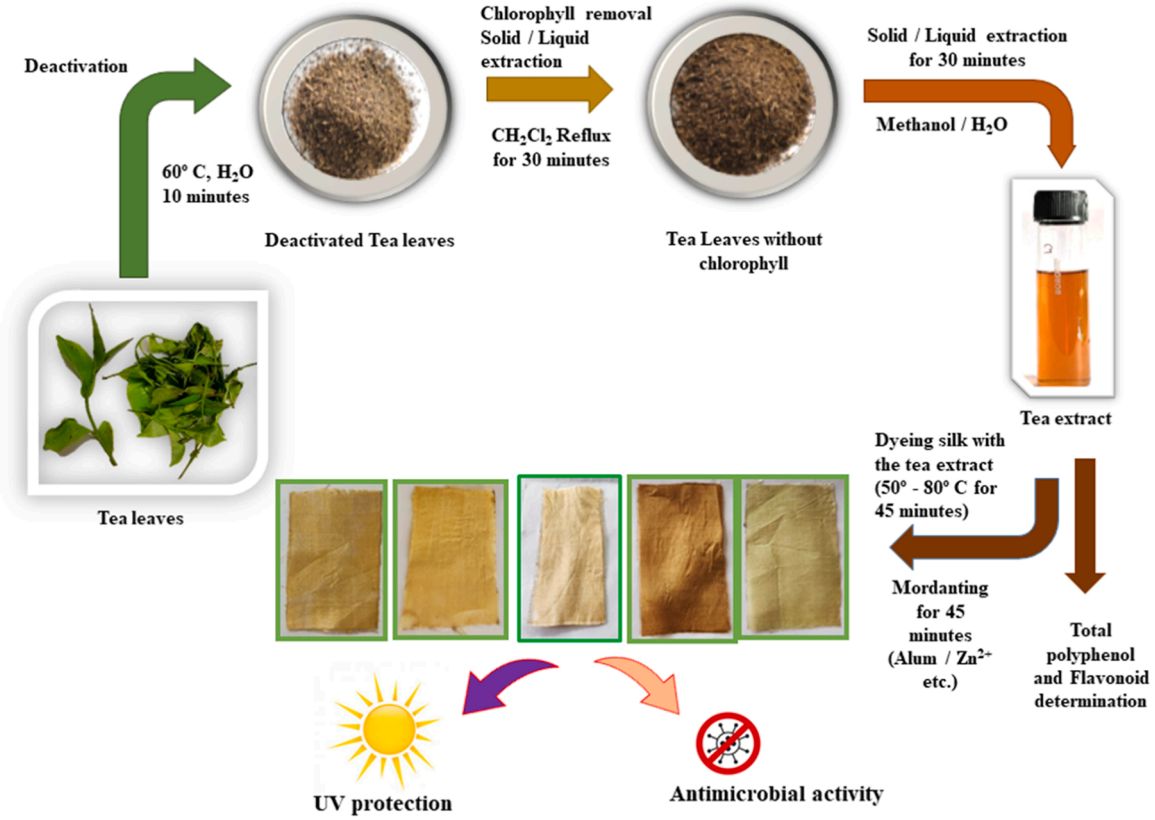


Fig. 1. The process of dye extraction from tea leaves and subsequent dyeing of the silk fabric. Extraction conditions: tea leaves: solvent: 50 g/L (water and methanol/water solvent systems), time: 30 min, reflux, pH: 3–9; Dyeing conditions: 80 ℃, 45 min, 0.2 g / 100 ml alum or zinc mordant.

Smirnov and Shapiro-Wilk tests were performed to check the normality of the data. Data analysis and statistical tests were performed using MS Excel 2016 and SPSS20 for windows. T-test was performed to analyse significant differences in parameter estimates. Correlation analysis was performed to determine the relationship between different parameters. The data were also subjected to statistical analysis of variance (ANOVA) following LSD to find the significance of the mean difference of data following normal distribution (differences were considered as significant at $p < 0.05$).

2.3. Characterization

2.3.1. Evaluation of colourfastness

The colourfastness to washing was evaluated according to a standard test method (ISO 105/C-1982. C01) (1982) using a laundrometer. The colour change observed after agitation of a textile specimen with stains of adjacent fabrics was determined with standard Grey Scale measuring from 1 to 5 grade only. The colour fastness to rubbing was measured with a Crockmeter rubbing fastness tester. It was used to evaluate the colourfastness of the dyed silk fabric to dry or wet rubbing and the result was expressed with standard Grey Scale measuring from 1to 5 grade only.

2.3.2. Colour characteristics

The colour values of the mulberry silk fabric dyed with green tea extract were assessed using the Computer Colour Matching system (SS 5100 H Spectrophotometer). The measurement method is in accordance with the literature (Cheng et al., 2019). When the value of a* is positive or negative, it represents the tincture of redder and greener shades, respectively. In comparison, b* represents the tincture of yellower and bluer shades when positive and negative respectively. Low a* /b* values represent dimness characteristics. The positive and negative DL* values represent the lightness or darkness of the colour shades respectively with respect to undyed fabric. DH* represents differences in hue and Dc* represents differences in chroma.

2.3.3. Zeta potential

The zeta potential of the silk fibre was determined using Malvern zeta sizer nano-zs90. Three observations were taken for each sample at the same pH value and the results were averaged for each one.

2.3.4. Measurement of UPF

The Ultraviolet Protection Factor (UPF) of the dyed silk fabric was assessed using the Gester GT-C30 UPF tester in accordance with AS/NZS4399 standards (Singh and Singh, 2013). Eleven samples of 10 cm × 10 cm were set and three observations were taken for each sample. The results were averaged for each of the samples. To assess the percent transmission of the samples a spectrophotometer was used.

2.3.5. Antimicrobial activity

Antibacterial activities of each differently dyed fabric were analysed via disc-diffusion method following (Wang et al., 2021) with minor modification against a Gram positive and a Gram-negative type-cultures namely *Staphylococcus epidermis* (MTCC-435) and *Escherichia coli* (MTCC-443) procured from Institute of Microbial Technology (IMTECH, India). Each fabric with diameter roughly 12 mm was sterilized under 1 h UV light irradiation and then transferred onto middle of the Mueller Hinton agar plate containing 100 μL of bacterial solution with 10^6 colony forming units per ml (CFU/ml). After incubating at 37 °C for 16–24 h, the inhibition zone size around fabric was recorded to evaluate the corresponding antibacterial ability if any. A plain fabric without dye was used as control.

2.3.6. Structural characterization

The FT-IR spectra of the silk fabric was recorded in the range of 4000–400 cm^{-1} using a spectrometer (Perkin Elmer, USA/Spectrum Two) in KBr pellets. X-ray photoelectron spectroscopy (XPS) analysis was performed using Thermo-Scientific spectrometer (Model: ESCALAB Xi^+) coupled with monochromatic Al Kα X-ray source. The samples of silk fabric were scanned using field emission scanning electron microscopy (FESEM) (Carl Zeiss-Sigma). Dyed and undyed samples were evaluated for visual appearance using Nikon ECLIPSE E200 phase contrast microscope with 10x magnification.

2.3.7. Semi empirical AM1 study

The Structure of catechin was modelled in Gaussian 09 software and carried out semiempirical AM1 optimization in different solvent systems such as water, methanol, ethanol as well as in vacuum phase (Labidi et al., 2018). The optimization of the structure in different solvents was carried out using default scrf method i.e., Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) (Wang and Zhang, 2005). From the obtained value of Gibbs free solvation energy, the stability of catechin in different solvent systems were determined (Mananghaya et al., 2012). Again, structures of silk fiber, mordanted silk fiber and premordanted silk fiber dyed with catechin were modelled using Gaussian 09 software. The structures were subjected for semiempirical AM1 level of calculation and interaction energy of the systems was calculated using the equation 4 given below (Huang et al., 2007; Sponer et al., 1996):

$$E_{\text{interaction}} = E_S - (E_1 + E_2) \quad (2)$$

where, E_S = Total energy of the whole system and E_1, E_2 = Total energies of the individual systems.

3. Results and discussion

3.1. Characterization of green tea extracts

The extraction of tea polyphenols varies with the nature of the solvents. The tea extracts show different absorbance values since solvents exhibit different dissolution power towards specific components (Bindes et al., 2019; Mai et al., 2017). Higher cavitation/bubbling occurs in the methanol/water solvent system than in water during the extraction process. Methanol has lower surface tension than water, increasing the extraction yield (maximum absorbance) (Rather et al., 2021). The UV-Vis analysis of different tea extracts under the conditions of reflux time (30 min) was performed in a spectrophotometer (Fig. 2). A broad peak around 280 nm in all the samples was observed due to the presence of tannin components, mostly catechins. The other characteristic peaks of tannins were also observed in around 246 and 326 nm. In the methanol/H_2O/Na_2CO_3 extract, an additional broad peak at λ_{max} 400 nm might be attributed to the presence of quercetin and rutin and is a result of redshift when the extraction solution pH was basic (Jurasekova et al., 2014; Zhou and Tang, 2017). Standard catechin shows λ_{max} at 280 nm, whereas caffeic acid and gallic acid shows λ_{max} at 239, 291, 313 nm and 268 nm, respectively, as shown in Fig. S2 of the supporting information. EGCG absorbs in the spectral region between 248 and 361 in water extract with λ_{max} 247 nm, and in other solvents, the spectral range is between 246 and 323 nm with λ_{max} 246 nm in methanol extract. The spectral range of ECG in water is from 246 to 363 nm with λ_{max} 273 nm and from 246 to 325 nm in other solvents with λ_{max} 277 nm in methanol extract. The spectral range of EGC in water extract is between 254 and 378 nm with λ_{max} 335 nm, and EC is between 252 and 328 nm with λ_{max} at 315 nm in water. The above results are similar to those reported by Atomssa and Gholap (2015) for the characterization of major catechins in green tea leaves using a UV-Vis spectrophotometer (Atomssa and Gholap, 2015).

The amount of polyphenols, flavonoids, and antioxidant activity of green tea extracts were determined (Table 2). Polyphenol and flavonoid content presented maximum efficacy in the methanol/water and water solvent system, whereas minimum estimation was observed for both the

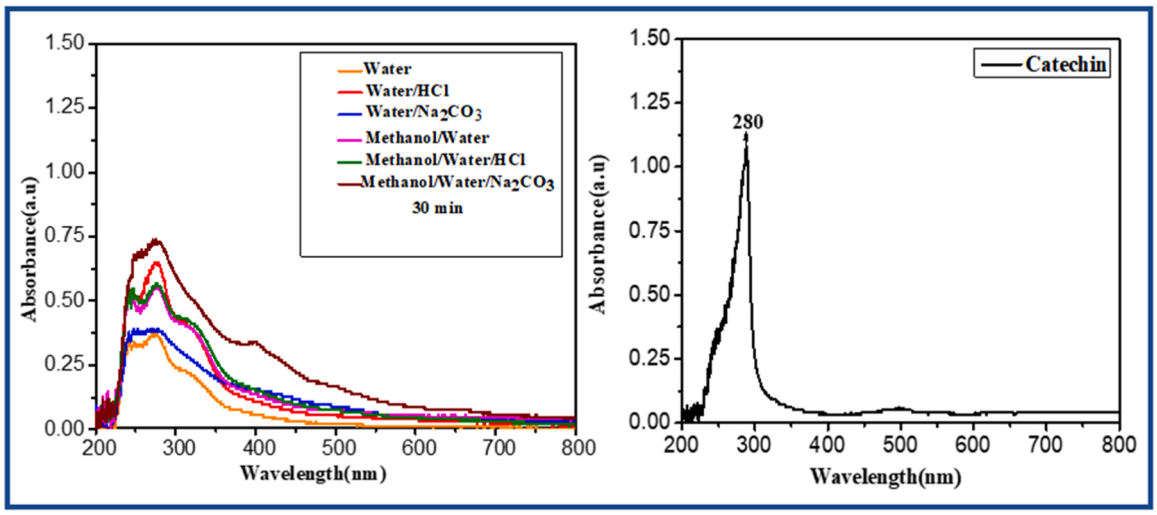


Fig. 2. UV-Visible absorption spectra of different green tea extracts: water (pH=6), water/HCl (pH=3), water/Na_2CO_3 (pH=9), Methanol/water (pH=6), Methanol/water/HCl (pH=3), Methanol/water/ Na_2CO_3 (pH=9), powdered tea leaves = 5 g, extraction time = 30 min; and UV-Visible absorption spectra of Catechin.

Table 2
Total polyphenols, flavonoids and radical scavenging activity (Mean ± Standard Error) of green tea extract in different solvent systems.

Solvent system	Amount of total polyphenols (mg/g extract)	Amount of total flavonoids (mg/g extract)	Antioxidant activity by DPPH (%)
Methanol/ Water	214.08 ± 2.89[a]	62.24 ± 1.77	74.73 ± 2.02
Methanol/ Water/HCl	174.00 ± 5.86[b]	48.77 ± 1.56[a]	43.40 ± 2.65[a]
Methanol/ Water/ Na_2CO_3	153.86 ± 5.94[c]	27.15 ± 2.05	35.23 ± 2.65[a]
water	204.00 ± 5.82[a]	51.74 ± 1.01[a]	63.63 ± 3.50[b]
water/HCl	174.42 ± 4.85[b]	37.70 ± 2.02[b]	59.58 ± 2.66[b]
water/Na_2CO_3	165.64 ± 4.44[b, c]	34.77 ± 1.56[b]	56.56 ± 2.67[b]

*Similar superscripts indicate that mean value is not significantly different

contents in methanol/water/Na_2CO_3 extract among the different solvent systems adopted. Maximum polyphenol content was estimated in methanol/water extract, followed by water extract exhibiting values 214.08 ± 2.89 and 204.00 ± 5.82 mg/g, respectively. Flavonoid contents exhibited maximum value in methanol/water extract (62.24 ± 1.77 mg/g) followed by water extract (51.74 ± 1.01 mg/g). Polyphenol and flavonoid content in the different solvent system showed significant positive correlation ($r = 0.89$; $p < 0.01$) in the dataset. Univariate tests showed that polyphenol content in the different solvent systems differed significantly (ANOVA; $p < 0.01$). LSD indicates that polyphenol content in methanol/water extract is near water extract ($p = 0.186$) but significantly higher than other solvent extracts ($p < 0.01$). Similarly, methanol/water/HCl extract exhibited close polyphenol content with water/HCl ($p = 0.95$). Alkaline extracts methanol/water/Na_2CO_3 and water/Na_2CO_3 lets in closer polyphenol estimates in the dataset (Table 2). Polyphenolic extraction was better in acidic extraction conditions due to the ease of prevention of oxidative changes by acids (Yoshida et al., 1999). Flavonoid content in methanol/water/HCl is close to water extract (LSD; $p > 0.05$). Likewise, water/HCl and water/Na_2CO_3 extract exhibited comparable flavonoid content, but the values were significantly different from the other solvent extracts (ANOVA; LSD; $p < 0.01$) in the study (Table 2). From the results, it may be concluded that methanol was more effective in extracting the dye components than water. The reason is that methanol is associated with polar C-O and O-H; however, water can only associate with O-H bonds during extraction. As compared to methanol, the two lone pairs of electrons of the oxygen atom in water are less available for participation in extraction (Rehan et al., 2022; Wizi et al., 2018). Polyphenol and flavonoid estimates in the current study reveal underestimation compared to the former estimation in the methanol extract exhibiting values of 255 mg/g and 99 mg/g for polyphenol and flavonoid content, respectively (Koláčková et al., 2020). Whereas in the present study, polyphenol content in the water extract (204.00 ± 5.82 mg/g) is considerably higher than the findings of (Theppakorn et al., 2014) (166 mg/g) rather than flavonoid content in the water extract (51.74 ± 1.01 mg/g) is comparable with the previous study of (Nibir et al., 2017) (50.10 mg/g). The dye extract from green tea leaves exhibited free radical scavenging activity from 35.23 ± 2.65% (methanol/water/Na_2CO_3) to 74.73 ± 2.02% (methanol/water) in different solvent extracts. Antioxidant activity in the different solvent systems differs significantly (t-test; $p < 0.01$). Whereas antioxidant activity in methanol/water/HCl and methanol/water/Na_2CO_3 extract did not vary significantly (ANOVA; LSD; $P > 0.05$). LSD further indicates that antioxidant activity in the water, water/HCl, and water/Na_2CO_3 extracts exhibited close values (Table 2). Antioxidant activity in the different solvent systems showed a strong positive correlation with polyphenol ($r = 0.76$ **) and flavonoid content ($r = 0.63$ **) in the dataset. It is expected that as the silk fabric possesses a small radical catching ability so mordanted dyeing of silk with green tea extract will be effective for increasing the antioxidant behaviour of silk. Antioxidant activity in the study exhibited similar values to the findings of (Trinovani et al., 2022) (74.55%) and (Lin et al., 2008) (77.70%) in methanol and water extract, respectively. Total polyphenol content and total flavonoid values can be directly correlated with the higher antioxidant activities in methanol/-water extract. Further, this correlation has been reflected in K/S values and UPF values of dyed silk fabric.

3.2. Property evaluation of dyed silk fabric

The colourfastness analysis of dyed silk fabric shows excellent results and is presented in Table S2 and described in the Text S1 of the supporting information. The ability of dyed fabric to maintain the colour shade on washing and rubbing or exposure to other physical and chemical conditions is referred to as fastness properties of dyed fabric. Fig. 3 shows the colour stability of unmordanted and mordanted with Al^{3+} and Zn^{2+} dyed fabrics, respectively, before and after washing. In methanol/water extract, methanol/water/HCl, water and water/HCl extracts the total polyphenolic components and total flavonoids were found to be highest as compared to methanol/Water/Na_2CO_3 and

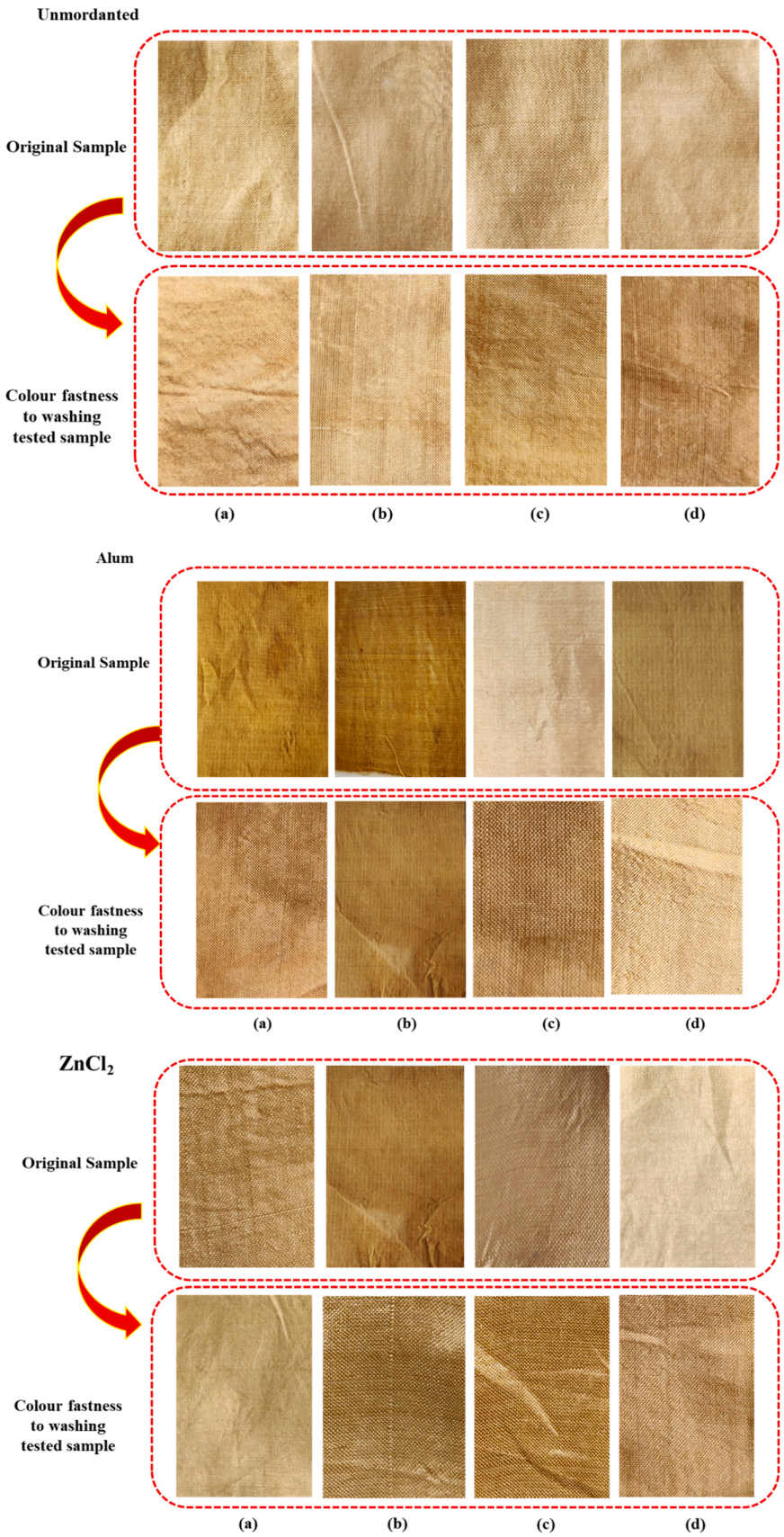


Fig. 3. Colourfastness stability of unmordanted, Al^{3+} mordanted and Zn^{2+} mordanted dyed fabrics with different solvent combinations before and after washing with 50 g/L a) Methanol/H_2O b) Methanol/H_2O/HCl c) H_2O d) H_2O/HCl.

water/Na_2CO_3 extracts. Moreover, the controlled experiments of dyeing with the basic extracts performed at pH 9 has not shown any significant colour in dyeing. So, we have reported the results of dyeing silk fabric with water and methanol/water solvent combinations at pH 3 and 6.

The effect of different solvent combinations on color and color characteristics values are presented in Table 3. It has been reported that the values of the isoelectric point of silk fibre vary from 1.4 to 5.2 depending on the nature of the silk (Ren et al. (2018); Hawley and Johnson (1930)). The zeta-potential measurements of the silk material for our study indicate the isoelectric point is in between pH 2–3. The value of the zeta potential at pH 2 was 1.03 mV and changed to − 5.32 mV at pH 3. The negative values of zeta potential increase to − 6.77, − 7.47, − 8.03, − 10.2, − 11.3, and − 16.4 mV at pH 4, 5, 6, 7, 9, and 10, respectively. The presence of the main functional groups in the form of carboxylic (-COO^-) and amino (-NH_2) on the silk surface provide reactive sites that connect the mordants and silk fiber with the dye molecules via chelation. The color strength in terms of K/S values was found to be 18.851 for methanol/water extract and 13.126 for methanol/water/HCl extract. In methanol/water extract, the total polyphenolic components and total flavonoids were highest, followed by methanol/water/HCl indicating the higher K/S values of the dyed silk. The tea polyphenols in different extracts may bind with the silk with interactive forces such as hydrophobic interactions, hydrogen bonding, and Vander Waal's forces (Haque et al., 2022; Tang et al., 2010). The higher concentration of polyphenols and flavonoids in the methanol/-water system also increases the K/S values of dyed silk fabric with that system due to the formation of a concentration gradient between dye solution and silk fabric (Rather et al., 2021). The silk fibres contain hydrophobic parts in amino acid structure, which interact with the hydrophobic aromatic rings of tea polyphenols by hydrophobic interaction (Tang et al., 2010). The mordanted samples show higher K/S values as compared to the un-mordanted one as the dye molecules form metal complexes with the positively charged metals. The transition metal complexes form strong bond with the tea polyphenols due to their ability to form coordination complexes and can thus produce a deep colour on the silk fabric. This coordination increases the interactions of the mordant dyed silk fiber, which in turn results in higher K/S values (Rather et al., 2015). Further, it has been observed that K/S values of the dyed silk exhibit a strong positive correlation with polyphenol concentration ($r = 0.78$; $p < 0.01$), flavonoid concentration ($r = 0.93$; $p < 0.01$) coupling influence on antioxidant activity ($r = 0.56$); $p < 0.05$) of different solvent extracts. It is evident from Table 3 that the colors obtained by direct dyeing are different from dyeing using alum mordant with varying hues and tones. The colour coordinates (a*, b*) of mulberry silk dyed fabric are located amidst redness and yellowness spaces. Dyeing with methanol/H_2O without mordant produced higher lightness shade (DL*), chroma (C*), and yellowish tincture (b*values) compared to the mordant-dyed silk fabric (Table 3). In mordant dyed silk with methanol/H_2O/HCl, the quality of yellowness (b* values) and redness (a* values) increased as compared to the unmordanted one. This might be due to the different dye-mordant-silk interactions occurring between the tea extracts, mordant, and silk fiber (Jabar et al., 2023). The chromophore of the dye molecules makes different interactions with the silk fabric and forms stable complexes via chelation with the mordants, which results in deeper colours with metal ions providing different shades (Cheng et al., 2019).

3.3. UV protection of dyed silk fabric

Considering the hazardous impact of UV radiation on human health, some natural UV-blocking agents are used as UV absorbers to convert it into less harmful radiation. Naturally occurring pigments are eco-friendly and safe for the dyeing of textiles and help in quenching this harmful UV radiation showing good UV protection properties (Gong et al., 2019). The Ultraviolet protective nature of undyed and dyed silk samples was investigated and is shown in Table 4. Naturally occurring polyphenols have excellent UV absorption capacity due to their conjugated systems and the presence of groups such as -OH, -NH_2, and -NH (Hou et al., 2017). Dyeing silk with polyphenols added UV protective capacity to the undyed one, which had nominal activities. High concentration of dye molecules results in a higher UV protection capacity of dyed silk fabric due to more dissipation of energy of the adsorbed molecules absorbing maximum radiation (Rehan et al., 2022). The transmittance rates of the undyed silk fabric in Ultraviolet A and Ultraviolet B were 33.18% and 20.39%, respectively, with an Ultraviolet Protection Factor (UPF) value of 6.84. The dyed silk samples with higher UPF values and lower transmittance rates indicate better protection levels (Feng et al., 2007; Rather et al., 2020). The high-energy UV radiation is quenched by the photochemical cleavage or the

Table 4
UPF of silk fabric dyed with green tea extract.

Type	Sample no.	Samples (dyed silk fabric)	UVA (%)	UV B (%)	UPF
Un mordanted	1.	Undyed	33.18	20.39	6.84
	2.	Catechin	32.03	20.77	6.85
	3.	Methanol/water	9.52	6.54	25.74
	4.	Methanol/water/HCl	13.07	8.55	18.25
	5.	water	5.58	2.39	62.87
	6.	water/HCl	5.96	2.00	51.66
Mordanted	7.	Catechin	26.34	15.96	8.97
	8.	Methanol/water	7.42	4.86	33.38
	9.	Methanol/water/HCl	7.53	5.05	31.86
	10.	water	8.70	5.37	29.08
	11.	water/HCl	18.68	10.52	14.49

UV represents Ultraviolet, UPF represents Ultraviolet Protection Factor

Table 3
Colour coordinates of unmordanted and mordanted silk fabric dyed with tea extracts.

Silk Type	Dye extract	a*	b*	c*	H*	DL*	Da*	Db*	Dc*	DH*	K/S
Unmordanted	Control	-0.664	6.387	6.421	95.969						1.309
	Catechin	0.076	4.387	4.388	88.972	-0.614	0.740	-2.000	-2.034	-0.641	3.241
	Methanol/water	1.513	9.041	9.167	80.467	0.589	2.177	2.654	2.745	-2.061	11.913
	Methanol/water/HCl	1.328	7.969	8.079	80.506	0.284	1.992	1.582	1.657	-1.930	9.759
	water	1.391	9.238	9.342	81.404	0.676	2.055	2.851	2.921	-1.955	6.194
	water/HCl	-0.166	7.575	7.577	91.291	0.911	0.826	3.713	3.589	-1.259	5.198
Mordanted	Catechin	0.914	4.645	4.734	78.836	-0.622	1.578	-1.742	-1.687	-1.636	4.409
	Methanol/water	1.561	8.308	8.453	79.327	0.379	2.225	1.921	2.032	-2.124	18.851
	Methanol/water/HCl	1.633	9.241	9.384	79.946	0.665	2.297	2.854	2.963	-2.155	13.126
	water	1.134	10.199	10.262	83.622	1.591	2.126	6.337	6.274	-2.304	10.656
	water/HCl	1.393	8.458	8.572	80.615	0.448	2.057	2.071	2.151	-1.974	7.662

a* represents red/ green coordinate, b* represents yellow/ blue coordinate, c* represents chroma, H* represents hue angle, DL* represents the lightness or darkness of the colour shades, Da* represents differences in red and green, Db* represents differences in yellow and blue, Dc* represents differences in chroma, DH* represents differences in hue, K/S represents colour strength of dyed mulberry silk fabric.

transformation reactions which take place within the hydrogen bonds present in flavonoids (Rather et al., 2021). The variations of UPF values in the dyed samples with different solvent extracts are due to the different levels of total polyphenols and flavonoids in the extracts, which contributes to the formation of conjugated bonds and other dye-mordant-silk interactions (Rather et al., 2020; Gong et al., 2019).

There is a good correlation between UPF and colour strength (K/S) values. The K/S values exhibit a positive correlation with the UV protection factor ($r = 0.91$; $p < 0.01$) of dyed silk fabric with different solvent extracts. The deeper the colour strength of the fabric better the UV protection capacity of the dyed silk fabric (Gong et al., 2019; Hou et al., 2017). These correlations are in accordance with the results observed for silk and wool dyeing using pigments extracted from Cinnamomum camphora silk and wool (Gong et al., 2019).

3.4. Antimicrobial activity

The results of the antibacterial activity of green tea-dyed silk fabric are shown in the Fig. S8 of the supporting information. During the antibacterial activity test of prepared fabrics, a zone of inhibition of about 1–2 mm around sample fabrics was recorded on Staphylococcus epidermis MTCC-435 plates for eight samples indicating the mild contact-killing ability of those fabrics. Direct dyeing without mordant with solvent extracts methanol/water/HCl, and water/HCl exhibited antibacterial activity. According to Rather et al. (2020), the use of mordant remains helpful in increasing antibacterial activity. Dyeing with alum mordant using water extract and mordanting with $ZnCl_2$ in solvent extracts of water, catechin, and water/HCl showed antibacterial activity. However, there was no inhibition zone found near the untreated fabric and other samples. Samples from all three conditions of dyeing, i.e., without mordant, with alum, and $ZnCl_2$ mordant showed activities against the type culture S. epidermis (MTCC-435); however, $ZnCl_2$ mordant was found to be more effective one as four samples treated with $ZnCl_2$ showed mild antibacterial activity. The formation of chelate complexes due to the interactions of dye molecules with the metal ions reduces the polarity of the metal ions. The lipophilic nature of the central metal atom is increased due to the distribution of electrons, further increasing the delocalization of π electrons on the whole chelating ring favouring its diffusion more effectively through the lipid layer and thus aggressively destroying them (Bouhdada et al., 2019; Rather et al., 2020). There was no inhibition zone recorded against Escherichia coli (MTCC-443) during the test. The Gram-negative bacteria contains an outer phospholipid membrane with negatively charged structural lipopolysaccharide components, which is less prone to the antibacterial action of the dyed silk compared to Gram-positive bacteria (Rather et al., 2016).

3.5. SEM analysis

The study of surface morphology is observed as one of the important parameters for dyed fabric which reveals the deposition of green tea components on silk surface. The morphological changes that have occurred by dyeing of silk fabric with tea polyphenol extracts were investigated and are shown in Fig. 4. From the Figure, it can be observed that the undyed silk has a cleaner and smooth plain surface. The silk dyed with green tea leaf extract shows roughness on the surface of silk fabric due to the deposition of dye molecules on the fibre during the process of dyeing (Saini et al., 2020). Therefore, these SEM images demonstrated the successful dyeing of silk fabric by green tea extract.

The elemental mapping analysis of the dyed and the undyed fabric shows the presence of many elements (Fig. 5). The undyed samples show the presence of evenly distributed carbon, nitrogen, and oxygen as the main elements arising from the silk protein. The dyed samples show the presence of a considerable amount of evenly distributed aluminium along with carbon and oxygen, which indicates that alum was used as a mordant in the dyeing process. The elemental compositions of the dyed and undyed silk from the EDS analysis are shown in Fig. S9 of the supporting information. The EDS spectrum of the undyed fabric showed that the weight amount of C, N, and O were 40.53%, 19.82% 31.84%, respectively, whereas the dyed fabric with methanol/water extract showed that the weight amount of C, O, Al were 54.57%, 36,70% and 0.58% respectively and weight amount of C, O, Al in catechin dyed silk were 53.37%, 35.95%, and 0.71% respectively as given in Fig. S9 of the supporting information. The increased amount of carbon and oxygen in dyed silk fabric might be attributed to the increase in phenolics after dyeing of silk fabric. The presence of other elements, such as Ca, Si, and

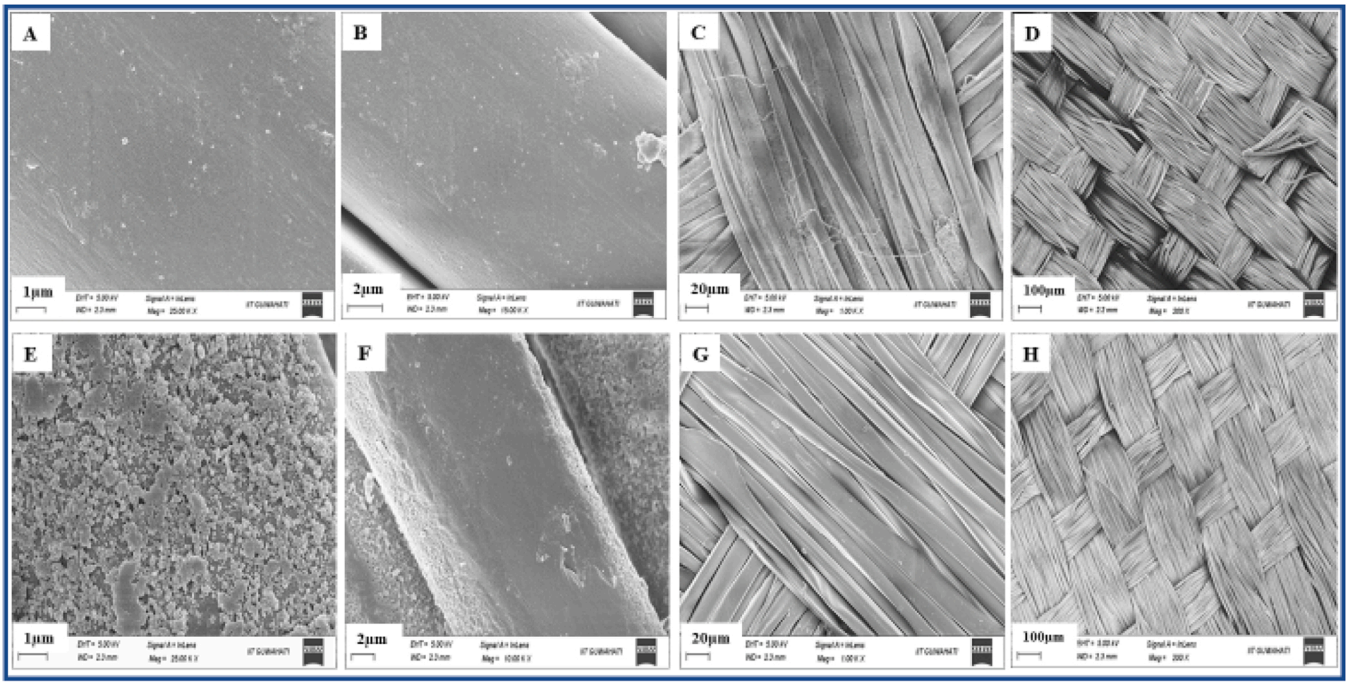


Fig. 4. FE-SEM images of undyed fabric (A-D) and dyed fabric (E-H) dyed with 50 g/L methanol/water tea extract using 0.2 g/100 ml alum mordant.

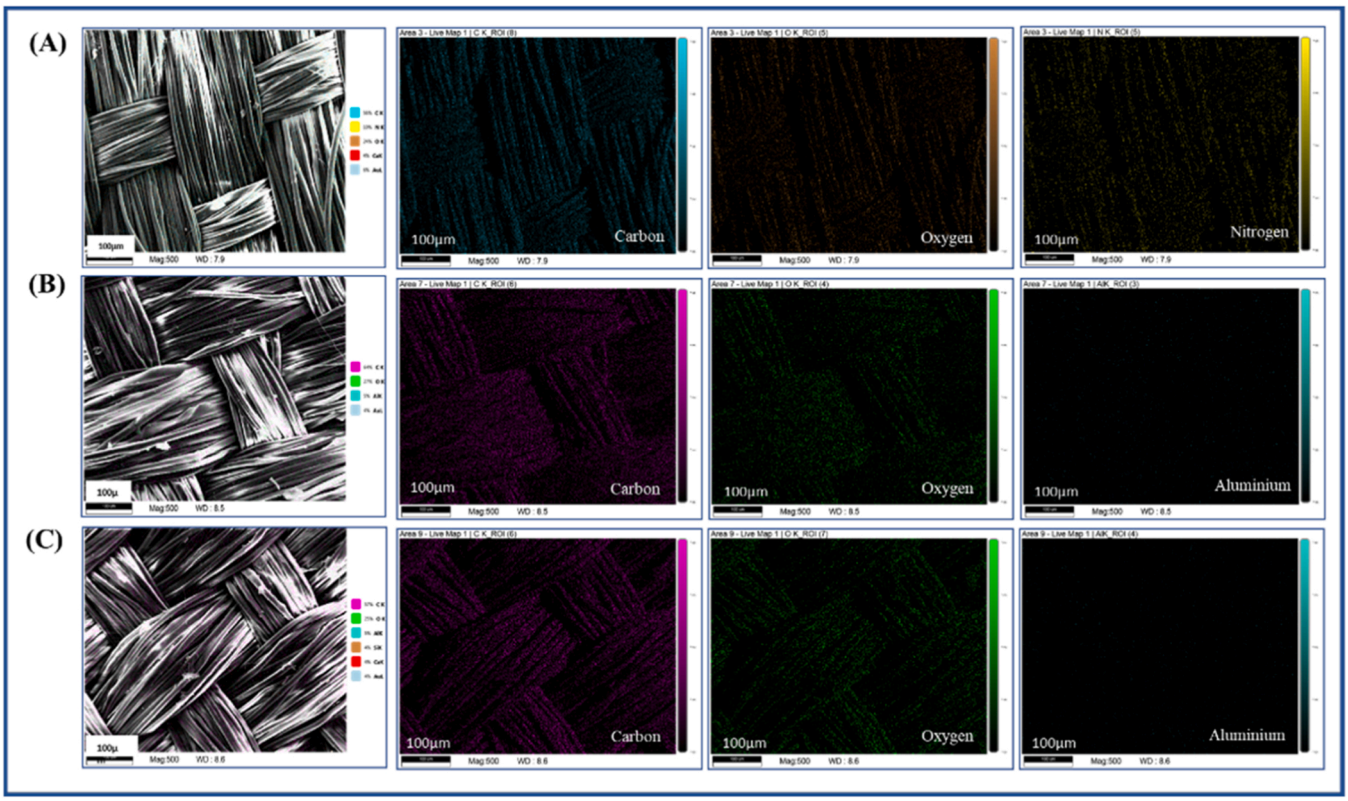


Fig. 5. EDS Elemental mapping of A) Undyed B) dyed with 50 g/L methanol/water tea extract catechin using 0.2 g/100 ml alum mordant. C) dyed with 10 mM catechin using 0.2 g /100 ml alum mordant.

Au, was also identified. Such elements may originate from additives or impurities during the dyeing process. Hence, we can conclude that they are not a part of the mordant composition used during the dyeing process. An optical microscopic analysis of the dyed and undyed silk is shown in Fig. S10 and described in Text S2 of the supporting information.

3.6. FTIR analysis of dyed silk fabric

The surface functionalities of silk before and after dyeing were analysed in FTIR and shown in Fig. 6 and Fig. S11 of the supporting information. Silk is a protein with -NH, OH and C═O functional groups present in its structure. Fig. 6 shows FTIR spectra of the undyed silk, which show peaks at 3287 cm^{-1} for the hydroxyl group of silk protein. A strong peak at 3274 cm^{-1} was seen in dyed silk, which corresponds to -OH stretch. The characteristic band at 1644 cm^{-1} in silk fabric was due to the asymmetric coupling of C═O stretching vibration of peptide bond associated with amide I. A bending vibration was observed in dyed silk at 1622 cm^{-1} (C═O stretch) linked with an aromatic group which represents the presence of flavonoid groups. The decreasing shift at 1622 cm^{-1} observed in dyed silk with methanol/water and water/HCl (Fig. S11) indicated that hydrogen bonding may have occurred between silk and tea polyphenols (Hwang et al., 2022). The peak at 1520 cm^{-1} is associated with amide II due to NH bending/CN stretching in undyed silk. The peak at 1516 cm^{-1} is ascribed to the -C-C- aromatic stretch peak in dyed one. The peak at 1440 cm^{-1} in undyed silk is due to protein chain COO^{-}, and the peak at 1241 cm^{-1} is attributed to amide III (CN stretching and NH in-plane bending) (Rani et al., 2018; Suanpoot et al., 2008). A peak at 1448 cm^{-1} represents the -CH out of plane bending vibrations and the existence of an aromatic system in dyed silk. The peak, which is seen at 1236 cm^{-1}, shows C-O-C stretching vibration in dyed silk samples. At 1063 cm^{-1} the spectra represent the C-O-C bond of polyphenols (Ren et al., 2016). Peaks around 690 cm^{-1} show C-O out of plane bending vibrations due to the presence of tannins (Rather et al., 2020).

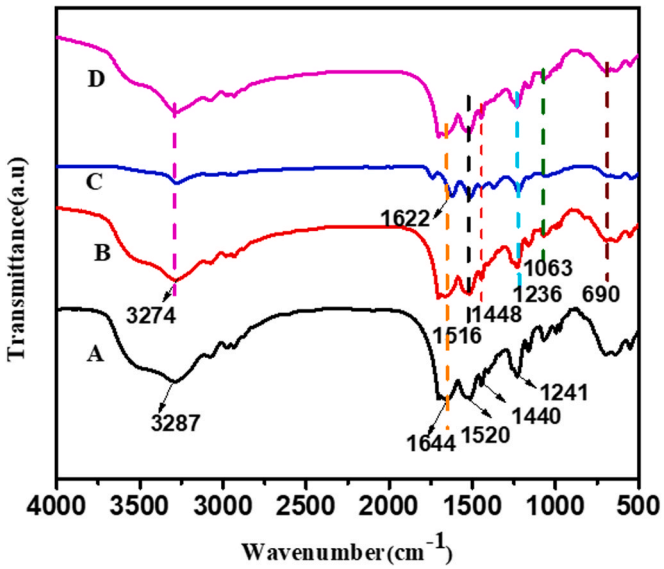


Fig. 6. FT-IR spectra of (A) Undyed (B) dyed with 10 mM catechin and dyed with 50 g/L of (C) Methanol/water (D) Methanol/water/HCl tea extract mordanted with 0.2 g/100 ml alum mordant.

3.7. XPS analysis of dyed silk fabric

To determine the chemical composition of silk before and after dyeing X-ray photoelectron spectroscopy (XPS) analysis was performed. The XPS wide survey spectra of undyed and dyed silk with methanol/

water and catechin are shown in Fig. 7. The peaks for binding energies at 284.8, 399.9, and 531.73 eV correspond to C1s, N1s, and O1s, respectively for undyed silk. For mordant dyed (Alum) samples with methanol/water extract and catechin the binding energies at 284.7, 400.2, 532.6 eV and 74.4 eV correspond to C1s, N1s, O1s, and Al 2p respectively. The elemental composition for both the undyed and dyed silk is presented in Table 5. It shows that the C, N, and O contents in the undyed silk fabric 66.83%, 9.8% and 23.37%, respectively, whereas those of the dyed silk were 69.93%, 2.28% and 27.35% for methanol/water. On relating the C, N, and O contents of the dyed and undyed silk, we could observe that the dyed silk exhibited a higher atomic percentage of carbon and oxygen, which may be due to the deposition of dye molecules on silk fabric through the formation of ether and ester linkage. The Gaussian peaks acquired through deconvolution of C1s, N1s, and O1s of undyed silk and methanol/water dyed silk are shown in Fig. 8. The Gaussian peaks for dyed silk with catechin and Al 2p peaks for both methanol/water and catechin are shown in Fig. S12 of the supporting information. The C1s peak of the spectrum can be deconvoluted into three peaks. For the undyed silk, the peaks assigned to 284.6, 285.8, and 288.1 eV could be ascribed to C-H/C-C, C-O, and C═O, respectively (Khatri et al., 2020). For dyed silk, the peak assigned to C-H/C-C, C-O and C═O corresponds to binding energies at 284.5, 286.0 and 288.4 eV respectively, which are considered within the standard range of XPS analysis. The relative content of C-H/C-C bond in undyed fibre is 52.63% and decreases to 42.83% and 49.05% in dyed silk with methanol/water and catechin respectively. The relative percentage of C-O bond in undyed fibre is 34.77% and increases to 49.14% and 43.74% in dyed silk with methanol/water and catechin respectively indicating the increase in phenolics on the surface of silk after dyeing. The O1s spectrum is also deconvoluted into three distinctive peaks of the undyed silk at 532.2, 531.3, and 533.6 eV, which could be consigned to C-O, O-H, and C═O, respectively (Khatri et al., 2020). The peak assigned to C-O, O-H and C═O of dyed silk fabric showed similar binding energies at 532.2, 531.0 and 533.2 eV respectively which are considered within the standard range of XPS analysis. The relative content of O-H group in undyed silk is 38.66% and decreases to 8.27% and 6.376% in methanol/water and dyed silk with catechin respectively. This decrease in relative content of O-H group in dyed silk is due to the fact that (-OH) of the carboxylic group present in silk and dye molecules bind with the positively charged metals forming a coordination complex (Rehman et al., 2022). This interaction also has been reflected in Scheme 1 of our dyeing mechanism. Similarly, the N1s spectrum of undyed silk was deconvoluted into peaks around 399.7, 399.9, and 401.0 eV revealing the presence of C-N-H, C-N, and NH_2 groups, respectively (Khatri et al., 2020). The

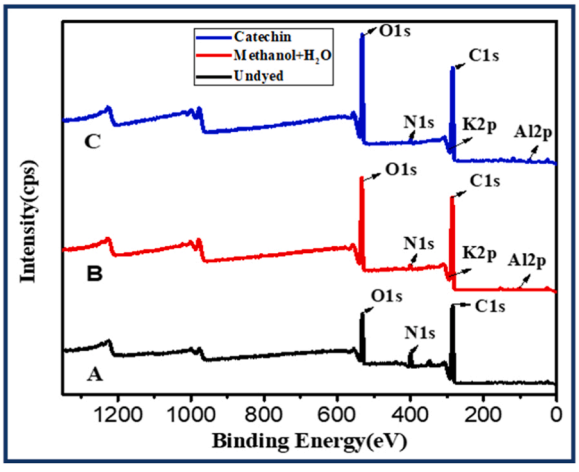


Fig. 7. XPS wide survey spectra of (A) undyed (B) dyed with 50 g/L of methanol/water extract (C) dyed with 10 mM catechin using 0.2 g / 100 ml alum mordant.

Table 5
XPS surface composition of silk fabric dyed with green tea extract and catechin.

Sample	Carbon (%)	Nitrogen (%)	Oxygen (%)	Aluminium (%)
Undyed	66.83%	9.8%	23.37	-
Methanol/water	69.93%	2.28%	27.35%	0.45%
Catechin	63.38%	1.76%	32.09%	2.77%

peaks ascribed to C-N-H, C-N and NH_2 groups of dyed silk fabric showed similar binding energies at 398, 400 and 402 eV respectively. The quantity of mordants is low, so it does not show any strong peak in the XPS spectra (Lee et al., 2013). The Al 2p spectrum was deconvoluted into two peaks in the catechin extract, with the main peak observed in aluminium is around 74.7 eV which is due to Al^{3+}. The other peak observed at 75.5 eV is due to aluminium sub-oxide formation (Song et al., 2015), shown in Fig. S12 of the supporting information. The XPS analysis of dyed silk fabric reveals the presence of aluminium since alum was added as mordant during the dyeing process.

3.8. Plausible mechanism for metal ion silk-dye interaction

The proposed mechanism and the interaction between dye and silk fabric is shown in Scheme 1. Silk fabric dyed with Al^{3+} mordant shows enhanced color strength and fastness properties. The green tea extract contains catechins as the accountable components responsible for coloring. Silk fabric makes a strong coordination bond with Al^{3+} after the dyeing and mordanting process. The main functional groups of silk exist in the form of carboxylic ($-COO^-$) and amino ($-NH_2$) and provides reactive sites that link the mordants and silk fibre with the dye molecules via chelation. The hydroxyl and carbonyl groups present in dye molecules of mangiferin and catechins can form metal complexes with the positively charged metals. The formation of coordinate bonds takes place between dye-metal complex and amino ($-NH_2$) groups on silk. Some coordination sites remain vacant when these mordants interact with the fibre while at the same time functional groups such as amino and carboxyl groups on silk fibre can occupy this site. Ternary complexes can be formed by the mordants on one site with the fibre and the other site with the dye molecules. These results in higher binding affinity silk fibre with the dye molecules (Uddin, 2015; Jabar et al., 2023). Mordants had a positive impact on the color characteristics of silk that had been colored with tamarind seed. The mordant draws the dye molecules together to form a complex structure that firmly binds the color to silk fibers. Red kidney bean water and copper sulfate or ferrous sulfate may interact with eri-silk yarn, according to a described mechanism. It was also investigated how mordants affected silk that had been dyed with grape seeds. Metallic salt mordanting improved the lightfastness qualities while having varying results on the other fastness parameters. Poor sweat and wet rubbing fastness in silk materials can be improved by using natural tea dye (Tepparin et al., 2012; Kampeerapappun et al., 2020; Guo et al., 2020; Cheng et al., 2019).

3.9. Modelling and optimization of catechin in different solvent systems

In order to study the stability of catechin in different solvent media and metal-dye silk interactions, semi-empirical calculations were carried out in Gaussian 09. The total energy value obtained for different solvent systems were $E_{vacuum} = -0.33850$ Hartree, $E_{methanol} = -0.35216$ Hartree, $E_{water} = -0.35259$ Hartree, $E_{ethanol} = -0.35193$ Hartree. Gibbs free energy of solvation for methanol, ethanol and water was found to be - 0.01365, − 0.01342, and − 0.01409 Hartree, respectively, as shown in the supporting information. Solubility of a given molecule in solvent requires a negative value of ΔG_{solv}. All the calculated ΔG_{solv} of the different solvents are negative, with ΔG_{solv} in water having the highest negative value. Therefore, the stability of catechin in different solvents will be in the following order catechin-water > catechin-methanol > catechin-ethanol (Mananghaya et al.,

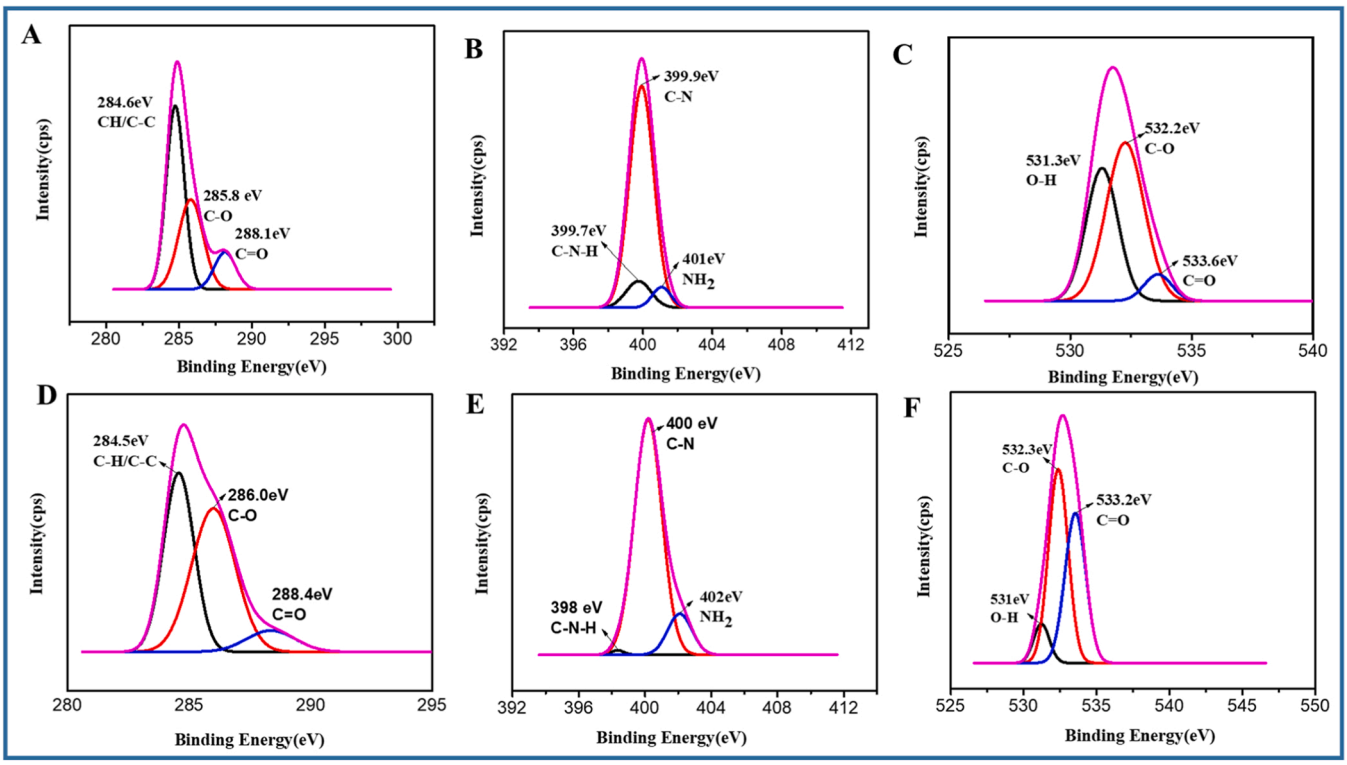
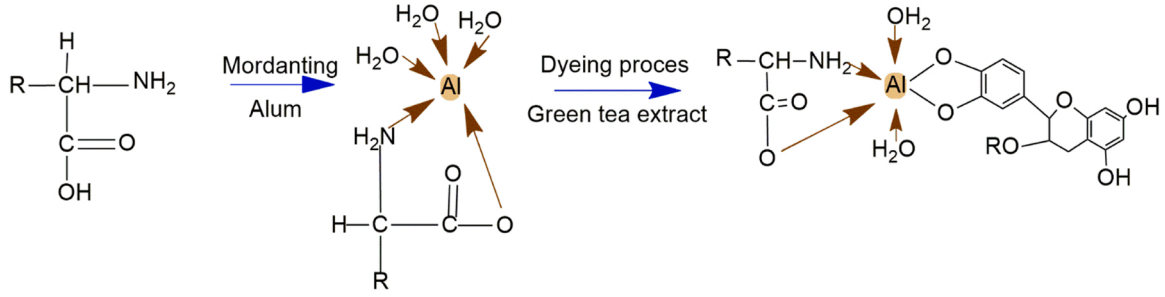


Fig. 8. XPS deconvoluted C1s spectra of undyed and 50 g/L of methanol/water extract dyed silk fabric (A, D); XPS N1s spectra of undyed and 50 g/L of methanol/water extract dyed silk fabric (B, E); XPS O1s spectra of undyed and 50 g/L of methanol/water extract dyed silk fabric (C, F) and mordanted with 0.2 g / 100 ml alum mordant.



Scheme 1. Metal ion-silk-dye interation.

2012; Wang and Zhang, 2005).

Again, we have modeled and optimized the silk fiber structure using same level of calculations and obtained a total energy value of − 0.16169 Hartree. Optimization of mordanted silk fiber was done as shown in Figure C of the supporting information and obtained total energy value of − 0.47699 Hartree. Similarly, pre mordanted silk fiber dyed with catechin as shown in Figure D of the supporting information, is optimized using semi-empirical AM1 level of calculation and obtained total energy of − 0.82076 Hartree. The interaction energy for catechin-mordant-silk interactions was found to be $E_{interaction} = -13.836$ kJ/mol. A negative value of interaction energy indicates good attractive interaction in the system, indicating good stability (Huang et al., 2007; Sponer et al., 1996).

4. Conclusion

This study presents a sustainable approach to dyeing silk using green tea extracts in both water and methanol/water solvent systems. The methanol/water solvent system exhibited higher total polyphenol, flavonoid, and antioxidant activity, which correlated with the color strength (K/S values) of the dyed silk fabric. By utilizing Al^{3+} or Zn^{2+} mordants, the dyeing process resulted in diverse colours with excellent colour strength (K/S value of 18.851) for the methanol/water solvent system. The mordant-dyed silk fabric displayed good colourfastness to washing, drying, and rubbing (above a rating of 3), as well as demonstrated antibacterial activity against Staphylococcus epidermis and UV protection properties. These outcomes were attributed to the strong interactions and bonds formed between dye molecules, mordant, and silk fabric, as revealed by XPS analysis. The binding mechanism of catechin-mordant-silk interactions was established by calculating the theoretical interaction energy, with negative values (−13.836 kJ / mol) indicating that the silk dyeing process would be favourable where catechins are the major constituent. Theoretical calculations of ΔG_{solv} indicated that catechin was more stable in water. Still, the dyed silk fabric exhibited satisfactory colour depth and desirable UV protection, antimicrobial activities, and colourfastness properties when using water and methanol/water solvent extracts. Developing dyeing methods from a sustainable source like tea is always advantageous to the textile industry, including generating employment opportunities and income for individuals in rural and sub-urban areas through tea farming and waste

utilization. Further, the results of this investigation will encourage the researchers to develop and design more greener dyeing methods for silk, cotton and other fabrics with applications in medical and energy fields.

CRediT authorship contribution statement

Shristirupa Borah: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Priyanga Manjuri Bhuyan**: Validation. **Swapnali Hazarika**: Resources. **Barrnali Sarma**: Resources. **Aniruddha Gogoi**: Resources, Writing – review & editing. **Parikshit Gogoi**: Conceptualization, Writing – original draft, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.There are no conflicts of interest to declare.

Data Availability

No data was used for the research described in the article.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2023.117517.

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