Environmental Science and Pollution Research (2022) 29:24035–24048
https://doi.org/10.1007/s11356-021-17341-5

RESEARCH ARTICLE

Waste black tea leaves (*Camelia sinensis*) as a sustainable source of tannin natural colorant for bio-treated silk dyeing

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Received: 3 September 2021 / Accepted: 29 October 2021 / Published online: 25 November 2021

Abstract

Environmentally friendly products are the need of the hour, particularly in this pandemic situation because synthetic products need such toxic chemicals for their formulation and finishing which are carcinogenic for the globe. The current study is the utilization of waste black tea leaf (BT)–based tannin brown natural colorant for silk dyeing using microwave treatment. Dye (tannin) has been isolated in various media before and after microwave treatment up to 6 min and applied at various conditions. It has been found that 30 mL of aqueous extract of 3.0 *p*H obtained from 6.0 g of powder containing 3.0 g/100 mL of salt as an exhausting agent after microwave treatment for 5 min, when employed at 55 °C for 45 min, has given good color yield onto silk. Iron (3%) and acacia extract (2%) as pre-chemical and bio mordant, iron (2%) and pomegranate extract (2%) as post chemical and bio-mordant, and Al (3 %) and pomegranate extract (3%) as meta chemical and bio-mordant have given new shades with good to excellent fastness ratings. It is inferred that waste black tea leaves (BTs) in an aqueous medium have an excellent potential to serve as a source of natural tannin brown dye for the coloration of surface-modified silk fabrics under the influence of cost, energy, and time-effective microwave treatment. Additionally, the utilization of a low amount of sustainable chemical and bio-mordants has valorized the dyeing of silk by developing soothing and sustainable shades with good fastness properties.

Keywords Bio-mordants · *Camelia sinensis* · Microwave · Silk fabric · Sustainability · Tannin

Introduction

Textile dyeing is one of the most environmentally damaging industries because of the wastes it causes. Excessive amounts of water and chemicals are used in dyeing processes using synthetic dyes (Khattab et al. 2020; Singh and Sheikh 2020). Harmful environmental effects of many different dimensions, such as global warming and air and water pollution that occur due to industrial development (Javaid and Qazi 2019; Khan et al. 2021), make it necessary to take into account the ecological dimension of production and research in every field (de Marco et al. 2019; da Silva et al. 2020). Ecological constraints, decreasing water resources, and chemical waste problems push the textile industry to look for different alternatives (Lachguer et al. 2021; Chen et al. 2020). In addition, the demands of consumers, who have to cope with many diseases with the introduction of synthetic materials and chemicals, are also in favor of natural products such as natural plant dyes (Lin et al. 2020). In order to protect the environment, different measures are taken in all branches of industry to maintain industrialization while fulfilling these principles (Söz et al. 2021). One of these industries is the textile industry (Singh et al. 2019; Giacomini et al. 2020). In this running decade, it will be possible to achieve the goals of sustainability and creating a better livable environment if sustainable goals are followed

Responsible Editor: Philippe Garrigues

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during the production processes (Mahdi et al. 2021; Haji and Rahimi 2020). Therefore, the "return to nature" trend is increasing all over the world that covers a wide range of researches from organic fiber election to environmentally friendly production methods and from bio-mordants to natural dyeing (Adeel et al. 2021a; Hosseinnezhad et al. 2020; Özomay et al. 2021).

In recent years, many commercial organizations have been dyeing and printing using natural dyes in coloring different textile materials. Natural dyes, which have a wide range of colors, are also an environmentally friendly method because they are biodegradable (Srivastava & Singh, 2019; Adeel et al. 2021b). Natural dyes are often non-substantive and are bound to textile material with the help of mordant substances, generally known as metal salts (Pratumyot et al. 2019). Today, bio-mordants, which are a more environmentally friendly approach, are preferred as an alternative to metal salts (Samanta, 2020; Werede et al. 2021). Plants such as acorn, turmeric, acacia, and pomegranate are mostly used as bio-mordant (Adeel et al. 2021b; Haji, 2019). One of the main reasons why bio-mordants are preferred in natural dyeing is the environmental factors as well as the improvement of the fastness properties of dyeing them (Özomay et al. 2019; Hosseinnezhad et al. 2021a; Wang et al. 2018). Shade fastness ratings are the most important parameters that show the efficiency of dyeing in textile materials (Rodiah et al. 2021; Chakraborty et al. 2020). Scientists are looking for ways to further improve the fastness properties of natural dyeing day by day by making use of new technologies (Abkenar, 2021).

One of the most modern methods among these technologies is to make use of microwave radiation (Baig et al. 2021). Microwave rays provide maximum interaction of bio-molecules with the solvent through a solid-liquid transfer mechanism (Chen et al. 2020). Also, microwave heating has the greatest advantage in that it causes more mass transfer into a solvent (Gong et al. 2020; Wang et al. 2021) through leveled and uniform heating process resulting in higher efficiency of colorant yield (Arain et al. 2021; Phan et al. 2020; Frose et al. 2019). This treatment tunes the fabric surface in such a way that it becomes completely prepared to accept the dye molecule which in turn makes the dyeing rate the highest (Majumder et al. 2021). During conventional heating, heat is transformed to the material surface undergoing several processes (conduction, convection, radiation), which forms it totally a time and energy-consuming process. Microwave is very rapid and uniform, resulting in energy and time-saving process. Another advantage is to reduce the size of equipment and waste and materials (Buyukakinci et al. 2021; Jafari et al. 2019).

In this study, silk fabric dyeing with extracts of spent tea leaves (Fig. 1a) has been investigated under microwave treatment. Tea (*Camellia sinensis*) is an agricultural plant from the Theaceae family that grows in humid climates, and its leaves and buds are used to produce beverages. Tea, which is widely used in the world, also has a high antioxidant feature (Ren et al. 2019; Abdelileh et al. 2021). The powder of tea leaves (Fig. 1b) contains many compounds, such as polyphenols (catechins and flavonoids), amino acids, caffeine, saponins, and volatile compounds (Huang & Liu, 2019), but tannin (Fig. 1c) is the main coloring component which imparts brown color onto fabrics. Its extract reduces the chances of heart attack, regulates the nervous system, and acts also as anti-cancer, anti-bacterial, anti-oxidant, anti-UV agent (Islam et al. 2020). Tannin is the main natural colorant that is being isolated from tea leaves (Singh et al. 2017) and is used to color natural fabrics. Of natural fabric, silk is remembered as the queen of natural fabrics. Silk fabric shows comfortableness, smoothness, softness, luster, breathing ability, and anti-crease characteristics (Haerudin et al. 2020). The main part of silk is fibroin, which contains amido linkage as a functional unit that interacts with mordant and dye to give color.

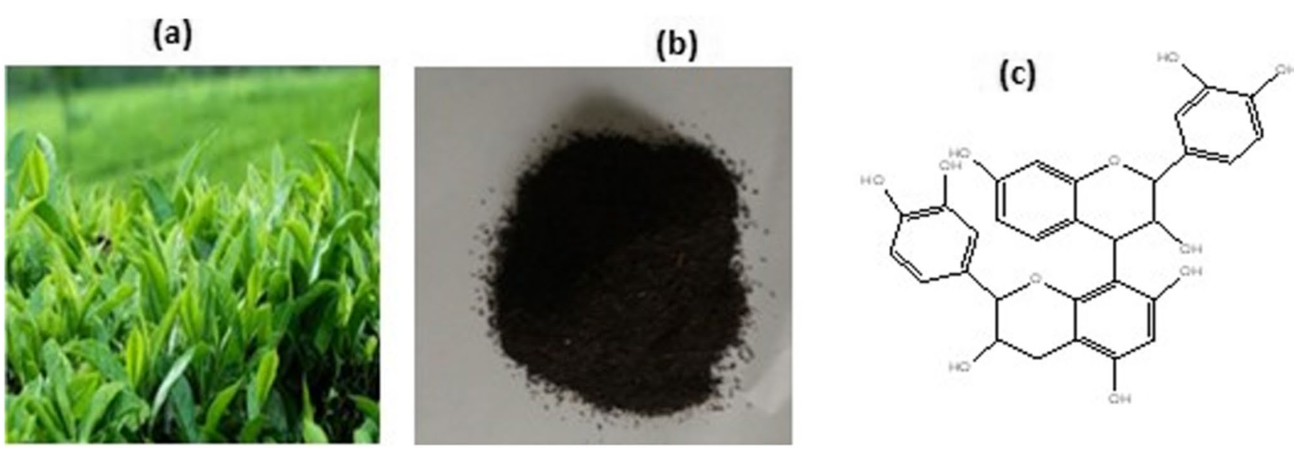


Fig. 1 Tea leaves (**a**), black tea powder (**b**), and tannin (c)

Hence, keeping in view the current scenario, the sustainable use of microwave treatment for isolation and utilization of sustainable bio-mordants for the valorization of natural dyeing process with colorfast shades, the current study has been aimed to achieve the following:

a. Improve the isolation of colorant from waste tea leaves in a suitable medium under the influence of microwave treatment
b. Observe the changes in surface morphology and chemical nature of fabrics before and after microwave treatment through SEM and FTIR analysis respectively
c. Develop new shades with good fastness properties using sustainable chemical and bio- mordants

Materials and methods

Material collection

Commercially available finely ground tea leaves (*C. sinensis*) were obtained from the herbal market Faisalabad. In the same way, sources of bio-mordants such as turmeric rhizomes, pomegranate peels, acacia bark, and henna leaves were treated and stored for further process. Plain white silk fabric procured was washed with neutral soap at 60 °C for 30 min and used for dyeing.

Dye extraction and irradiation process

Using a powder-to-medium ratio of 1:25 (4.0 g), the leaves of *C. sinensis* were boiled with 100 mL of aqueous (neutral), aqueous (alkaline), and aqueous (acidic) media for 45 min for the extraction of natural colorant (tannin). In comparison, using a powder-to-medium ratio of 1:25, methanolic (organic) extract was also prepared by refluxing powder (4.0 g) with 100 mL of solvent for 45 min. Both silk fabric and respective extracts were given MW irradiations for 1, 2, 3, 4, 5, and 6 min, with an interval of 1 min, using Orient Microwave irradiator at high power. After irradiation, MW-irradiated (RE) and un-irradiated extracts (NRE) were used to dye MW-irradiated (RSF) and un-irradiated silk (NRSF) keeping extract to silk fabric ratio (E:SF) of 1:25 at 80 °C for 45 min. The detailed scheme of extraction and dyeing has been presented in Table 1. Two-way ANOVA designed as a statistical tool has been employed to observe the significance of the results.

Optimization of dyeing variables

Dyeing variables have been optimized by utilizing optimum irradiation and extraction conditions. In the first series amount of powder (2–10 g/100 mL) with an interval of 2.0 g/100mL, extract volume (10–50 mL) with an interval of 10.0 mL, and extract pH (1–5) with a difference of 1.0 *p*H have been employed. In another series, for maximum exhaustion, 1.0–5.0 g/ 100 mL with an interval of 1.0 g/100 mL has been employed at given conditions. In another series, the dyeing of silk with optimum tea extract has been done at 55–95 °C with an interval of 10.0 °C for 25–65 min., with a difference of 10.0 min.

Mordanting treatment

For the preparation of plant-based mordants, 1.0–5.0 g of crude powder was boiled with 100 mL of aqueous medium for 45 min, keeping bio-mordant source to an aqueous medium ratio (BM:AM) of 1:25. Three useful chemical mordants (1.0–5.0 g/100 mL) namely salts of Al^{3+}, $(Al_2(SO_4)_3$, and Fe^{2+} $(FeSO_4)$ and 1.0–5.0 g/100 mL of tannic acid (T.A.) were used for producing colorfast shades by following the already-cited methods of Adeel et al. (2021a, b, c).

Optimization of dyed and un-dyed fabrics

Selected extract and silk fabrics before and after irradiation for 5 min were subjected to FTIR analysis for viewing any change in characteristics peak of amido-linkage and tannin. For the surface morphology of silk fabric, SEM images were taken through scanning electron microscopy. The dyed

Table 1 Extraction and coloring conditions for silk fabric using *waste black tea leaves*

Fabric used	Sample code	Microwave irradiation time	Dyeing conditions
Silk	NRE/NRNF	1–6 min	Extraction medium= aqueous, acidic, alkaline, and organic (methanolic)
	RE/NRNF	1–6 min	6 g/100mL waste tea powder (BT)
	RE/RNF	1–6 min	30 mL of extract volume of *p*H=3
	NRE/RNF	1–6 min	for 45 min. at 55 °C, 3g/100mL of table salt
	MAD	1–6 min	

NRE non-radiated extract, *NRSF* non-radiated silk fabrics, *RE* radiated extract, *RSF* radiated silk fabric, *MAD* microwave-assisted dyeing), *BT* black tea leaves fabrics were assessed through Data Color SF 600 and ISO Standards for light (105-B02), washing (105-C03), and rubbing fastness (105-X-12) which were used onto optimum chemical and bio-mordanted dyed fabrics, and the results were assessed at grey scale to get the final rating.

Results and discussion

Effect of radiation on extraction

Microwave treatment has given excellent results by isolating the colorant (tannins) from tea leaves in the aqueous medium (Rabia et al. 2019; Ticha et al. 2021). It has been found that the extract obtained in the aqueous medium (RE) after microwave treatment for 5 min has given good color depth when applied on non-radiated (NRS) silk fabric (Fig. 2a). On changing the medium from aqueous to acidic (Fig. 2b), the results show that the irradiation of silk fabric (RSF) for 6 min has given excellent results when dyed with non-radiated acidic extract (NRE).

During the utilization of alkaline extract, low color depth (K/S) has been observed (Fig. 2c). This is because the actual behavior of the colorant is disturbed because tannin being a natural colorant found in black tea is mildly acidic in nature. Its isolation in a basic medium may cause disturbance in the actual potential of coloration. Also, other phytochemicals such as catechin, epicatechin, and gallic acid are isolated which affects the shade strength (K/S) during the coloration process. Hence dyeing of silk with alkaline extract under microwave treatment (MAD) for 5 min has given excellent results. On changing the medium from aqueous to organic (methanolic), it has been found that the non-radiated silk fabric (NRSF) has given excellent results using irradiated extract (RE) for 6 min (Fig. 3d). Low irradiation time did not isolate the colorant by rupturing the cell wall whereas high irradiation time may have facilitated the isolation of other bio-molecules which may have affected the shade strength during dyeing (Dutta et al. 2021). Hence, the extract irradiated for 5 min may effectively isolate the colorant from tea leaves, which gives high color strength upon dyeing. In comparison, for high color yield, the colorant should be isolated in the aqueous medium followed by microwave treatment for 5 min (RE) and should be used to dye un-irradiated silk fabric (NRS).

Spectral images given in Fig. 3(a, b) reveal that microwave radiation has not changed the chemical nature, i.e., characteristic peak of amido linkage; however, SEM images displayed in Fig. 4(a, b) reveal that after microwave treatment its surface has been scratched. This process has

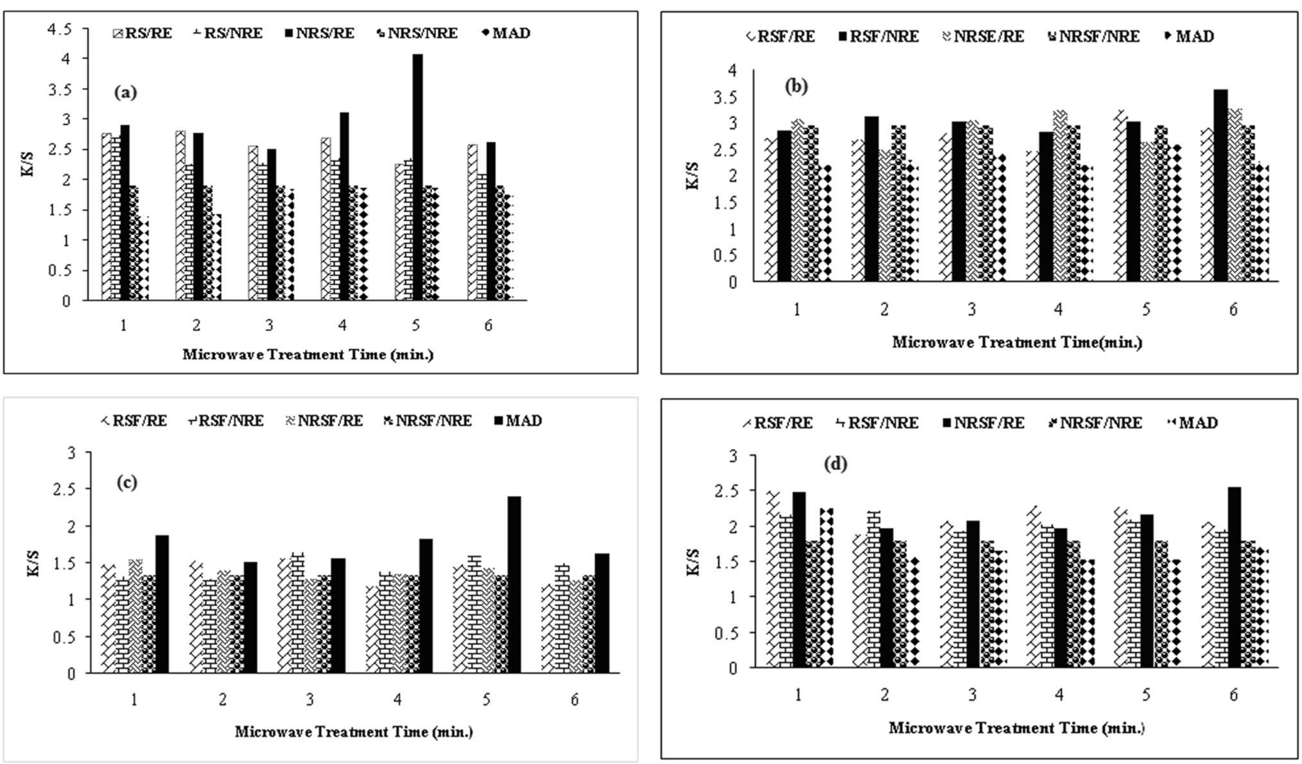


Fig. 2 Isolation of colorant from black tea leaves (BT) in aqueous (**a**), acidic (**b**), alkaline (**c**), and organic (**d**) media and dyeing of silk before and after microwave treatment

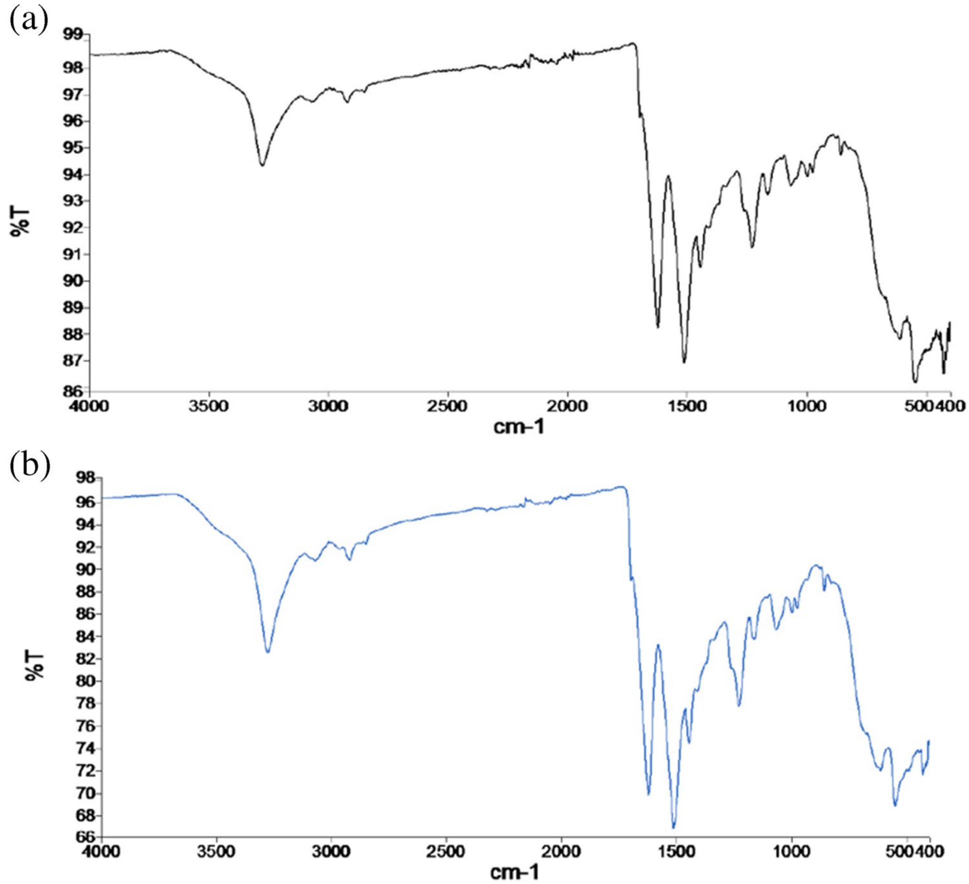


Fig. 3 FTIR spectra of silk fabric before (**a**) and after (**b**) microwave treatment

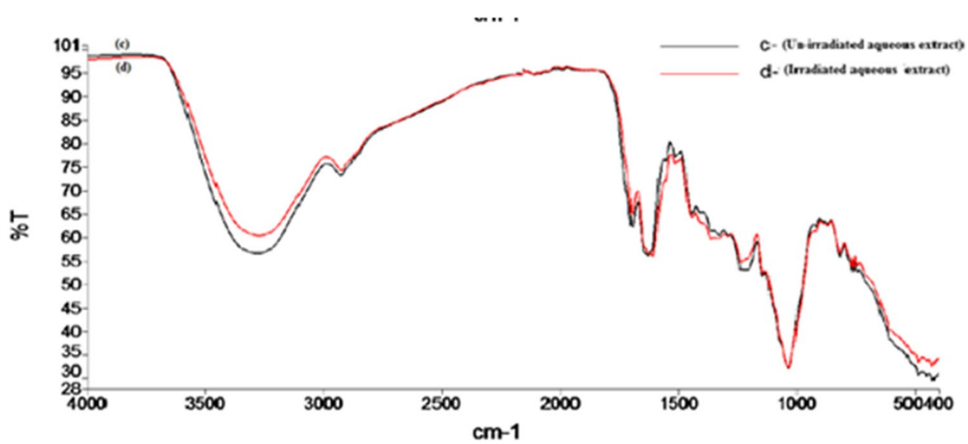


Fig. 4 SEM images of silk fabric before (**a**) and after (**b**) microwave treatment

enhanced its sorption behavior due to which more uptake of colorant in terms of color strength (K/S) has been observed. Also, the FTIR spectrum of aqueous extracts before and after microwave treatment (Fig. 5c, d) shows that tannin is present in black tea leaves whose characteristic peak has also not been changed. Hence, microwave treatment for 5 min to extract and fabric reveal that without harming the physiological nature of colorant (tannin) and without changing the functional nature of silk, this eco-friendly source (MW) has enhanced the colorant yield onto silk fabric.

The color coordinates given in Table 2 indicate that the optimum fabric dyed with aqueous extract is brighter in shade (L^*= 62.65) having more reddish yellow tone (a^*=10.71, b^*= 14.88). Using an acidic medium, the shade is also brighter (L^*= 68.15) in shade with more redder yellow tone in appearance (a^*=14.30, b^*= 17.85). Dyeing using alkaline medium under microwave treatment for 5 min has given brighter shade but with less reddish yellow tone (L^*= 85.85, a^*=3.86, b^*= 7.70). In comparison, using methanolic extract, the shade has moved

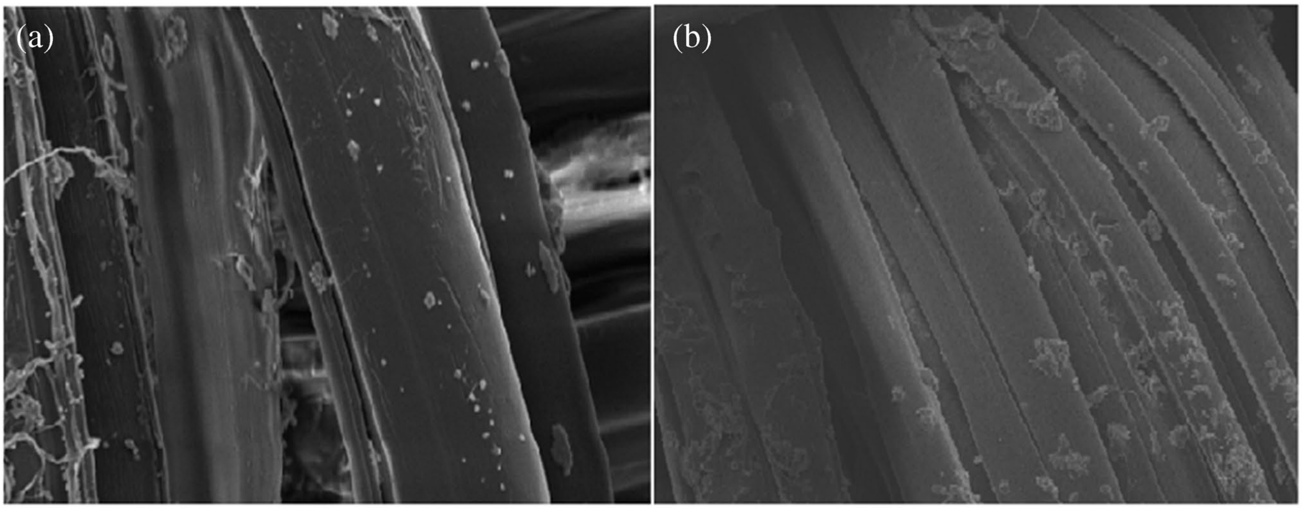


Fig. 5 FTIR spectra of aqueous extract before (**c**) and after (**d**) microwave treatment

Table 2 Color coordinates of selected dyed silk fabrics before and after microwave radiation

Radiation used	Medium used	Optimal condition	*L**	*a**	*b**
Microwave (MW)	Aqueous	NRSF/RE (5min)	62.65	10.71	14.88
	Acidic	RSF/NRE (6 min)	68.15	14.30	17.85
	Alkaline	MAD (5min)	85.85	3.86	7.70
	Methanolic	NRSF/RE (6 min)	80.98	4.58	15.91

NRE non-radiated extract, *NRSF* non-radiated silk fabrics, *RE* radiated extract, *RSF* radiated silk fabric, *MAD* microwave-assisted dyeing, *L**= lighter/darker*;* *a**= redder/green*;* *b**= yellower/ bluish; *BT* black tea leaves

towards less brightness with less reddish but more yellow tone (*L**= 80.98) and less reddish but more yellowish tone (*a**=4.58, *b**= 15.91). It has been found that dyeing of irradiated silk with aqueous extract of tea after microwave treatment for 5min should be done.

Statistical analysis presented in Table 3 shows that irradiation of fabric and extract (sample codes) is highly significant (p= 0.000), whereas the role of other parameters such as temperature, time, and pH is also significant (p= 0.000). Hence, irradiation of fabric and extract to get good yield should be done, whereas selection of parameters should also be done to get acceptable results.

Effect of powder and extract volume

The amount of powder decides the mark of extreme extraction of colorant in terms of color yield (K/S), because the usage of tea powder below optimal level (6 g/100 mL) yields less color strength, whereas its usage above optimal level (6 g/100 mL) may involve other phytochemicals during isolation process which disturbs the coloration process resulting into low color strength (Adeel et al. 2021b). It has been found that from the Fig. 6a that 6g of powder used for the extraction of colorant in 100mL of the aqueous medium

Table 3 Two-way ANOVA as statistical analysis of microwave treatment of silk and black tea (BT) powder extract versus color strength

Source	*Type III sum of squares*	*df value*	*Mean square*	*F value*	*Sig. (p value)*
Corrected model	6.990[a]	9	0.777	8.039	0.000
Intercept	158.758	1	158.758	1643.398	0.000
MW radiation time	.338	5	0.068	.699	0.630
Samplecode1	6.652	4	1.663	17.214	0.000
Error	1.932	20	0.097	-----------	----------
Total	167.679	30	-------------	------------	-----------
Corrected total	8.922	29	------	---------	------

[a]R squared = .783 (adjusted R squared = .686); dependent variable: K/S

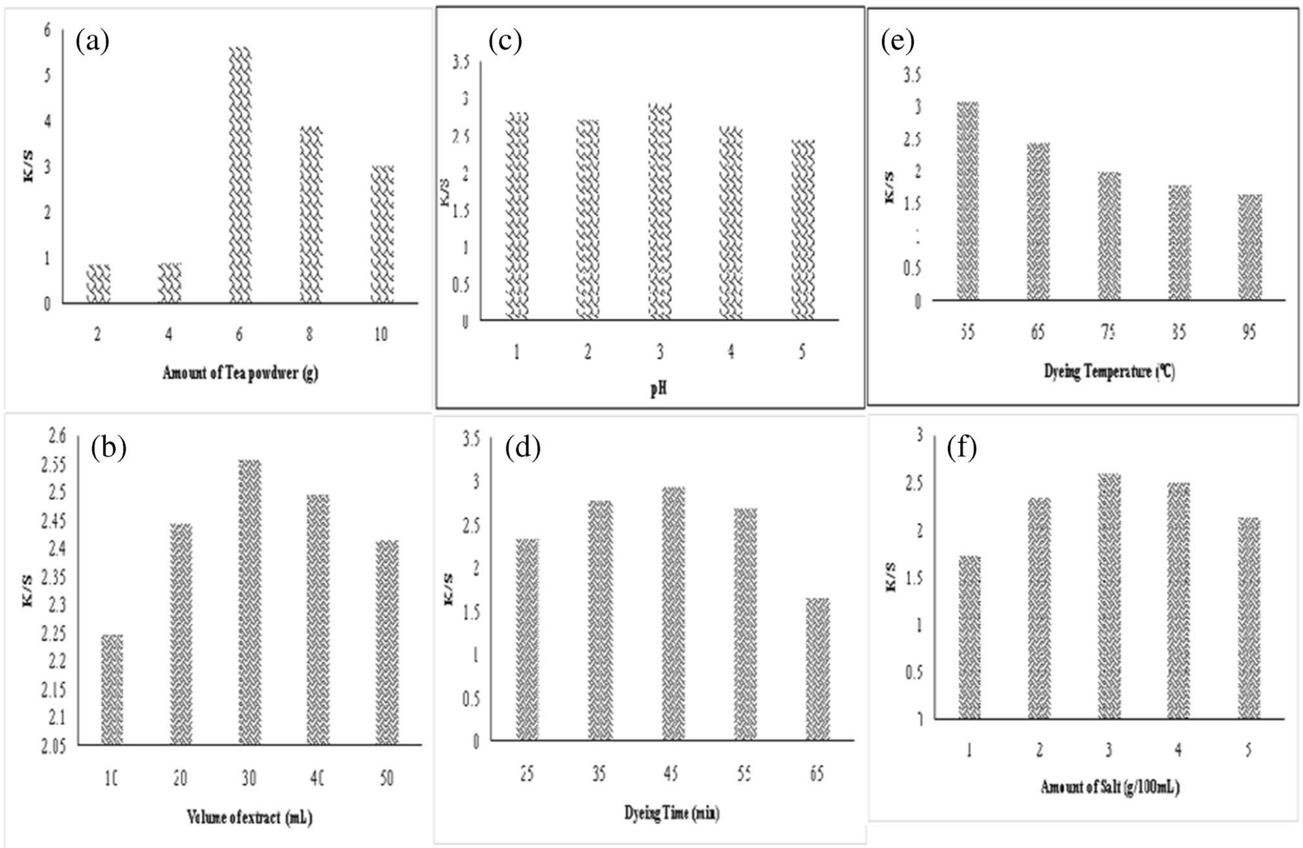


Fig. 6 Optimization of powder (**a**), extract volume (**b**), extract pH (**c**), dyeing time (**d**), dyeing temperature (**e**), and salt amount (**f**) for coloration of silk with microwave-treated aqueous black tea (BT) leaf extract

Table 4 Color coordinates of selected silk fabrics dyed using black tea (BT) powder extract at optimum conditions

Optimum parameters	*Level*	*L**	*a**	*b**
Powder	6 g/100 mL	81.78	5.14	13.06
Extract volume	30 mL	81.76	5.07	13.21
Extract *p*H	3	79.09	6.65	9.46
Salt amount	3 g/100 mL	81.67	1.56	18.43
Temperature	55 °C	69.63	14.81	16.01
Time	45 min.	72.87	11.03	16.40

after microwave treatment for 5min has given excellent color strength onto radiated silk fabric (RSF). The color coordinate data given in Table 4 indicate that the fabric dyed with the aqueous extract obtained from the selected amount of powder (6 g/100mL) is much brighter in shade (*L**= 81.78) having a reddish yellow tone (*a**=5.14, *b**= 13.06). After powder amount, the extract volume was optimized, where it has been found that from that 30 mL of extract obtained from 6 g powder has given high color strength (Fig. 6b). The lab values given in the Table 4 reveal that the fabric dyed with 30 mL of extract obtained from 6 g powder after microwave treatment for 5 min is brighter in the shade (*L**= 81.76) with less reddish but more yellowish tone(*a**=5.07, *b**= 13.21). It can be seen that microwave treatment has reduced the amount of powder and extract volume, which reveals its cost-effective nature.

Effect of extract pH and salt

Dyeing of silk fabric needs an acidic dye bath to sorb the colorant more effectively. This is due to the existence of amino linkage (COOH- and NH_2- group) as a main functional site which interacts with a colorant (Adeel et al. 2021c). It has been found from Fig. 6c that 30 mL of aqueous extract of 3 *p*H obtained from 6 g powder after microwave treatment for 5 min has given excellent color strength onto silk fabric. This is due to the movement toward the alkalinity (pH> 3); the NH_2- group becomes dominant, which leads to weak interlinkage with the –OH group of colorant (Huang and Liu 2019; Wang et al. 2018). From the color coordinate data given in Table 4, it can be seen that the fabric dyed at optimal pH is brighter in shade (*L**= 79.09), having a more reddish yellow hue (*a**=6.65, *b**= 9.46). Salt amount also plays its role to get maximum exhaustion. In this study, it has been found that 3g/100mL of salt (Fig. 6f) was used during dyeing of silk with 30 mL of aqueous extract of *3 pH* obtained from 6 g of black tea powder (B.T.) after microwave treatment for 5 min has given good results. The color coordinates given in Table 4 show that fabric dyed after achieving maximum exhausting is brighter in shade (L^*= 81.67), having less redder but more yellower hue (a^*=1.56, b^*= 18.43).

Effect of contact levels

Dyeing of silk fabric using an aqueous extract of black tea powder (BT) is time-dependent. Coloring for low time gives less tint strength, whereas long contact time may cause movement of equilibrium of coloring process from fabric towards dye bath. In both cases, the firm sorption of colorant onto fabric is not obtained, and after washing, a lot of colorants are stripped, thereby giving lowering tint strength (K/S). The decrease in the dyeing time shows that microwave treatment is time effective tool for silk dyeing. It has been found that from Fig. 6d, when irradiated silk fabric (RSF) is dyed with irradiated aqueous extract for 45 min., maximum color strength is obtained. Lab values given in Table 4 show that the fabric dyed for 45 min is brighter in shade (L^*= 72.87) having reddish yellow tone (a^*=11.03, b^*= 16.40). Similarly, apart from contact time, in the dyeing of silk, dyeing temperature (heating) is also an essential parameter because the optimum temperature established the equilibrium in the dye bath to give excellent color strength (K/S). A low heating level may lead to less sorption of colorant onto fabric, while a high heating level may cause either desorption or hydrolytic degradation of colorant (Kovačević et al. 2021; Nonso et al. 2019). It has been found that dyeing of fabric for 45 min at 55°C using 30 mL of aqueous extract of 3pH containing 3g/100mL of salt as an exhausting agent has given good results (Fig. 6e). Lab values given in Table 4 show that the fabric dyed at 55°C for 45 min is darker in shade (L^*= 69.63), having more reddish yellow tone (a^*=14.81, b^*= 16.01). Again, it can be seen that microwave radiation has reduced dyeing time and heating level, which shows its time and energy effective nature for dyeing of silk with plant materials

Effect of bio-mordants

The results displayed in Fig. 7 (a) reveal that silk fabric pre-mordanted with 1% henna leaves extract followed by bio-coloration has given good color depth (K/S) and good to better fastness properties. Henna leaves have colorant Lawson which utilizes its functional sites (–OH and –C=O group) interact with amido linkage of fabric and –OH of tannin present in tea leaves via additional H–bonding to give firm shades (Martınez-Ramos et al. 2020; Adeel et al. 2021d). The proposed general interaction of bio-mordant with fabric amide linkage and OH of tannin from tea leaves has been displayed in Fig. 8a. The lab values given in Table 5 reveal that samples treated with 1% henna leaves extract before dyeing are lighter in shade (L^*=71.81) and less redder (a^*=9.23) but more yellower (b^*=12.16) in hue. Similarly, during post mordanting, fabric treated with 3% henna leave extracts after dyeing is brighter (L^*=67.88) in shade but more redder (a^*=13.91) and yellower (b^*=16.02) in hue and has given good color strength (Fig. 7b). For meta-mordanting, it has been observed that the addition of 4% henna leaf extracts during dyeing has given better color strength (Fig. 7c) and good colorfastness properties. The lab values presented in Table 5 reveal that fabric dyed during the addition of henna extract is looking darker (L^*=80.96) in shade but less redder (a^*= 12.71) and much yellower (b^*= 15.96) in hue. Turmeric is another bio-mordant having curcumin that has been employed in these studies. It has been found that fabric impregnated with 3% turmeric extract has good color strength with acceptable fastness characteristics (Fig. 7a). The color coordinates given in Table 5 show that 3% pre-mordanted sample with turmeric is much brighter (L^*=76.61) in shade and less-redder (a^*=7.23) but excellent yellow (b^*=39.02) in hue. The application of 2% turmeric extract after dyeing has also given good color characteristics (Fig. 7 b), where color coordinates given in Table 5 show that dyed fabrics are also brighter in shade (L^*=74.78) and less-redder (a^*=3.79) but more yellow (b^*=26.88) in tone. The addition of 4 % turmeric extract during dyeing (meta) has given good results (Fig. 7c), whereas color characteristics reveal that fabric dyed after meta-mordanting is brighter in shade (L^*=75.39), having less-redder (a^*=4.31) but more-yellower (b^*=35.09) hue. The reason is the same as discussed in our previous work that curcumin utilizes its –OH group as a functional site to bind with amide linkage of silk and –OH of colorant (tannin) from tea leaves to give acceptable results (Huang and Liu 2019).

Acacia (*Acacia Nilotic*) is said to be the evergreen natural source which has excellent herbal characteristics due to the presence of quercetin which interacts with colorant and fabric to develop firm shades with good to excellent color characteristics. It has been found that application of 2% acacia bark extract before dyeing has given good color strength (Fig. 7a) with brighter shades but less redder and more yellow hue (L^*=77.01; a^*= 9.12; b^*=18.91). In comparison, the utilization of 4% of acacia bark extract after dyeing has given high color strength (Fig. 7b) with a little darker shade (Table 5) having a yellowish red tone (L^*=69.23; a^*= 12.91; b^*=18.39). Similarly, the addition of 2% of acacia bark extract during dyeing has also produced good color yield onto fabric (Fig. 7c) with a darker shade (Table 5) having yellowish red tone (L^*=65.68; a^*= 12.89; b^*=15.02). Pomegranate is also considered an excellent bio-mordant as well as a dye source. It contains tannin called punico-tannic

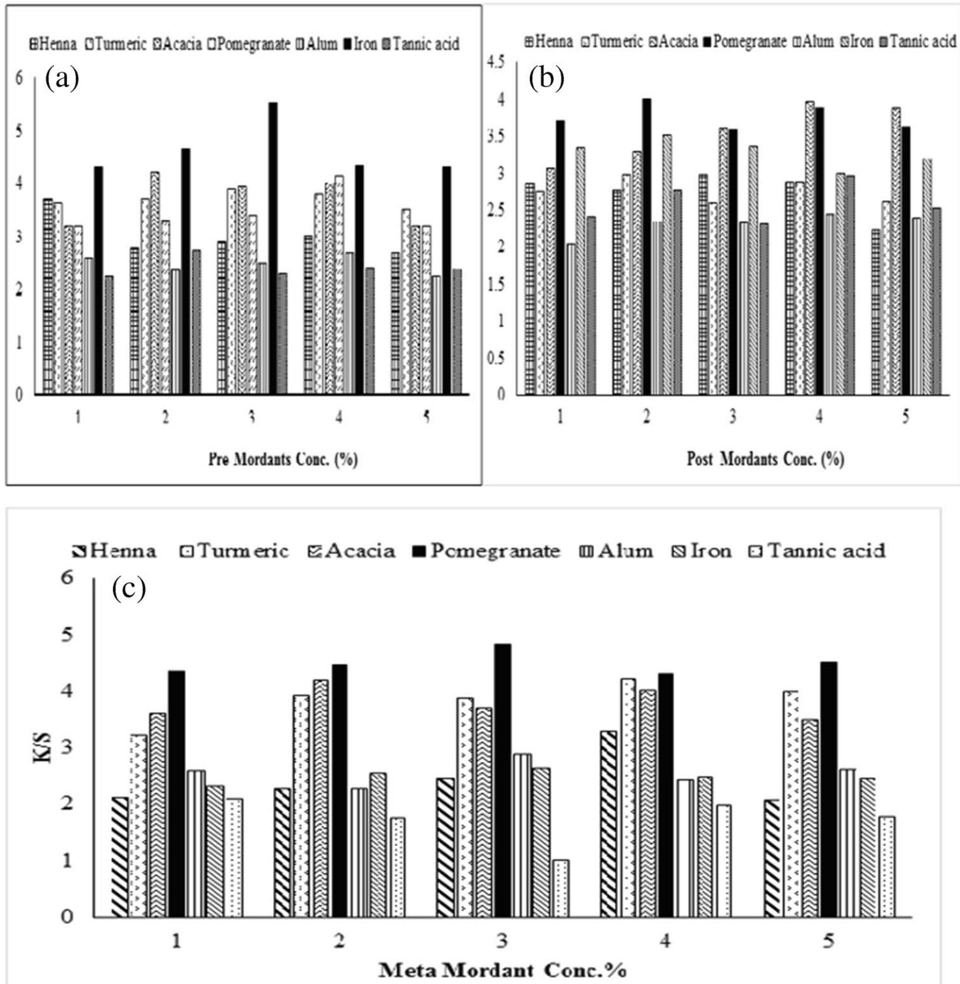


Fig. 7 Utilization of sustainable chemical and bio mordant before (**a**), after (**b**), and during (**c**) dyeing of silk with microwave-treated aqueous black tea (BT) leaf extract

acid which has the ability to act as both mordant and dye. The results given in Fig. 7a show that application of 4% pomegranate extract before dyeing has given good color strength with bright shade (Table 5) having more reddish yellow tone (L^*=75.23, a^*=8.89, b^*=17.61). The addition of 2% pomegranate extract after dyeing has also given good color yield (Fig. 7b) with less redder (Table 5) but more yellow tone (L^*=71.98, a^*=8.99, b^*=21.89). In comparison, the addition of 3% of pomegranate extract during dyeing has also given good results (Fig. 7c) with brighter shade (L^*=74.81) having a reddish yellow tone (a^*=8.52; b^*=23.41).

Effect of chemical mordants

Aluminum is considered a good chemical mordant because of its ability to give brighter and stable shades (Huang and Liu 2019). The color coordinates given in Table 6 reveal that the application of aluminum salt solution (4% Al) before dyeing has given brighter shades (L^*=76.89), having a reddish yellow tone (a^*=6.04; b^*=8.15). Similarly, upon utilization of aluminum salt solution (2% Al) after dyeing of the fabric, the shade obtained is too much brighter (L^*=83.18), having a reddish yellow tone (a^*=5.34, b^*=9.88). In comparison, the application of aluminum salt solution (3% Al) during dyeing of silk with tea extract at optimum conditions, the shade obtained was pretty brighter (L^*=82.82), with a reddish yellow hue (a^*=6.43; b^*=9.98). Overall, it has been found that when Al used as meta-mordant gives better color strength as compared to pre- and post-mordanting (Fig. 7c).

Iron is said to be one of eco-friendly mordants because it neither causes any carcinogenic effect on the environment nor disturbs fabric chemistry except making shade darker or dull via metal-dye complex formation through a coordinate covalent bond (Islam et al. 2020). The results given in Fig. 7a reveal that application of iron salt (3% Fe) before dyeing has given excellent color strength onto silk fabric, whereas the color coordinates given in Table 6 show that dyed fabric is darker (L^*=58.55) in shade with less-redder (a^*= 4.71) but more yellow tone (b^*=13.47). During post-mordanting (Fig. 7 b), it has been found that the utilization of iron salt (2% Fe) has given good color strength, whereas

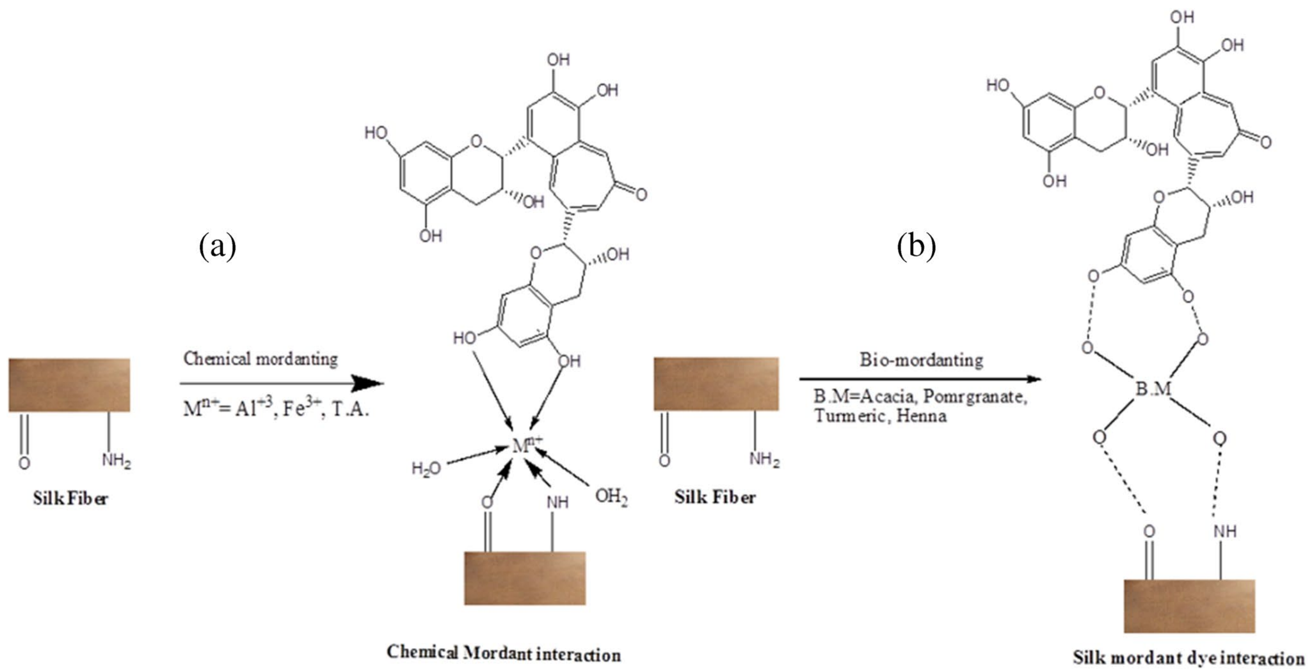


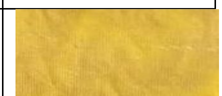
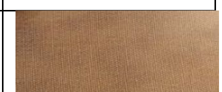
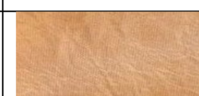
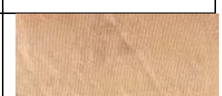
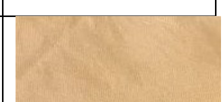
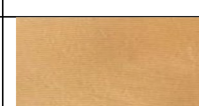
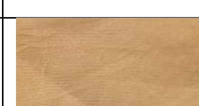
Fig. 8 Proposed interactions of chemical (**a**) and bio-mordant (**b**) with dye and fabric

lab values given in Table 6 show that the sample dyed after mordanting is less-darker (L^*=66.53) in shade and less-redder but more-yellower in hue (a^*=4.88, b^*=8.92). In comparison, the application of iron slat (3% Fe) during dyeing has given better color strength (Fig. 7c) whose shade analysis shows that the shade is brighter (L^*= 72.80) with a bluish greener tone (a^*= 2.17, b^*= 3.71). Hence, the utilization of iron salt (3% Fe) before dyeing silk with tea extract at selected conditions has given high color strength with darker shades having reddish yellower tone.

Tannic acid is another one of the good sustainable and eco-friendly chemical mordant used for dyeing fabrics, because tannin plays a major role in developing shade through H– bonding. The results displayed in Fig. 7a show that the application of tannic acid (2% pre) before dyeing has given high color strength, whereas the shade analysis given in Table 6 show that dyed fabric darker (L^*= 71.98), having reddish yellow (a^*= 7.61; b^*= 5.79) tone. The application of tannic acid after dyeing (4 % post) has given good color strength (Fig. 7b) with a brighter shade (L^*=77.35) having a reddish yellow tone (a^*= 7.76, b^*= 12.86). In comparison, the application of tannic acid (1%) during dyeing better color strength has been achieved (Fig. 7c), where the shade analysis displayed in Table 6 shows that meta mordanted fabric is much brighter in shade (L^*= 83.17) having a greenish blue (a^*= 5.04, b^*= 5.78) tone. Hence, the utilization of tannic acid (2% TA) before dyeing of silk with tea extract at selected conditions has given high color strength with darker shades having reddish yellower tone. The proposed metal-dye interaction with amido linkage of silk fabric has been displayed in Fig. 8b. It can be seen that microwave radiation has also reduced the amount of mordants used before, after, and during dyeing of silk with tea leaves extract and has produced firm shades, which again shows that this sustainable tool (MW-rays) is cost-effective in nature.

The fastness ratings for pre, post, and meta mordanting displayed in Tables 5 and 6 show that chemical mordants via firm bonding onto silk fabric through complex formation have given good to excellent properties. Light fastness depends upon mode of interaction as between –OH of colorant and amido linkage (–CO, $-NH_2$) of silk and nature of metal used (Dulo et al. 2021; Hosen et al. 2021). So coordinate bond is formed by metal (Al and Fe) or H-bonding between –OH of tannic acid and amido linkage (–CO, $-NH_2$) of silk and –OH colorant as a bridge to hinder the color to fade. Similarly, such bonding also shows a good to excellent resistance for detergents and corrosion. Hence, chemical mordanting before and after dyeing at optimal conditions gives acceptable fastness characteristics. Bio-mordants are newly developed tools for the introduction of new shades and improving fastness properties. It has been found that functional active molecules present in pomegranate, i.e., tannin, Lawson in henna, and curcumin in turmeric used as pre, post, and meta mordants, give new shades with an excellent rating. This is due to extra H-bonding which may be formed by interaction of functional site of bio-mordants, amido

Table 5 Color analysis of silk fabric dyed with waste tea leaves extract before, after, and during bio-mordanting

Mordant used	*Optimal condition*	*L**	*a**	*b**	*LF*	*WF*	*DRF*	*WRF*	Dyed Mordanted Fabrics
Turmeric (*Curcuma longa* L)	3% Pre	76.61	7.23	39.02	5	4/5	5	4/5	
	2% Post	74.78	3.79	26.88	5	5	5	4/5	
	4% Meta	75.39	4.31	35.09	5	5	5	4/5	
Henna (*Lawsonia inermis*)	1% Pre	71.81	9.23	12.16	5	4/5	5	4/5	
	3% Post	67.88	13.91	16.02	5	4/5	5	4/5	
	4% Meta	80.96	12.71	15.96	5	4/5	5	4/5	
Acacia (*Acacia nilotica*)	2% Pre	77.01	9.12	18.91	5	5	5	4/5	
	4% Post	69.23	12.91	18.39	5	5	5	4/5	
	2% Meta	65.68	12.89	15.02	5	5	5	4/5	
Pomegranate (*Punica granatum* L)	4% Pre	75.23	8.89	17.61	5	5	5	4/5	
	2% Post	71.98	8.99	21.89	5	5	5	4/5	
	3% Meta	74.81	8.52	23.41	5	5	5	4/5	

*L**= lighter/darker; *a**= redder/green; *b**= yellower/ bluish; *LF* light fastness; *WF* wash fastness; *DRF* dry rubbing fastness; *WRF* wet rubbing fastness

linkage (–CO, $-NH_2$) of silk, and –OH of colorant (Hosseinnezhad, et al. 2021b; Wang et al. 2018). Thus, the color after mordanting becomes deeper and shows less resistance, which might be attributed to the metal complex formation between metal, dye, and their covalent binding with fibers (Adeel et al. 2021b; Khan et al. 2021). It has been observed that without mordanting on light exposure, the colorant may take photolytic degradation and results in low rating. Hence, overall bio-mordanting in comparison with chemical mordanting shows a good rating of fastness.

Table 6 Color analysis of silk fabric dyed with waste tea leaves extract before, after, and during chemical mordanting

Mordant used	*Optimal condition*	*L**	*a**	*b**	*LF*	*WF*	*DRF*	*WRF*	*Dyed-Mordanted Fabrics*
Al^{3+} (Potash Alum)	4% Pre	76.89	6.04	8.15	5	5	5	4/5	
	2% Post	83.18	5.34	9.88	5	5	4/5	4	
	3% Meta	82.82	6.43	9.98	5	5	4/5	4	
Fe^{2+} (Iron sulphate)	3% Pre	58.55	4.71	13.47	5	4/5	4/5	4	
	2% Post	66.53	4.88	8.92	5	4/5	4/5	4	
	3% Meta	72.80	2.17	3.71	5	4/5	4/5	4	
T.A. (Tannic Acid)	2% Pre	71.98	7.61	5.79	4/5	4/5	4/5	4	
	4% Post	77.35	7.76	12.86	5	4/5	4/5	4	
	1% Meta	83.17	5.04	5.78	5	4/5	4/5	4	

*L**= lighter/darker; *a**= redder/green; *b**= yellower/ bluish; *LF* light fastness; *WF* wash fastness; *DRF* dry rubbing fastness; *WRF* wet rubbing fastness

Conclusion

Plant-based potential molecules as natural colorants are currently gaining fame, where the valorization of waste materials under the effect of sustainable isolation tools such as microwaves is on the way. Spent tea leaves as a source of natural tannin brown dye for silk coloration have been explored. It has been found that 30 mL of aqueous extract of 3.0 *p*H obtained from 6 g of powder containing 3.0 g/100 mL of salt as an exhausting agent after microwave treatment for 5 min when employed at 55 °C for 45 min., has given excellent results onto irradiated silk (RSF). Also, the introduction of plant-based mordants as an alternative to toxic chemical anchors has been employed to develop soothing shades with improved fastness characteristics. It is recommended that waste materials such as leaves, dried flowers, barks, seeds, and roots of plants should be explored as a source of natural dyes for textiles under sustainable isolation sources such as microwaves, ultrasonic, plasma, and the inclusion of herbal-based mordants along with sustainable chemical mordants should also be employed for getting soothing and sustainable shades with good fastness.

Author contribution Dr. Shahid Adeel is the supervisor, where Dr. Fazal-ur-Rehman has co-supervised the work of M.Phil studies. Mr.

Tayyab Hayat and Ms. Nimra Amin have conducted the experiments. Dr. Fatima Batool has analyzed the dyed fabrics and Dr. Meral Ozomay analyzed the extract and fabrics through FTIR and SEM techniques. The significance of the method utilized in this study was statistically analyzed by Dr. Tanvir Ahmad.

Availability of data and materials The whole data is present in M. Phil thesis.

Declarations

Ethics approval We approve that this manuscript is part of M. Phil studies.

Consent to participate and publish We give consent to publish our work of M. Phil studies, which is jointly contributed by all authors.

Competing interests The authors declare no competing interests.

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