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Green Dyeing of Wool Fibers with Madder: Study of Combination of Two Biomordant on K/S and Fastness

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Abstract: Nowadays, using sustainable dyeing process has become a necessity, but does not meet performance requirements. Application of biomordants was recommended to enhance the quality of dyeing. Tannin-based biomordants appeared advantageous in green dyeing; meanwhile, unconditional affinity towards fibers of different types has attracted the attention of researchers. We introduce the idea of using combination of natural mordant as a new technique for sustainable dyeing of wool and a model natural fiber. In this study, Iranian madder was used as green dye and Yellow Myrobalan (YM) and Black Myrobalan (BM) employed as biomordant. FTIR-ATR spectra of the washed, mordanted, and mordanted-dyed wool fibers confirmed appropriate bonding among wool fibers, green mordant, and dye molecules. The superior color strength of wool fibers dyed with 4 %YM+6 %BM and 40 % madder was featured by *K/S* value of 35.77 and was obviously higher than that of madder by sumac, 9.5. Fastness properties (light, wash, and rub fastness) of wool dyed with combination of YM and BM were good.

Keywords: Sustainable dyeing, Natural dyes, Myrobalan, Biomordant, Fastness properties

Introduction

Dyeing is a main process in textile technology and dye plays an important role in dyeing of textile, fibers or fabrics [1]. Natural and synthetic dye can be used in dyeing process; so, the use of natural dyes has recently been increased due to their renewability and biodegradability [2,3]. The majority of natural dyes could not be directly used in dyeing process due to their low affinity [4]. The mordanting process could solve this limitation. Mordants, which have affinity towards both fibers and dye molecules, can be used, whenever there is low affinity between dye and fiber. There are three methods for mordanting process as pre-, meta-, and post-mordanting and mordants are divided in two classes, which contain metal and natural material [5,6].

Yusuf *et al.* studied the effect of tin(II) chloride on wool dyeing. They dyed woolen yarn with natural dyes extracted from henna leaves and madder roots. The color strength has been found to be good in all dyed fibers. The fastness properties were medium to good for dyed woolen yarns [7]. Yusuf *et al.* in other studies used a biomordant in wool dyeing. In this work, Acacia Catechu and Rubia Cordifolia were used as biomordant and natural dye, respectively. The results showed that the all dyed wool present red tones shade with excellent color fastness properties. The pre-mordanting method found more overdriven effects compared to the meta-mordanting and post-mordanting methods overall [8]. Ul-Islam *et al.* investigated the effect of pomegranate peel extract as biomordant on dyeing process. The investigated biomordants show different interactions with coloring compounds of Butea monosperma (palas) dye resulting in deep brown, olive green, dark brown, cinnamon, burgundy, and yellowish hues on wool. The natural mordant, which was used in this study, improved dye affinity with good fastness properties [9]. Rather *et al.* investigated the effect of Acacia nilotica bark extract as natural mordant in wool dyeing using pre-mordanting method. The hue of developed color was found to be in yellow-red coordinate of color space diagram with appropriate fastness properties [10]. Hosseinnezhad *et al.* dyed silk fibers in the presence of Sumac as biomordant using pre-mordanting techniques. The FT-IR ATR spectra of the washed, mordanted, and mordanted dyed silk fibers showed bonding between silk fibers and green materials. The fastness of dyed samples was investigated by ISO standard test method and resulted in good results [11].

In this work, we investigate the effect of biomordant combination as the new method for dyeing wool carpet yarns as model fibers. We evaluated the structure of various sorts of natural sources and recognized that Myrobalan is fertile in tannin; therefore, we applied it in dyeing wool helping Iranian madder natural dyes. At first, we first extracted Yellow and Black Myrobalan as biomordant through a chronological procedure, and applied in dyeing of wool fibers with selected natural dyes. The color strength, color coordinates, wash, light and rubbing fastness of dyed wool fibers in the presence of combination of Yellow and Black Myrobalan extracts are evaluated with and without

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mordanting and the results are investigated. The approach implemented in this work is a big step towards green production of Iranian carpet using new tannin-rich first generation of biomordants together with local natural dyes.

Experimental

Materials and Method

The 100 % wool carpet yarn (215 tex/2 fold) is a natural protein-based fiber, which has been used in Persian carpets or rugs for thousands of years. Madder is the main sources of natural dyes obtained from vegetable for wool dyeing. Madder is one of the oldest natural dyes, which is known as the queen of red colors with common name of Rubia Argyi, which belongs to Rubiaceae family. Natural dyes (Madder) and Yellow and Black myrobalan fruit with scientific name terminalia chebula, as natural mordants, were extracted from underbrush grown in the north and in the center of Iran. The madder was innovatively extracted and was fully characterized in our pervious study [11].

For the analysis of chemical bonding between ingredients, FTIR-ATR spectra were collected on a spectrometer (Perkin Elmer, USA) equipped with a ZnSe crystal to help qualitative evaluation of changes in the main characteristic group absorption bands in the mordanting wool as well as dyed wool yarns. The FTIR-ATR spectra were obtained using a single reflection horizontal ATR accessory with a ZnSe crystal fixed at an incident angle of 45 °. The Color-Eye 7000 spectrophotometer from Gretag Macbeth was utilized to capture the reflectance spectra of the dyed fibers within 380 to 750 nm at 10 nm intervals, while the measurement geometry was d/8 and the specular component as well as the standard illuminant's UV content were included. The CIEXYZ tristimulus values and the colorimetric specification of samples in CIELAB and CIELCH color spaces were computed under D65 standard illuminant and CIE1964 standard observer. Heidolph rotary evaporator (Hei-VAPValue digital, Germany) was used to get the supersaturated solution extraction. Light fastness was conducted on a Hanau Xenotest 150S according to ISO 105-B02:2014(en). Wash and rub fastness properties of the dyed yarns were determined according to ISO 105-C10 2006(en) and ISO 105-X12 2016 standards.

Extraction Procedure of Yellow and Black Myrobalan

The dried yellow Myrobalan (YM) and black Myrobalan (BM) were grounded in a mixer and were stored in a glass bottle at room temperature (25-27 °C). The fine powder of material (50 g) was extracted with 200 m*l* of ethanol on a shaker for 20 h. The residue was extracted three more times to complete the extraction. The total extract was heated to boil and allowed to stand overnight and was filtered again. The clear filtrate was concentrated under vacuum using the rotary evaporator instrument and the obtained semi-solid mass was diluted with distilled water. The precipitate was subsequently dried in an oven and collected in powder form.

Mordanting Procedure

Wool fibers were mordanted by pre-mordanting technique using different double mordant combinations (5 % YM+5 % BM, 2.5 % YM+7.5 % BM, 7.5 % YM+2.5 % BM, 4 % YM+6 % BM, 6 % YM+4 % BM) for investigating the effect of mordant on hue and tone. Before mordanting, wool fibers were washed by non-ionic detergent solution to enhance surface wettability. The washed wool fibers were added to the mordant solutions, while temperature increased

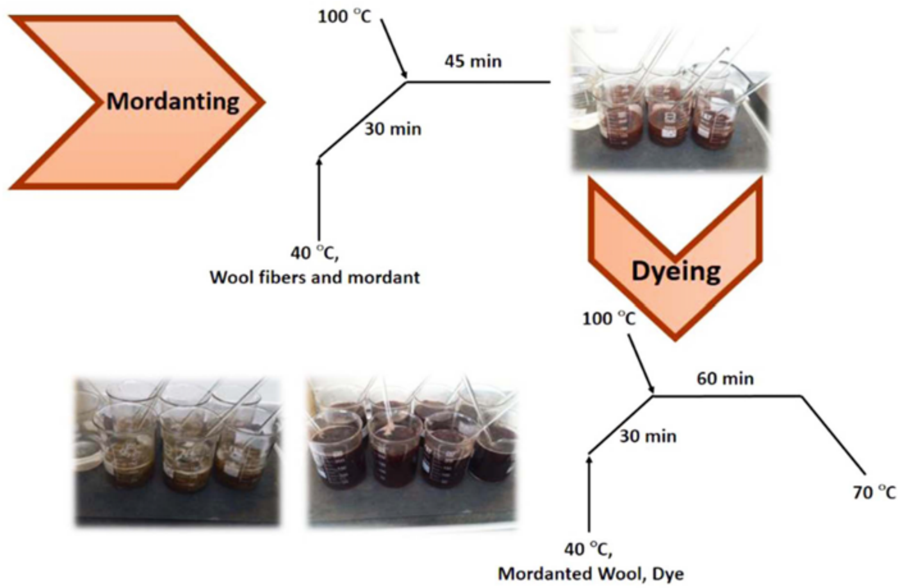

Figure 1. Mordanting and dyeing samples.

up to 100 °C in 30 min and were kept for more 60 min. Finally, the mordanted yarns were drained with water to remove weakly adsorbed mordants. Figure 1 shows mordanting samples.

Dyeing of Wool Yarns

Mordanted fibers were dyed with L.R. 40:1 and the build-up properties of the natural dyes on wool fibers were evaluated by dyeing fibers with 1, 5, 10, 20, and 40 % o.w.f of madder solutions. Dyeing was done by raising the dye bath temperature from 40 up to 100 °C at a heating rate of 2 °C/min, by holding the bath at this temperature for 60 min, and then by cooling down to 70 °C during 40 min. The wash, light, and rubbing fastness properties of the dyed fibers were measured according to the ISO105-C10:2006, ISO105-B02:2014, and ISO105-X12 2016 protocols, respectively. Figure 1 indicates dyeing samples.

Results and Discussion

Rubia tinctorum, which is commonly named madder, is a food plant used as a natural red dye for leather, wool, cotton, and silk. Since madder is polar molecule with hydroxyl groups which show low affinity towards wool fibers, this limited affinity can be refined using mordant. As the YM and BM mordants are known as eco-friendly and the demand for the greener textiles is increasing, the improvement of biomordants such as YM and BM is gaining popularity [8]. Myrobalan contains 32 % of tannin of pyrogallol (hydrolyzable) type composed of 14 components of hydrolyzable tannins (gallic acid, chebulic acid, punicalagin, chebulanin, corilagin, neochebulinic, ellagic acid, chebulegic acid, chebulinic acid, 1,2,3,4,6-penta-O-galloyl-β-D-glucose, 1,6-di-O-galloyl-D-glucose, casuarinin, 3,4,6-tri-O-galloyl-D-glucose, and terchebulin). The tannin content varies with the geological variation. Flavonol glycosides, triterpenoids, coumarin conjugated with gallic acid called chebulin, as well as phenolic compounds were also isolated. In addition, ethyl gallate and luteolin were isolated from the fruit of T. chebula. Also, it consists of nutrients such as vitamin C, protein, amino acids, and minerals [12]. Figure 2 represents the chemical structure of gallic acid. The YM and BM were extracted and identified by FT-IR technique. FTIR (KBr) (cm^{-1}): 3624: OH str., 3010: CH str. Ar., 1608, 1492: C=C str. Ar.

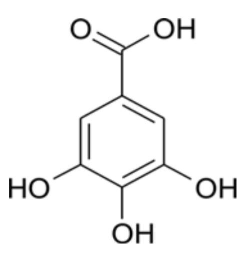

Figure 2. Chemical structure of gallic acid.

FTIR-ATR spectra of the wool fiber indicate absorption peaks of functional groups and peptide bonding, which is the characteristic of wool. Elemental analyses showed amino acid-rich structure of wool [13]. FTIR-ATR spectra of the washed and mordanted wool indicate very similar bands, which were formed between 3000 to 3500 cm^{-1}, and can be attributed to hydrogen bonded hydroxyl groups (O-H). Such broad peaks are the result of free and/or inter-/intra-molecular hydroxyl bounds, which are possibly merged with each other in an intricate way formed between wool fibers and mordanting agents [14,15]. Table 1 indicates the FT-IR results. Our previous research shows that 10 % is a good amount to use the YM and BM mordant. In this study, we intend to investigate the combination effect of these two mordants. Figure 3 shows the SEM image of wool fiber, mordanted wool with 2.5 % YM+7.5 % BM and dyed mordanted wool with madder 40 %.

Mordanting agents can control the fastness and color

Table 1. FTIR peaks of washed and mordanted wool fibers

Sample	OH (cm^{-1})	C-N (cm^{-1})	C=O (cm^{-1})
Washed wool	3415	1227	1726
5 %YM+5 %BM	3428	1222	1736
2.5 %YM+7.5 %BM	3425	1227	1735
7.55 %YM+2.5 %BM	3432	1225	1736
4 %YM+6 %BM	3428	1221	1739
6 %YM+4 %BM	3429	1225	1738

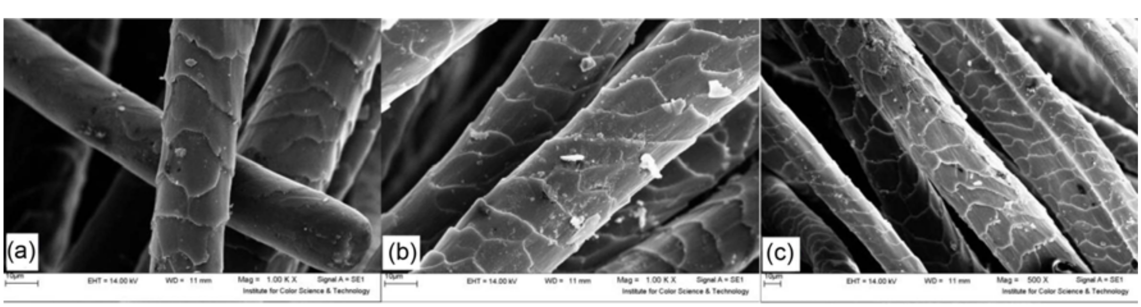

Figure 3. SEM of (a) the washed, (b) natural mordanting, and (c) dyed of wool fibers.

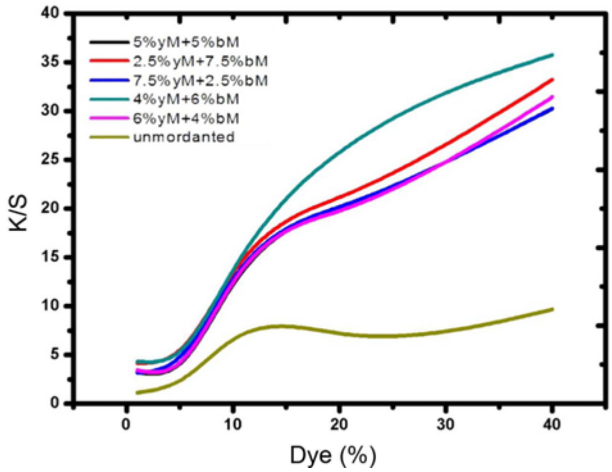

Figure 4. Effect of mordant combination on K/S of dyed wool fibers.

strength values of fibers dyed with natural reagents [11]. Typically, mordanting process helps strong interaction between dye molecules and fibers through formation of chemical complexes. Mordanting methods applied in dyeing including pre-mordanting were compared based on *K/S* values of the dyed wool (Figure 4). A comparative shade depth analysis of madder dyed wool samples confirmed higher color strength, as was featured by a higher *K/S* value. In agreement with this observation, FTIR spectra of the dyed wool yarns notified the disappearance of all C-N peaks due to synergistic interaction between fibers, mordanting agent, and dye molecules [10,16].

The *K/S* values are 1.11, 2.38, 6.56, 7.19, and 9.66 for dyed fibers in the absence of mordant. The results suggest that the addition of mordant extract to dyeing bath leads to a higher K/S value for wool compared to the natural dyed fibers in the absence of mordant. The mordants anchored to the surface of wool can improve fixation properties similar to natural mordants used in previous studies [17,18]. Correspondingly, tannin-based biomordants with 5 % Babul, which were applied in wool dyeing, resulted in *K/S* value of 4.14 [13]. The use of Gallnut as tannin-based in pre- and post-mordanting methods resulted in *K/S* values of 16.09 and 14.66, respectively [19].

In addition to *K/S* value, CIELAB is affected by mordanting methods and the type of used mordants (Table 2). All dyed samples were conditioned to the first hue area (red-yellow quarter) of the CIELAB color space benefiting from the yellow appearance. Then, the dyed samples were placed in the fourth hue area (red-blue quarter) of the CIELAB color order system and appeared as red. As it was expected, using more amounts of natural dyes in these samples resulted in darker colors, where there was no significant difference between the chroma attributes of dyed samples with 20 and 40 (wt.%) of the applied natural dyes in the pre-mordanting methods. Similar results are reported for Emblica officinalis, which is used alone and in combination with copper sulfate as mineral mordant on cotton and silk fabrics representing higher *K/S* and color strength [20]. Elsewhere, a shade range was attached on wool by madder and gallnut biomordant, which indicates color coordinates situated in red-yellow quadrant of the CIELab color space and satisfactory color depth and fastness [19].

ISO105-C10, ISO105-B02, and ISO105-X12 were considered to study wash, light, and rubbing fastness of dyed fibers, respectively (Table 3). The results suggest that washing fastness of samples was very good (4-5 to 5) in the presence of mordants. The staining of green dyed samples revealed good fastness with grade 5. The dyed yarns showed moderate light fastness in the presence of mordants.

Table 3. Fastness properties of the dyed wool fibers

Mordant	Light fastness	Wash fastness		Rubbing fastness	
		Change	Staining	Change	Staining
Un-mordant	2	2	2	4	4
5 %YM+5 %BM	4-5	4-5	5	4-5	4-5
2.5 %YM+7.5 %BM	4-5	4-5	5	4-5	4-5
7.55 %YM+2.5 %BM	4-5	4-5	5	4-5	4-5
4 %YM+6 %BM	4-5	4-5	5	4-5	4-5
6 %YM+4 %BM	4-5	4-5	5	4-5	4-5
Alum 1 %	5	5	5	4-5	4-5

Light fastness rating: (1) poor, (2) fair, (3) moderate, (4) good, (5) better, (6) very good, (7) best, and (8) excellent. Wash and rubbing fastness rating: (1) poor, (2) fair, (3) good, (4) very good, and (5) excellent.

Table 2. Color value of dyed fibers in the presence of combination of bio-mordant

Mordant	5 % Dye			20 % Dye			40 % Dye		
	L^*	a^*	b^*	L^*	a^*	b^*	L^*	a^*	b^*
5 %YM+5 %BM	55.67	32.54	33.97	40.17	35.06	36.39	32.17	39.42	33.28
2.5 %YM+7.5 %BM	53.15	31.14	31.80	38.41	34.82	37.69	30.76	41.87	35.47
7.55 %YM+2.5 %BM	55.17	32.09	32.47	39.62	33.79	36.12	31.84	39.74	33.76
4 %YM+6 %BM	52.87	30.81	31.43	40.46	34.65	38.06	30.27	42.12	34.87
6 %YM+4 %BM	54.73	31.19	33.21	38.90	33.80	36.79	31.64	39.85	33.42

However, the light fastness was increased for all the dyed yarns that experienced pre-mordanting with a mixture of natural and mineral mordant. The similar results have been reported by Prabhu *et al.* [20] for light fastness of dyed wool, cotton, and silk. Ren *et al.* used natural dye, which was extracted from tea for dyeing wool fabrics. The results illustrated that rubbing and washing fastness values of all dyed fabrics were increased and pH value had direct effect on light fastness [21]. All dyed fibers showed good rubbing fastness due to the ability of the dye molecules to self-associate through intermolecular hydrogen bonding because of the presence of primary amino grouping dye molecules [16,22]. Such a green process based on green ingredients enables clean production of Iranian carpet using locally available green compounds. Green dyeing of wool with madder extract in the presence of Acacia catechu biomordant resulted in shades on pre-mordanting wool of red tones with good to excellent color fastness properties [19]. The use of 5 % of Babul in dyeing wool ended in the light, wash, and rub fastness values of 5, 4, and 4-5, respectively [10]. Using Gallnut as tannin-based mordants was also studied in pre- and post-mordanting. The results suggested similar light, wash, and rub fastness values for pre- and post-mordanting in the ranges of 4-5, 3-4, and 3-4, respectively [23].

In some works, we discussed about the effect of tannin mordants on dyeing. Myrobalan is a famous fertile plant in tannin and is a suitable biomordant for dying. The *K/S* value of dyed fibers in the presence of metal-rich mordant was higher than myrobalan due to the formation of a complex structure in metal-rich extract. Polypeptide structures, which are present in wool fibers, provide the matter with so many active sites containing NH_2 and COOH functional groups that bridge the dye molecules with the fiber [19,24-26].

Vankar *et al.* observed that Eurya acuminata mordant in conjunction with R. cordifolia dye can enhance the dyeability of the silk fabric through chelation on the basis of high content of aluminum present in the Eurya acuminata leaves [27]. In another study, copper-rich Pyruspashia resulted in acceptable dye adherence because of strong chelation to flavone/flavonol dyes extracted from Delonix [28]. Tannin-rich A. catechu enhances dyeability of textiles. In addition, the use of plants as a natural green alternative to metallic mordants is a very promising concept, which may help to decrease the enormous environmental risks associated with metal salt mordants [29,30].

Conclusion

Green materials, systems, and technologies are receiving much more attention every day. Using of plants is considered a safe and clean route to the synthesis and development of green dyeing processes. Combinations of Yellow and Black Myrobalan with scientific name as terminalia chebula extract and the member of tannin rich biomordants were utilized as natural mordant for green dyeing wool fibers with natural dyes. The ratio of biomordants combination are as follow: 5 % YM+5 % BM, 2.5 % YM+7.5 % BM, 7.5 % YM+2.5 % BM, 4 % YM+6 % BM, and 6 % YM+6 % BM. FTIR-ATR spectroscopy was used to investigate chemical bonding of mordants and fibers and mordanted fibers with natural dyes. FTIR-ATR spectra of the washed and mordanted wool indicate very similar formed bands in 3000 to 3500 cm^{-1} region, which can be attributed to hydrogen-bonded hydroxyl groups (O-H). The colorimetric (CIE $L^*a^*b^*$) and *K/S* of dyed fibers were investigated and the results show that colorimetric and *K/S* values were improved in the presence of biomordants. The highest *K/S* value was achieved for ratio of 4 % YM+6 % BM. The wash, light, and rubbing fastness of the dyeing on fibers was found to be enhanced when biomordants were used in dyeing processing. Such a green procedure could be promising enough to be easily industrialized, thanks to the abundance of the local natural dyers towards clean production of Iranian carpets with a reasonable economic cost.

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References

1. M. Hosseinnezhad, K. Gharanjig, S. Belbasi, and S. H. Seied Saadati, *Prog. Color Colorant Coat.*, **10**, 129 (2017).
2. A. Ahmad Khan, N. Iqbal, S. Adeel, M. Azeem, F. Batool, and I. Ahmad Bhattic, *Dyes Pigm.*, **103**, 50 (2014).
3. A. Cerrato, D. De Santis, and M. Moresi, *J. Sci. Food Agric.*, **82**, 1189 (2002).
4. M. Chairat, J. B. Bremner, and B. Chantrapromma, *Fiber. Polym.*, **8**, 613 (2007).
5. S. N. Chattopadhyay, N. C. Pan, A. K. Roy, S. Saxena, and A. Khan, *J. Text. Inst.*, **104**, 808 (2013).
6. W. Hadder, I. Elksibi, N. Meksi, and M. F. Mhenni, *Ind. Crops Prod.*, **52**, 588 (2014).
7. M. Yusuf, M. Shahid, M. Ibrahim Khan, S. Ahmad Khan, M. Ali Khan, and F. Mohammad, *J. Saudi Chem. Soc.*, **19**, 64 (2015).
8. M. Yusuf, F. Mohammad, M. Shabbir, and M. Ali Khan, *Textiles and Clothing Sustainability*, **2**, 1 (2016).
9. S. Ul-Islam, L. J. Rather, M. Shabbir, J. Sheikh, M. Nadeem Bukhari, M. Ali Khan, and F. Mohammad, *J. Nat. Fibers*, **16**, 512 (2019).
10. L. J. Rather, M. A. Khan, and F. Mohammad, *J. Nat. Fibers*, **16**, 275 (2019).
11. M. Hosseinnezhad, K. Gharanjig, S. Belbasi, S. H. Seied Saadati, and M. R. Saeb, *Fiber. Polym.*, **19**, 1908 (2018).
12. S. Muhammad, B. Ali Khan, N. Akhtar, T. Mahmood, A.

Rasul, I. Hussain, H. Khan, and A. Badshah, *J. Med. Plant Res.*, **6**, 4772 (2012).
13. R. M. Kozlowski, “Handbook of Natural Fibres”, Vol. 1, pp.171-194, p.202, Woodhead Publishing, UK, 2012.
14. E. Sakhai, “Persian Rugs and Carpets: The Fabric of Life”, Antique Collectors' Club, Woodbridge, Suffolk, UK, 2008.
15. M. R. Sanjay, P. Madhu, M. Jawaid, P. Senthamaraikannan, S. Senthil, and S. Pradeep, *J. Cleaner Prod.*, **146**, 512 (2017).
16. M. Hosseinnezhad, K. Gharanjig, S. Moradian, and S. Tafaghodi, *Arabian J. Chem.*, **12**, 2069 (2019).
17. Y. Yin, J. Jia, and T. Wang, *J. Cleaner Prod.*, **149**, 637 (2017).
18. N. Jahan and E. A. Datta, *IOSR J. Polym. Text. Eng.*, **2**, 5 (2015).
19. M. Yusuf, S. A. Khan, M. Shabbir, and F. Mohammad, *J. Nat. Fibers*, **14**, 597 (2017).
20. K. H. Prabhu and M. D. Teli, *J. Saudi Chem. Soc.*, **18**, 864 (2014).
21. Y. Rena, J. Gong, F. Wang, .Z Li, J. Zhang, R. Fu, and J. Lou, *Dyes Pigm.*, **134**, 334 (2016).
22. L. Mehrparvar, S. Safapour, M. Sadeghi Kiakhani, and K. Gharanjig, *Int. Environ. Sci. Technol.*, **13**, 2569 (2016).
23. L. J. Rather, S. Islam, M. Shabbir, M. N. Bulchair, M. Shahid, M. A. Khan, and F. Mohammad, *J. Environ. Chem. Eng.*, **4**, 3041 (2016).
24. K. H. Prabhu, M. D. Teli, and N. G. Waghmare, *Fiber. Polym.*, **12**, 753 (2011).
25. M. Dodangeh, K. Gharanjig, and M. Hosseinnezhad, *Prog. Color Colorants Coat.*, **11**, 173 (2018).
26. L. J. Rather, S. Islam, M. Shabbir, M. N. Bukhari, F. Mohammad, and M. A. Khan, *J. Nat. Fibers*, **15**, 611 (2018).
27. P. S. Vankar, R. Shanker, D. Mahanta, and S. C. Tiwari, *Dyes Pigm.*, **76**, 207 (2008).
28. P. S. Vankar and R. Shanker, *Color. Technol.*, **125**, 155 (2009).
29. H. F. Mansour and S. Heffernan, *Clean Technol. Environ. Policy*, **13**, 207 (2011).
30. M. Shahid, A. Ahmad, M. Yusuf, M. Ibrahim Khan, S. Ahmad Khan, N. Manzoor, and F. Mohammad, *Dyes Pigm.*, **95**, 53 (2012).