Microwave-Assisted Appraisal of Neem Bark Based Tannin Natural Dye and Its Application onto Bio-Mordanted Cotton Fabric

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ABSTRACT: *The current study is aimed to utilize the microwave for isolation of colorant from neem bark and its application onto chemical & bio-mordanted cotton fabric. For the purpose aqueous, acid and organic media have been employed to isolate the colorant and to make its application onto surface modified and bio-mordanted cotton fabric followed by microwave treatment up to 6 min. It is found that using optimum extraction and dyeing conditions, acceptable fastness properties have been rated when 9% of Al & 7% of Fe & tannic acid as pre chemical, 7% of acacia & pomegranate, 9% of henna & 5% of turmeric extract as pre bio-mordants were employed. Similarly, 5% of Al & Fe, 9% of T.A as post-chemical, 7% of pomegranate & 9% of turmeric, acacia & henna extracts as post bio-mordants has given acceptable fastness ratings. It is recommended that isolation of colorant & dyeing under MW treatment has not only improved the natural dyeing process but also the addition of herbal-based bio-mordants have made the dyeing process more sustainable & ayurvedic. So it is concluded that microwave treatment has not only explored the coloring potential of neem bark but also made possible use of bio-mordants for making process greener with excellent color characteristics under reduced optimal conditions.*

KEYWORDS: *Bio-Mordant; Cotton; Microwave Radiation; Neem Bark; Tannin.*

INTRODUCTION

Currently worldwide environmental concerns have developed a special interest among buyers, consumers and traders for eco-friendly textiles [1-3]. This is as a result of inflexible environmental standards imposed

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by many countries in a response to the toxic and allergic reactions associated with synthetic dyes [4]. No doubt, the bright and cheerful shades of synthetic dyes fascinate the human eye but, one must remember the bitter fact of synthetic dyed products and their effluents that cause alarming issues to global community and ecosystem [5- 7]. Natural dyes comprise the colorants which are obtained from natural sources without any chemical procedure [8, 9]. Around the globe, today natural dyes have captured all attention of researchers as they indeed exhibit anti-oxidant, anti-allergic, superior biodegradability and eco-friendly properties [10-13]. Due to having wide range of shades and harmonized nature, natural dyes have revolutionized the world of textiles, cosmetics and medicines [14-19].

However, these natural colorants are facing more problems like less extract yield and poor fastness properties. Researchers are trying to modify the extraction and dyeing process either by improving the isolation process or by tuning the fabric through modern technique. A lot of modern methods for extraction and modification of fabric surface such as gamma radiation [20], ultrasonic radiation [21- 23], microwave radiation [24, 25], plasma radiations [26, 27] and ultraviolet radiation [28, 29] and cationization [30, 31] and enzyme treatment [32, 33] have been employed.

However, among these methods microwave treatment is a clean, uniform, volumetric, levelled and selective heating source which shows an easy penetration of colorant by following the principle of mass transfer kinetics [34, 35]. Previously, it has been above found that microwave radiation enhances the dyeing process by increasing the diffusion and sorption of colorant [36, 37]. It not only strengthens the color depth in short period and increases the color affinity but also reduces process time, energy and effluent load. These advantages have compelled the researchers to use microwave radiation in isolation of colorant and in tunning fabric surface for enhancing the uptake ability and color characteristics [38].

For current study, neem bark (*Azadirachta indica*) has been selected for exploration as a source of natural colorant (tannin) for cotton dyeing. Neem bark is a real blessing of God for a human society as it provides a variety of functional properties such as anti-oxidant, anti-allergic, anti-carcinogenic etc. [39]. Being the most useful, traditional and medicinal plant, it is considered as the village dispensary and the nature's medical store. Due to its miraculous biological activity to cure viral, bacterial, allergic, carcinogenic, mutagenic, diabetic, ulcer and tumor infections, its bark is one of the essential parts of ayurvedic system [40]. Its bark has biological active components such as protein, glycosides, saponin, flavonoids, steroids, anthraquinone, alkaloids, minerals, polysaccharides, phenols, terpenoid, etc. [41]. The Neem bark also contains tannin as the main coloring agent (Fig.1), which can be used for coloration of textiles [42- 44].

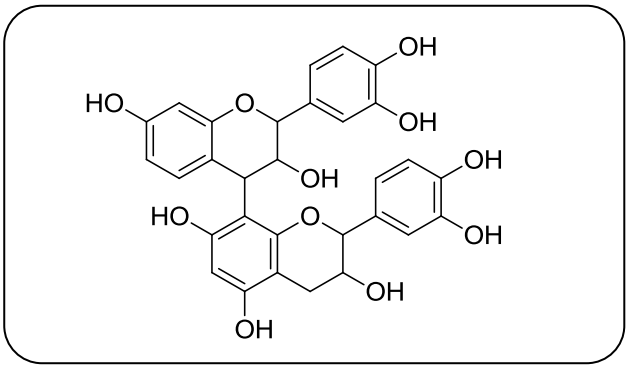

Fig. 1: Neem bark (tannin).

To authors knowledge no such detailed work has been done on exploration of neem bark as a source of natural tannin dye for coloration of cotton. Our research is a complete study, starting from microwave assisted isolation of colorant, optimization of dyeing variables and mordanting process followed by evaluation of color characteristics. Under optimal conditions, the addition of herbal based bio mordants to improve the color characteristics has given a new way to researchers, readers and the traders to make dyed fabric more therapeutic.

EXPERIMENTAL SECTION

Material collection

Barks of neem plant (*Azadirachta indica*) were procured from Jhang Bazar of Faisalabad, cleaned with water to remove the dust and dried. Dried barks were chopped into small pieces and were subjected to grind followed by sieving to get equal particles size powder. Pretreated cotton was provided by Harris Dyes and Chemicals, cut into small pieces (1 g each) and washed with non-ionic detergent at 60 ^{o}C for 30 min and dried in oven. Commercial available chemicals were used for extraction, dyeing and mordanting. Four eco-friendly

sources of bio mordants such as Turmeric rhizomes (*Curcuma longa*) containing curcumin, Henna leaves (*Lawsonia inermis*) containing lawson, Accacia bark (*Accacia nilotica*) containing quercetin and Pomegranate peels (*Punica granatum*) containing tannin were also obtained from local herbal market of Faisalabad.

Isolation of dye and irradiation process

Six states of solvents such as (aqueous, alkaline, acidic, methanol, acidify method and basic methanol basic) have been employed for isolation of colorant (tannin) from neem bark by heating 4 g of powder with 100 mL of respective solvent at boiling for 60 min, keeping solid to solvent ratio of 1:25. Upon boiling, the respective mixtures were filtered through fine cloth and cooled under air open. Extracts and cotton were irradiated for 1,2, 3, 4, 5 and 6 min using microwave irradiator of Orient (power of 220 V and frequency of 450 MHz). For achieving maximum color strength, irradiated (RC) and un-irradiated (NRC) fabric were dyed separately for 60 min keeping fabric to liquor ratio of 1:25 using irradiated (RE) un-irradiated extract (NRE). For comparison, Microwave Assisted Dyeing (MAD) was also carried out in microwave oven for 1-6 min. After dyeing all samples were hot and cold washing three times to remove any unfixed dye and subjected for evaluation in CIE lab system computed in data color (spectra flash SF 600).

Optimization of dyeing parameters

After getting optimal extraction condition, it is necessary to find out amount of powder used for isolation of colorant in optimal solvent. For the purpose, 2, 4, 6, 8 and 10 g of powder was used to isolate the colorant in acidic medium at boiling for 60 min. keeping solid to liquor ratio of 1:25. In another set, volume of dye bath was investigated by keeping 20-70 mL of acidic extract under microwave treatment for 4 min. As colorant is acidic in nature, so *p*H of dye bath was also evaluated by using extract of 1-7 *p*H for dyeing. To achieve maximum exhaustion, 1-10 g/ 100 mL of Table Salt (T.S) and Glauber's Salt (G.S) have been employed.

Effect of bio and chemical mordants

For making dyeing of cotton more sustainable, bio-mordanting process was used. For the purpose curcumin from turmeric, Lawson from henna, quercetin from acacia, tannin from pomegranate was isolated by following already documented method. For the purpose 1,3,5,7,9,10 g of respective powder was used to isolate the bio-mordanting from reproductive source, keeping powder to solvent (aq) ratio of 1:25. For comparison of bio-mordanting, three sources of ecofriendly chemical mordants such as Al (Posh Alum), Fe ($FeSO_4$) and tannic acid have been employed keeping 1-10% at given conditions.

Evaluation of color characteristic of dyed fabric

Surface morphology of irradiated (RC) and un-irradiated fabrics (NRC) have been analyzed using scanning electron microscopy (SEM). Finally, the color strength (K/S), L, a and b values of all dyed fabrics has been investigated in CIE Lab system computed in spectra flash SF 600 with an illuminant of D 65 10^o observer at Department of Chemistry Govt. College University Faisalabad, Pakistan. The rating for colorfastness properties of the optimum dyed fabrics has been evaluated using ISO standard methods. ISO 105-B02 for light, ISO 105-X12 for rubbing, ISO 105 C03 for washing fastness, and ISO 105 D01 for dry clean fastness, at quality control Laboratory of Noor Fatima Textile (PVT) Faisalabad, Pakistan has employed [41].

RESULTS AND DISCUSSION

Effect of microwave radiation on extraction of colorant

Microwave assisted extraction and dyeing is now a day gaining wide spread popularity because it not only saves energy, time and solvent consumption but also via mass transfer kinetics gives excellent color characteristics reference [45]. The result given in (Fig. 2a), using extract in aqueous medium show that microwave assisted dyeing (MAD) for 5 min has given good color strength. Upon changing medium from aqueous to acidic, it is found, microwave assisted dyeing (MAD), for 4 min has also given excellent results given in (Fig. 2a, 2b). Similarly upon using extract obtained in alkaline medium the irradiation for 2 min. has given good color strength onto un-irradiated fabric (NRC) in (Fig. 2c). Hence, among aqueous media (acidic, alkaline, aqueous) used, acidic medium has been found good when dyeing of cotton under microwave treatment (MAD) for 4 min. In other series, when media is changed from aqueous to organic,

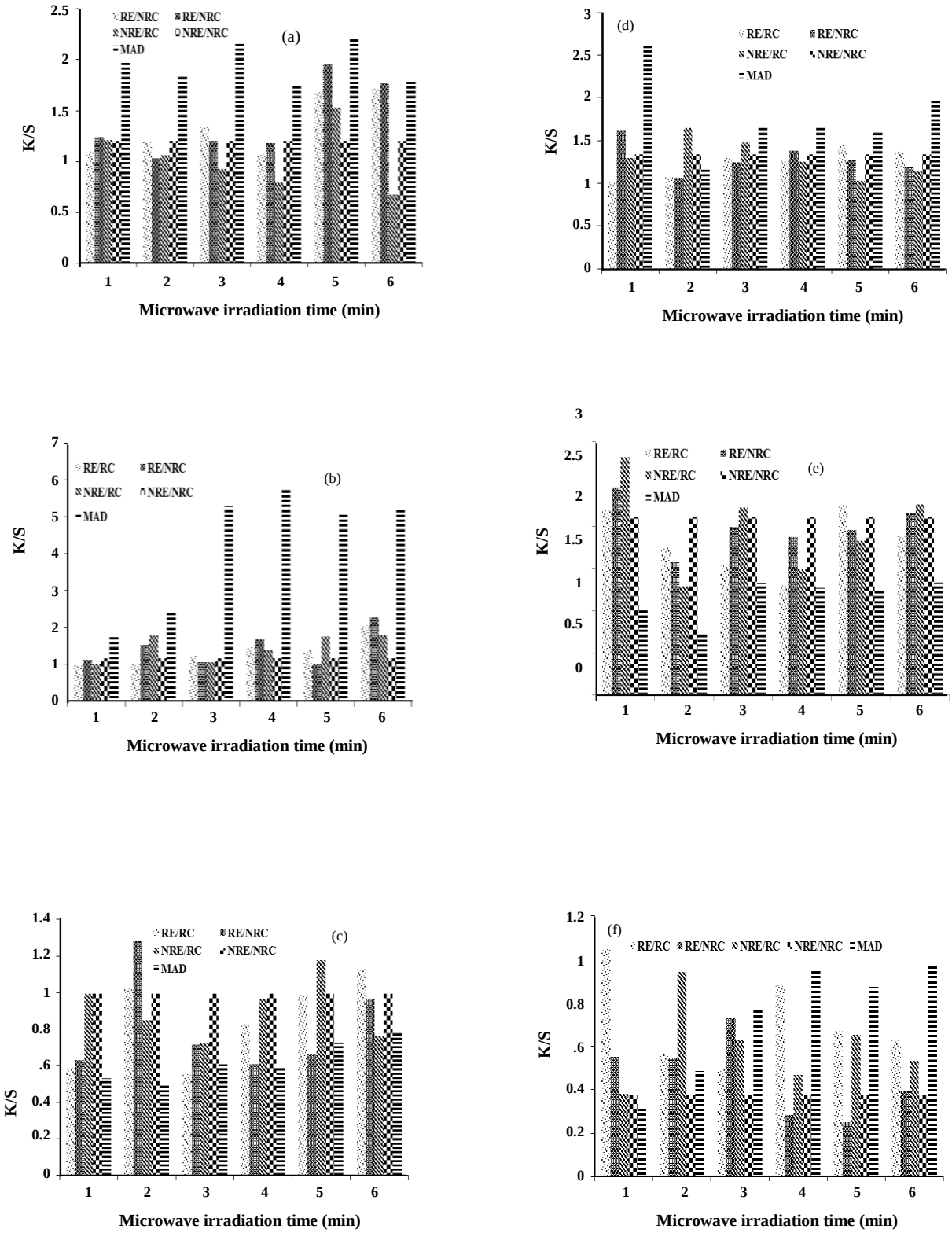

Fig. 2: Effect of microwave treatment on aqueous (a), acidic (b), basic (c) methanolic (d), acidified methanolic (e) and basic methanolic (f) extraction of colorant from neem bark.

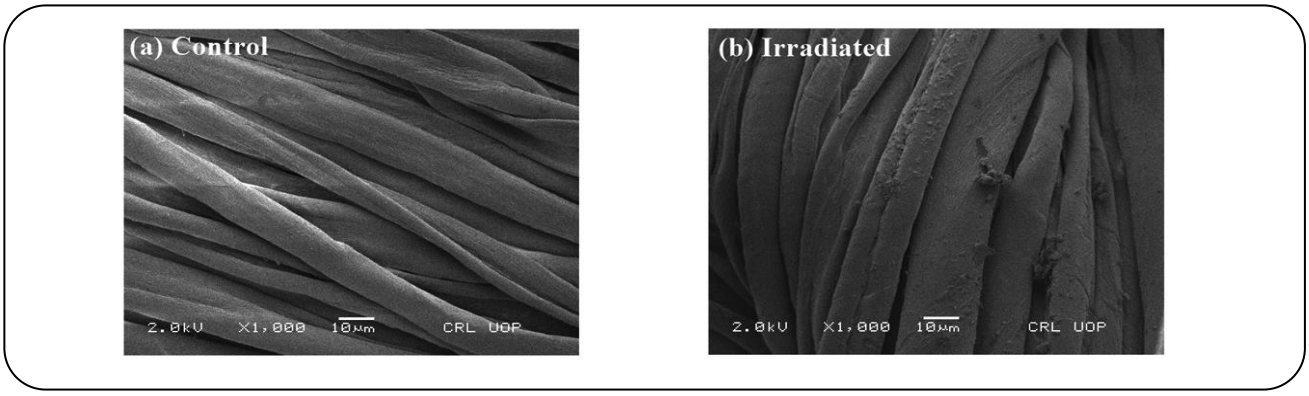

Fig. 3: Effect of SEM analysis on control (a) and irradiated (b) cotton dyed with irradiated acidic extract of neem bark.

the results displayed in (Fig. 2d-2f), reveal that colorant isolated in acidified methanolic medium has given excellent results after microwave radiation for 1 min instead of using acidic methanolic or basic methanolic media. But overall, the Microwave Assisted Dyeing (MAD) for 4 min using acidic extract has given excellent color strength onto fabric. Irradiation for low time does not stimulate the colorant to evolve out from cell wall, whereas for high time irradiation, the other functional moieties are isolated along with the colorant and during dyeing promisingly affect the shade [42]. Irradiation for 4 min. followed by Microwave Assisted Dyeing (MAD) gives high color strength because not only kinetic energy of the system is raised, but also significant diffusion is obtained *via* mass transfer kinetics. Hence, dyeing of cotton using acidify medium under microwave irradiation for 4 min gives acceptable results.

Effect of microwave radiation on surface morphology

Apart from extract, the irradiation of cotton is also important factor as it may modify the fabric, it has been found that MW irradiation has modified the fabric surface in such a way that its absorptivity diffusion efficiency and uptake-ability have been improved [45] upon dyeing under microwave treatment; more color strength has been found. The images of surface of fabric before and after irradiation (Fig.3) taken through scanning electron microscopy (SEM) show the significant changes at surfaces.

Effect of powder amount

In natural dyeing processes, it has been observed that amount of powder has the great influence on the isolation of functional moiety (colorant) in suitable medium

It is found that 8 g of neem bark powder has been optimized

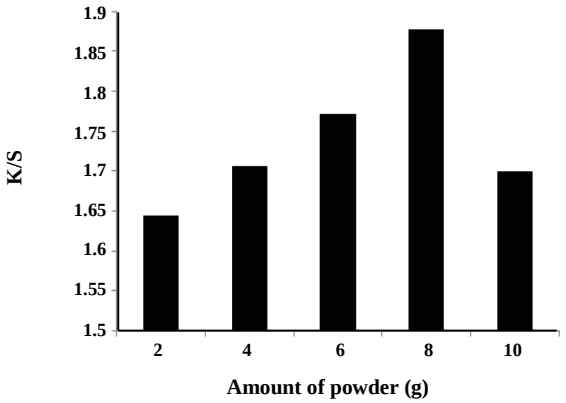

Fig. 4: Impact of powder amount on isolation of colorant from neem bark in methanolic medium.

to isolate the colorant (tannin) in acidic medium as the extract obtained has given good color strength (Fig. 4). Low amount of powder gives the less yield of colorant, whereas above optimal amount, other phytochemicals may also be isolated along with colorant (tannin) which during dyeing affects the color strength. Hence microwave treatment has reduced the amount of powder, which shows that it is cost effective tool.

Effect of pH and volume of dye bath

*p*H of dye bath is very important because the nature of colorant shows its maximum sorption onto fabric. It is found that acidic extract (*p*H 2) of neem bark has given darker shades upon dyeing of cellulose under Microwave Assisted Dyeing (MAD) process (Fig. 5). Upon gradual change in dye bath medium the nature (acidic) of colorant has been disturbed where the tannin may face hydrolysis process in alkaline medium and after dyeing under microwave treatment for 4 min, less K/S is observed.

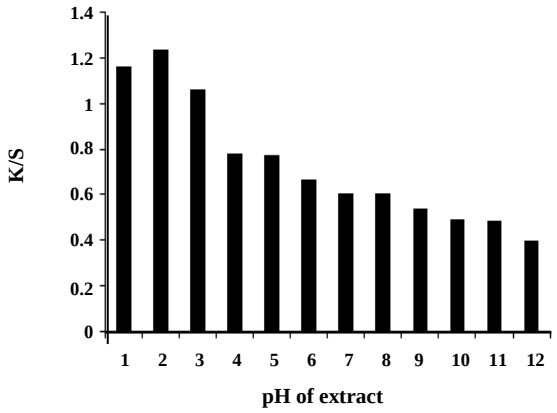

Fig. 5: Impact of extract volume of acidic medium on dyeing of cotton fabrics.

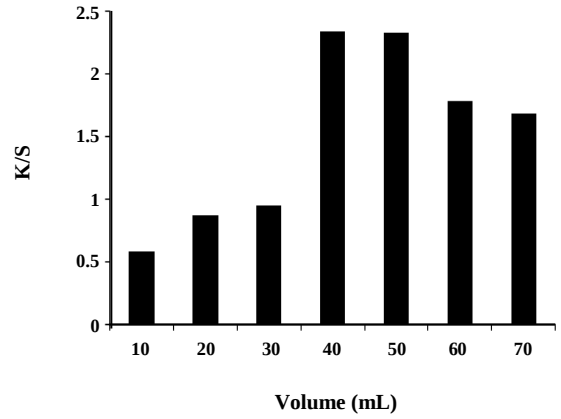

Fig. 6: Effect of exhausting agent on dyeing of irradiated cotton using acidic extract of neem bark.

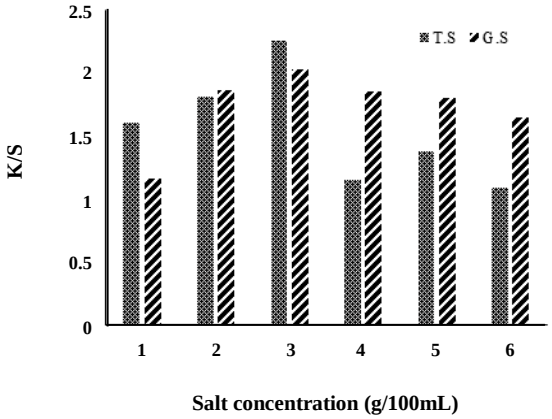

Fig. 7: Effect of pH on dyeing of cotton using acidic extract of neem bark.
(1=1g/100mL; 2=3g/100mL; 3=5g/100mL; 4=7g/100mL;5= 9g/100mL; 6= 10g/ 100mL)

Hence it is observed that dyeing of cellulose should be done in acidic dye bath of 2 pH, which has been taken from 8g of crude powder followed by microwave treatment for 4 min. Volume of dye bath also influence the coloration of cotton fabric under influence of microwave treatment. The results displayed in Fig. 6 shows that 50 mL of acidic extract (pH 2) obtained from 8g of powder after microwave treatment for 4 min has given maximum color strength onto cotton fabric while employing microwave assisted dyeing (MAD) process.

Effect of salt concentration

Similarly, effect of salt the addition of salt as exhaustion agent has played a vital role because it creates the interacting atmosphere between fabric and dye molecules within short range of attractive forces. Low amount of salt does not exhaust well whereas above optimal amount the over exhaustion of colorant may cause. Unevenness or gathering of aggregate at the surface where upon cold and hot washing, the unfix dye is. Hence it is observed that 5 g/100 mL of table salt and Glauber salt (G.S.) has given darker shades, but table salt (T.S.) has given excellent results (Fig. 7). The utilization of reduced amount of Table salt in microwave dyeing show that microwave treatment is cost effective tool.

Effect of chemical and bio mordanting

The results given in Fig. 8 show that among chemical mordants used show that 9% of Al, 7% of Fe and tannic acid (T.A.) has given excellent results. Similarly, among suitable bio mordants, 7% of acacia, 9% of henna, 7% of pomegranate and 5% of turmeric extracts have shown excellent results. This is because the salt contains metal as chemical mordants which form stable metal dye complex onto cotton fabric via covalent interaction [42]. Similarly, the functional moieties present in bio mordants have –OH group which interacts with the –OH of colorant. Terminal –OH of cotton fabric to form strong bond via hydrogen bonding interaction [43]. This extra bonding as well as – conjugated system of bio mordant have enhanced the stability of – in turn improved color strength [21, 46, 47]. Depending upon the dyeing methodologies, during post mordanting, 5% of Fe and Al and 9% of TA have given excellent results. However, as compared to pre- mordants, Al has given low

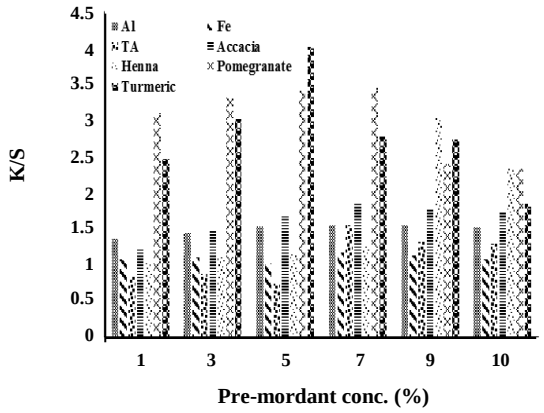

Fig. 8: Effect of pre-bio and chemical mordanting on color strength of irradiated cotton dyed with irradiated acidic extract of neem bark.

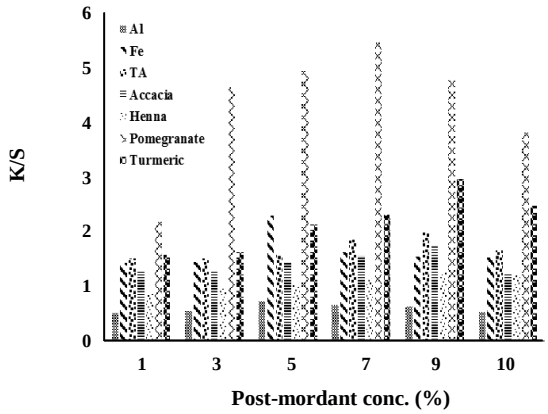

Fig. 9: Effect of post-bio and chemical mordanting on color strength of irradiated cotton dyed with irradiated acidic extract of neem bark.

results where as T.A. has given good results during post mordanting (Fig. 9). Similarly, upon utilization of bio mordants, 9% of turmeric, acacia and henna and 7% of pomegranate has given excellent results. Among mordanting methods, post mordants has given good results. Hence over all bio-mordanting has given excellent results and made the process eco-friendlier and more sustainable.

Rating of color fastness

The rating results given in Table 1 for chemical mordant and Table 2 for bio-mordant reveal that the fastness properties have been improved when neem bark extract is used to dye pre- and post chemical mordanting. The improvement in fastness properties before and after bio-mordanting is due to the presence of extra conjugation and additional H-bonding or covalent bonding with functional group (-OH) and fabric functional site (-OH). Greater the conjugation extension more is the rating and hence lower is the fading of colored fabric. Similarly, excellent fastness properties during chemical mordanting are due to stable metal dye complex formation, even dyeing, nature of metal and potential efficiency of complex formation of metal. Upon application of agencies such as heat, light, detergents, crocking and dye cleaning agents, more resistance is offered by fabric and good rating is obtained [7, 48]. However, over all bio mordanting have given excellent rating as compared to chemical mordanting. Hence it is concluded that MW treatment has improved the texture of dyed fabrics using neem bark extract upon bio-mordanting at reduced optimal conditions. Moreover, the introduction of bio-mordants, have not only given new shades with good rating but also make the process more sustainable, therapeutically and eco-friendly.

CONCLUSIONS

Investigation of sustainable products for green dyeing has welcomed by the community around the globe. Due to the awareness created by world renowned environmental and trade associations. Current study was also under taken to appraise neem bark as source of natural colorant (tannin) for cotton dyeing under the influence of MW treatment. The utilization of first application of bio-mordants with excellent ayurvedic nature has made the dyeing of surface modified cotton fabric more therapeutic and sustainable. It has been found that isolation of tannin from 8g of bark powder in acidic medium has given darker shades with good color depth by dyeing surface modified fabric under MW for 4 min. keeping 50 mL dye bath of 2 pH in presence of 5 g/100mL of Table salt as exhausting agent. Excellent color strength and rating of fastness have been found when extract of bio-mordants have been employed under mild condition as compared to chemical mordants used. It is concluded that microwave radiation has a great efficacy to explore new dye yielding plants and to modify the surface of fabric for enhancing its uptake ability. The addition of new bio-mordants in enhancing the color characteristics of cellulosic fabrics has proved the eco-friendliness of dyeing process of cotton fabrics.

Table 1: Effect of pre (a) & post chemical mordanting (b) on fastness rating of cotton fabrics dyed with irradiated acidic extracts at optimal condition.

Pre-mordanting

Mordant Conc. (%)	Al						Fe						Tannic acid					
	L F	WF		D R F	W R F	D C F	L F	WF		D R F	W R F	D C F	L F	WF		D R F	W R F	D C F
		C S	C C					C S	C C					C S	C C			
1	4	4/5	5	5	4/5	4	4/5	4	4/5	5	4/5	4/5	4/5	4	4/5	5	4/5	4/5
3	4	4/5	5	5	4/5	3/4	4/5	4	4/5	5	4/5	4/5	4	4	4	4/5	4	4/5
5	4/5	4/5	5	5	4/5	4/5	5	4/5	5	5	4/5	5	4	4	4	5	4/5	5
7	4/5	4	4/5	5	4/5	4/5	4/5	4	4/5	5	4/5	4	4/5	4	4/5	5	4/5	4
9	4	4	4/5	5	4/5	4/5	4	4/5	5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5	4/5
10	4/5	4	4/5	5	4/5	4	4/5	4/5	5	4/5	4/5	4/5	4	4/5	4/5	5	4	4/5

Post -mordanting

Mordant Conc. (%)	Al						Fe						Tannic acid					
	L F	WF		D R F	W F F	D C F	L F	WF		D R F	W R F	D C F	L F	WF		D R F	W R F	D C F
		C S	C C					C S	C C					C S	C C			
1	4/5	4/5	5	5	4/5	4	4	5	4/5	5	4/5	5	4	4	4/5	4/5	4/5	4/5
3	4/5	4/5	5	5	4/5	3	4	5	4/5	5	4/5	4/5	4/5	4	4/5	5	4/5	4/5
5	4/5	4/5	5	5	4/5	4/5	4/5	4/5	4	5	4/5	4/5	4/5	4/5	4/5	4/5	4	4
7	4	4	4/5	5	4/5	4/5	4/5	5	4/5	5	4/5	4/5	4	4/5	4	4/5	4	4/5
9	4	4	4/5	5	4/5	3/4	4/5	4/5	4	4/5	4/5	4/5	4	4	4/5	5	4/5	4
10	4	4	4/5	5	4/5	4	4/5	4/5	4	4/5	4/5	4/5	4/5	4/5	4/5	5	4/5	4/5

LF= Light Fastness, WF= Wash Fastness, CS= Color Stain, CC= Color Change, DRF= Dry Rub Fastness, WRF= Wet Rub Fastness, DCF= Dry Cleaning Fastness.

Table 2: Effect of pre (a) & post bio-mordanting (b) on fastness rating of cotton fabrics dyed with irradiated acidic extracts at Optimal condition.

Pre-biomordanting

Mordant Conc. (%)	Acacia						Henna						Pomegranate						Turmeric					
	LF	WF		DRF	WRF	DCF	LF	WF		DRF	WRF	DCF	LF	WF		DRF	WRF	DCF	LF	WF		DRF	WRF	DCF
		CS	CC					CS	CC					CS	CC					CS	CC			
1	¾	4	5	5	4	4/5	3	4	5	5	4/5	4/5	4/5	4	5	5	4/5	4/5	3	4	5	4	4/5	5
3	4	4/5	4/5	5	4/5	4	4	4/5	4/5	5	4/5	5	4/5	4/5	4/5	5	4/5	4/5	2	4/5	4/5	4/5	4/5	4/5
5	4	4/5	5	5	4/5	4/5	4	4/5	4/5	5	4/5	4/5	4	4/5	4/5	5	4/5	5	3/4	4/5	4/5	4/5	4/5	4
7	3	5	5	5	4/5	3/4	4/5	4/5	4/5	5	4/5	4	5	4/5	5	5	4	4/5	4/5	4/5	5	4/5	4	4/5
9	4	4/5	5	5	4/5	4/5	3/4	4/5	5	5	4/5	3/4	4	4/5	5	5	3/4	4/5	3/4	4/5	4/5	5	4/5	4/5
10	4	4/5	5	5	4/5	5	4	4/5	4/5	5	4/5	4/5	4/5	4/5	5	5	4	4/5	3/4	4/5	4/5	5	4/5	4/5

Post-biomordanting

Mordant Conc. (%)	Acacia						Henna						Pomegranate						Turmeric					
	LF	WF		DRF	WRF	DCF	LF	WF		DRF	WFF	DCF	LF	WF		DRF	WRF	DCF	LF	WF		DRF	WRF	DCF
		CS	CC					CS	CC					CS	CC					CS	CC			
1	3/4	4/5	4/5	5	4/5	4/5	4	4	5	4/5	4/5	4/5	3/4	4	5	5	4/5	4/5	2/3	4	5	5	4/5	4/5
3	4	4/5	5	5	4/5	4	4	4/5	4/5	5	4/5	5	4/5	4/5	4/5	5	4/5	4/5	2/3	3	4/5	5	4/5	3/4
5	4	5	5	5	4/5	4/5	5	4/5	4/5	5	4/5	4/5	4	4/5	4/5	5	4/5	4/5	2/3	3	4/5	5	4/5	3/4
7	3/4	4/5	5	4/5	4	3/4	2/3	5	4/5	5	4/5	5	4/5	4/5	4/5	5	4	4/5	3	2/3	4/5	5	4/5	3/4
9	4	4/5	4/5	5	4	4/5	4	4/5	4/5	5	4/5	4/5	4/5	4/5	4/5	5	3/4	4/5	3	4	5	5	4/5	4/5
10	4	4/5	4/5	4/5	4/5	4/4	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	4/5	5	4	4/5	3	3	4/5	5	4/5	4/5

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