

Green Miles in Dyeing Technology Metal-Rich Pumpkin Extracts in Aid of Natural Dyes

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Research Article

Keywords: Green dyeing, Bio-dyes, Pumpkin, Bio-mordant, Fastness.

Posted Date: June 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-579578/v1>

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Abstract

To reduce environmental pollution, it is essential to use green processes in dyeing and meet its requirements. One of the common methods to get better results in dyeing is to use mordant. To get a green dyeing, using natural mordant (bio-mordant) is very effective, but the search for an alternative having a higher stability and absorption interval, along with an absolute affinity towards natural fibers of various kinds was central to the focus of studies in the meanwhile. Pumpkin extract as a natural source metal-rich can be used as a bio-mordant in green dyeing of natural fibers such as wool fibers. Two natural dyes native to Iran; Reseda luteola and Madder were employed in this study. The effectiveness of bio-mordant presence on fibers was evaluated by FTIR-ATR test from mordanted and mordanted-dyed wool samples. Fastness performance of wool dyes with pumpkin alternated from good to excellent depending on natural dye type and concentration, due to the formation of complex structures that compensated for the lack of affinity-characteristic of tannin-based first-generation biomordants, at best with good fastness.

1. Introduction

Patents evidence that variety of materials, methods, and systems are born every day for the HITECH incentives. The orientation of technological developments towards sustainability needs are reflected more level headedly in the future picture of advanced systems enlivened by the scientists working in the era of energy harvesting materials. To come across requirements for a cleaner planet, green materials and technologies are developing too quickly, but still there are unsolved problems associated with materialization, mainly because of the materials used in manufacture of energy harvesting devices not being either efficient or environmental friendly. Dyeing process with green colorants has received a great deal of attention in recent decades. Because of their renewability and biodegradability, natural dyes are crucial elements in textile, food and drug coloration nowadays (Rather et al., 2016). Though natural dyes can be derived from different sources such as invertebrates and minerals, plants are the commodity natural dyes used in this sense (Shen et al., 2014; Mehrparvar et al., 2016). Nevertheless, only a few among natural dyes could be directly applied in coloring procedure because of their low affinity towards textile fibers—what demands mordanting as compliment to dyeing process (Hadder et al., 2014). A mordant principally ties textile fibers with dyes by a coordination complex to compensate for the lack of affinity, but a few natural dyes yield good fastness properties, hence optimizing dyeing process remained an unsolved problem (Indi et al., 2016).

Examples of natural dyes examined on dyeing are: Emblica officinal used in dyeing silk and cotton fabrics in the presence of different kinds of nature-inspired dyes that resulted in acceptable fastness properties when pre-mordanting was utilized (Prabhu et al., 2011); Gallnut (*Quercus infectoria* olive) extract used in dyeing wool that resulted in a proper depth of shade and good fastness in the presence of alum mordant (Shahid et al., 2012; Hosseinneshad et al., 2018); Manjistha, annatto, ratanjot and babool extracts used in dyeing wool showing good hue of dyed fabrics and washing fastness (Chattopadhyay et al., 2013); Red calico leaves extracts used in dyeing wool that resulted in acceptable fastness as well as an

extraordinary antibacterial character featured by a high-strength-fiber, and gamma irradiation declined the amount of bio-mordant and dyeing time(Ahmad Khan et al., 2014); Mulberry (*morusrubra*) extracts used in dyeing cotton fabrics under different conditions showing good fitness properties (Wang et al., 2016); Pomegranate extracts used in dyeing silk showing higher fastness properties rather than metal salts(Hosseinnezhad et al., 2017); and particularly attempts being made by Rather and coworkers in using acacia nilotica (Babul) in conjunction with Kerrialacca (Rather et al., 2017a), gallnut, pomegranate and babool (Rather et al., 2017b) in bio-mordant-aided green dyeing of wool and silk.

We believe that above-mentioned bio-mordants with good dyeing performance can be categorized in a general class of tannin-rich dyes, denoted as first-generation bio-mordants. Still there is another class of bio-mordants, say second-generation natural extracts, which should be underlined for their excellent fastness and unconditional fiber affinity brought about from their metal-rich structure (Fig. 1).

In this work, we introduce pumpkin extract as the first member of the second-generation bio-mordants for dyeing wool yarns as. Evaluation of various natural sources showed that pumpkin can be used as a suitable option to present the metal naturally in dyeing. As a result, in this study, pumpkin extract was used to dye wool fibers with two colors of Madder and Resedaluteola. Through a chronological procedure, we first extracted pumpkin bio-mordant and applied it separately, in dyeing of wool yarns with Madder and Resedaluteola. The Color and fastness performance of two types of wool yarns dyed in the presence of second-generation pumpkin extracts are evaluated with and without mordanting and the results are compared with previous studies related to tannin-based first-generation natural mordants.

2. Experimental

2.1. Materials and instruments

The chemical materials were provided from the Merck Co., Kenilworth, New Jersey, U.S.A. Reseda, madder, and pumpkin were selected and provided as natural resources of Iran. Absorbance and the reflectance data were obtained using the PerkinElmer micro-plate reader, and the Gretag Macbeth 7000A Color-Eye spectrophotometer, respectively. The light fastness test was performed using a Xeno-test 150s apparatus (Hanau, Germany) according to ISO standards.

2.2. Extraction procedure

Dried Walnut husk were extracted using ultrasound-microwave-assisted (UMA) via ultrasound-microwave bath ($F = 30$ KHz) and water as solvent of extraction. The extraction process was accomplished at 35°C , 20 min, 30 W (the power of Microwave) and during the extraction process, the temperature was kept constant using ice cube. Finally, the mixture was filtered and concentrated with rotary. The madder and reseda extraction process were performed similar the pervious study (Kozlowski et al., 2012; Cerrato et al., 2002; Mehrparvar et al., 2016).

2.3. Mordanting procedure

Pre-mordanting methods were applied in this study to prepare mordanting yarns with extracted pumpkin as natural mordant together with alum solution with a L:R = 20:1. Wool yarns were treated with a mordant solution containing 30 wt.% pumpkin extract and 5 wt.% alum and a combination of pumpkin:alum of 15:2 ratio with respect to the weight of fiber (o.w.f%). The washed wool yarns were employed to the mordant solutions whilst temperature rose up to 100°C. Mordanting samples are shown in Fig. 2.

2.4. Dyeing of wool yarns

Mordanted yarns were dyed in an IR dyeing apparatus machine (Xiamen Rapid) with L:R 40:1. Mordant concentrations (pre-mordanting) of 5%, 10%, and 20% and dye concentrations of 5%, 10%, and 20% were selected. Mordanting by a pre-mordanting method and dyeing were performed with the help of ultrasonic energy in an aqueous medium (Fig. 2). The mordant and dye extraction were stirred at room temperature for five min, then wool yarns were added. The dyeing of the wool yarn was concluded at 45 °C for 15 min with continuous stirring. Afterward, the dyed yarn was washed and analyzed.

3. Results And Discussion

The FTIR technique was employed to investigate the properties of mordanted and dyed yarns. The most significant chemical group of wool yarns is the peptide group, which was strongly seen in the FTIR results (Sakhai et al., 2008). The peptide bonds (Fig. 3), containing three different types of amines, have been reported in many papers (Jahan et al., 2015; Chairat et al., 2007; Kozlowski et al., 2012; Sakhai et al., 2008). The presence of a hydroxyl group in the spectrum of mordanted and dyed yarns are of the utmost importance in the spectrum of washed yarns. The extraction of pomegranate peel is brimming with tannin and the spectrum of mordanted yarns shows the interactions well (Sanjay et al., 2017).

The use of mordant in the dyeing process has an undeniable effect on increasing color stability and yield. Mordant application alters and enhances dye and fiber interactions. In the presence of metal mordant, metal complexes are formed on the surface of the fiber, which increases the color strength. The amount of K/S of dyeing samples is illustrated in Fig. 4. It is apparent from the figure that increase of natural dye concentration (either madder or Reseda) from 10 to 20, and then 40% boosted color strength. The results show that the amount of K/S for Reseda luteola -dyed samples is higher than the madder-dyed samples. All peaks related to the CN group in the FTIR test results of the dyed samples have been removed (Rather et al., 2017a).

The pumpkin extract to dyeing bath give rise to a higher K/S value for wool with respect to the natural fabrics dyed in the absence of pumpkin. Second-generation biomordants used in this work also helped delving into the depth of dyeing in aid of mineral components present in pumpkin extracts. There is evidence that metal ions contribute to formation of complex with dye molecules leading to enhanced fixation and affinity of dyed fibers/fabrics-what caused a rise in the value of K/S (Prabhu et al., 2014; Yin et al., 2017). In another study, Babul extract was employed as tannin-based mordant in wool dyeing with K/S about 4.14 (Kozlowski et al., 2012). Employing of Gallut (tannin-rich) in pre- and post-mordanting technique resulted in K/S values of 16.09 and 14.66, respectively (Yusuf et al., 2017). This is an

indication of the fact that dyeing in the presence of tannin-based first-generation bio-mordant gives K/S values relatively lower than that of metal-rich pumpkin ones.

Two characteristics of dyed natural fibers that change in the presence of mordants are: K/S and CIELAB. Dyed fibers with Reseda and Madder are placed in the savior of red-yellow and red-blue quarter, respectively. Except the wool yarns dyed with Reseda in the presence of alum mordant, by increasing the natural dyes concentration the chroma attribute (C^*) of samples increased, while the corresponding lightness values (L^*) decreased. In other words, while applying more contents of the used natural dyes in producing darker and more saturated colors, increase of Reseda concentration in the presence of alum mordant could not produce wool yarns with more saturated yellow appearance. By contrast, except the wool yarns dyed with madder in the presence of 15% pumpkin and 2% alum, increase of dye content from 20 to 40 wt.% ended in a substantial fall in the lightness attribute. It means that applying twice amounts of Reseda and madder dyes leads to producing darker colors, with a roughly the same chroma value. The silk and cotton fibers were dyed using mineral mordant, namely copper sulphate and *Emblicaeofficinalis* as bio-dye and obtained the similar results for K/S properties (Prabhu et al., 2014). In other study, gallnut was used as new bio-mordant for wool dyeing employing madder as natural dye. The new shade range in red-yellow quadrant was achieved and all samples presented good fastness properties (Yusuf et al., 2017).

ISO105-C10, ISO105-B02 and ISO105-X12 were selected to study wash, light and rubbing fastness of dyed samples, respectively (Table 1). Considering color affinity towards wool, as featured by K/S value, the column corresponding to such characteristic is painted from pale yellow to red for visual representation of the performance of metal-rich pumpkin extract in dyeing wool fibers in terms of concentration and type of the used natural dyes. The results of the meta-mordanting method are given in parentheses. The results illustrated that washing and staining fastness of samples was very good (4–5 to 5) and good (5) in the presence of mordants, respectively. The use of mordant is also effective in improving light fastness, but this amount is lower compared to mineral mordant. The results reported by Prabhu et al. (Prabhu et al., 2014) for dyeing of natural fibers (wool, cotton and silk) with natural dye are similar to the results obtained in this study. The tea as natural source was extracted for dye preparation and resulted extraction was employed for wool dyeing. The results showed that tea does not require mordanting due to the presence of large amounts of tannins and the fibers dyed with it have good fastness properties. Of course, the fastness properties of dyed fibers depend on pH value (Rena et al., 2016). Generally, the using of mordant improve the fastness properties due to the ability of the dye molecules to self-associate through intermolecular hydrogen bonding (Hosseinnezhad et al., 2015). Yusuf et al. extracted safflower as a natural dye for silk fabric dyeing. The dyeing was done in microwave conditions for three minutes. Turmeric and henna were selected as bio-mordanted and applied using pre and post-mordanting techniques. All the fastness properties of the dyed fibers were significantly increased by mordanting. The fastness properties of samples using natural mordants were very close to metal mordants (Yusuf et al., 2017). 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 (Rather et al., 2017a). Hosseinnezhad *et al.* investigated the combination of two natural mordants on dyed fiber properties. Yellow and black myrobolan as tannin-

rich mordants were selected for wool dyeing. The optimal ratio of the two mordants is yellow myrobolan: black myrobolan = 4:6. The highest K/S was obtained in this ratio (Hosseinnezhad et al., 2020). The chemical bonding between the fiber and the tannin is different from the mordant containing metal elements (Fig. 5). More interestingly, second-generation natural mordants are promising for the future ahead of green dyeing process (Mansour et al., 2011).

4. Conclusion

One of the main problems of many industries is the production of wastewater and environmental pollution. Therefore, this is one of the most important issues regarding the reduction of pollution. Natural materials (dyes and mordants) use reduces wastewater pollution. In this study, the dyeing properties of wool fibers were evaluated using the two natural dyes of madder and Reseda. Madder, Reseda, and pumpkin extraction efficiencies were 23%, 33%, and 27%, respectively. Wool yarns were chosen for dyeing because wool is a widely used and important fiber in the handmade carpet industry. FTIR techniques were used to investigate the extracts obtained and to identify the changes in the fibers. Examination of the amount of K/S value showed that by increasing the concentration of the dye, the amount of K/S increased. The latest ISO standards were followed to evaluate the fastness properties. The wash, light, and rub fastness of dyed yarns were good, moderate, and good, respectively.

Declarations

Ethical Approval

We approve that this manuscript is part of research studies about green dyeing.

Consent to Participate and Publish

We give consent to publish our work of natural dyeing studies and is jointly contributed by all authors.

Authors Contributions

Dr Mozhgan Hosseinnezhad is supervisor of research, where Prof. Kamaladin Gharanjig is co-supervisor of the work in whose lab practical work has been done. Mrs. Narjes Razani has conducted the experiments and analyzed the data of the work critically. Dr. Razieh Jafari analyzed dyed samples from colorimetric point of view. Dr. Mohammad Reza saeb finalized the manuscript scientifically and literary.

Funding information

This work was not received any kind of grant.

Competing Interests

There is no conflict of interest among authors

Availability of data and materials

As this is the part of green dyeing studies so whole data is present in research report.

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Tables

Due to technical limitations, table 1 is only available as a download in the Supplemental Files section.

Figures

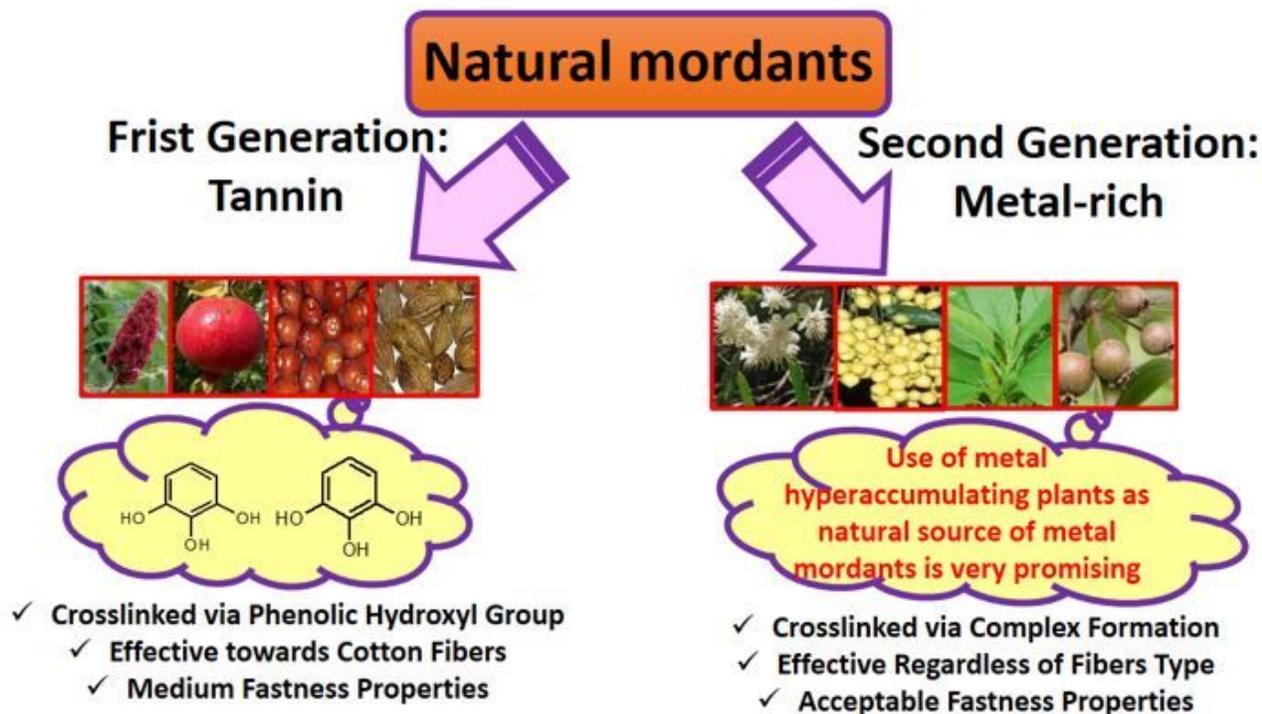


Figure 1

A brief comparison between two generations of natural mordants

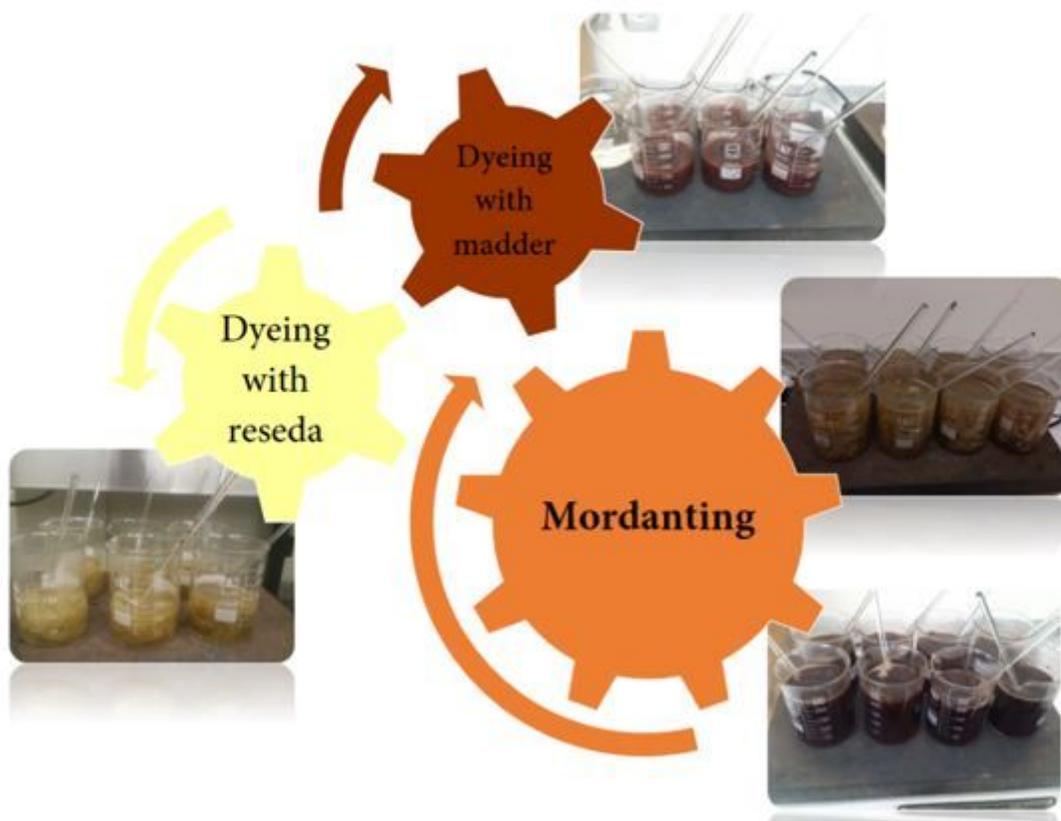


Figure 2

Mordanting and dyeing samples

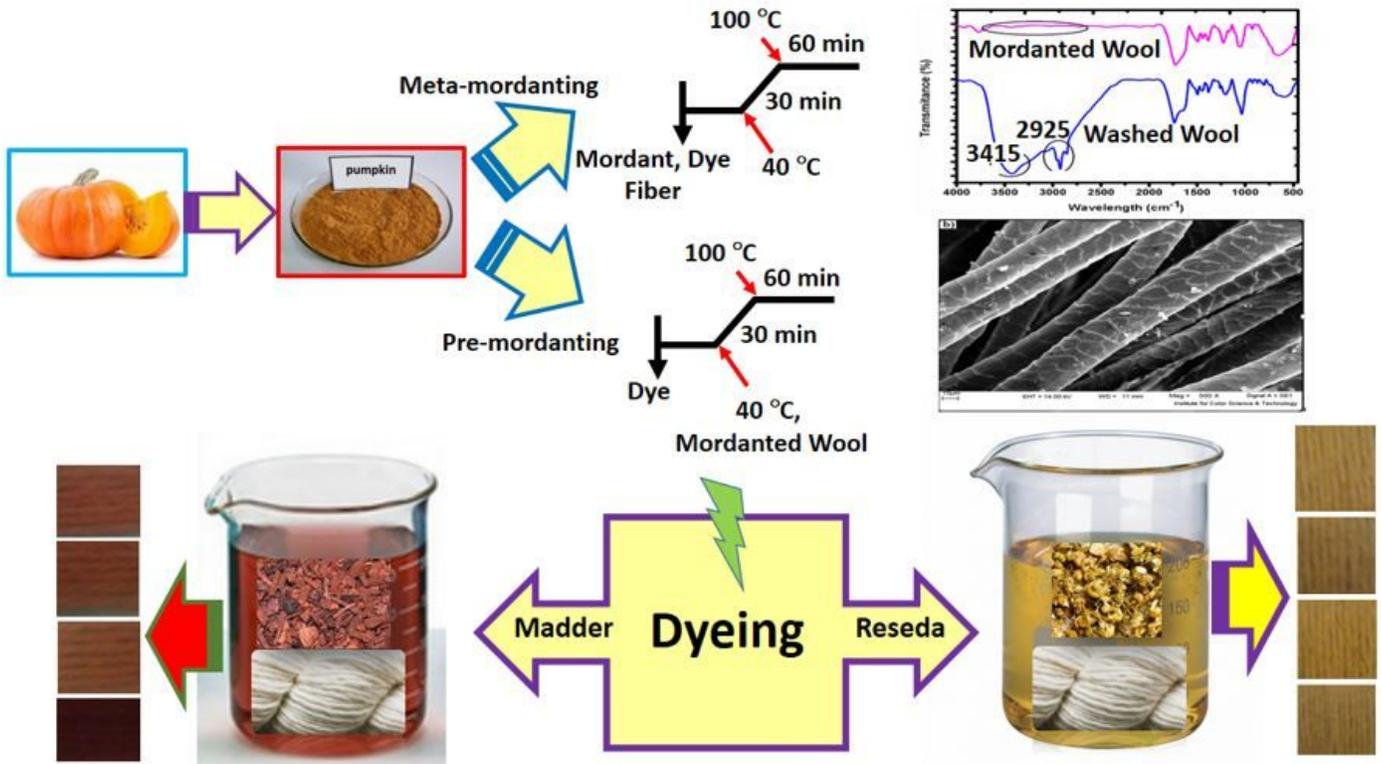


Figure 3

Procedure followed in mordanting and dyeing of wool fibers

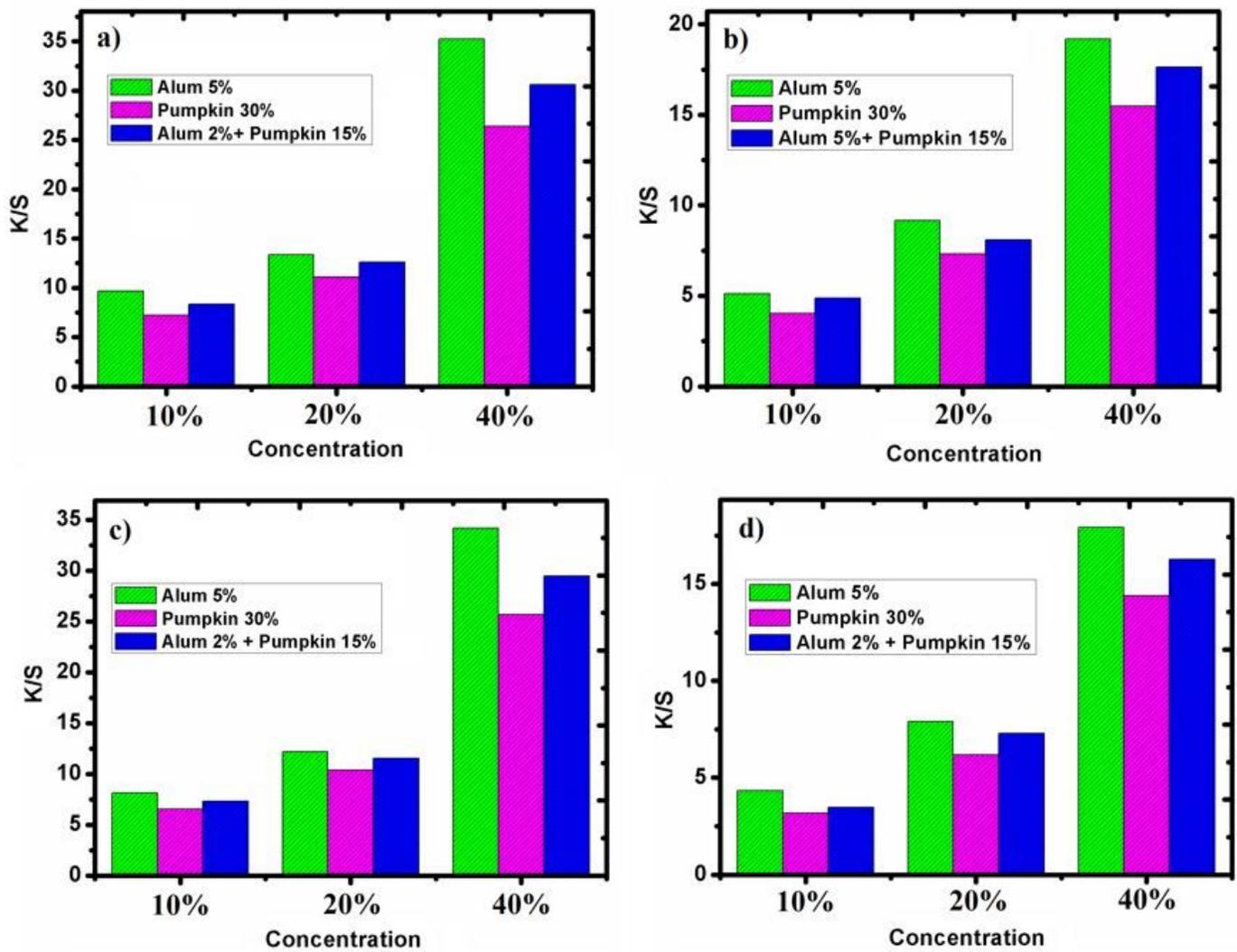


Figure 4

The effect of o.w.f (%) on the K/S of samples with madder (a), Reseda (c)[pre-mordanting]; and meta-mordanting of samples with madder (b) and Reseda (d)

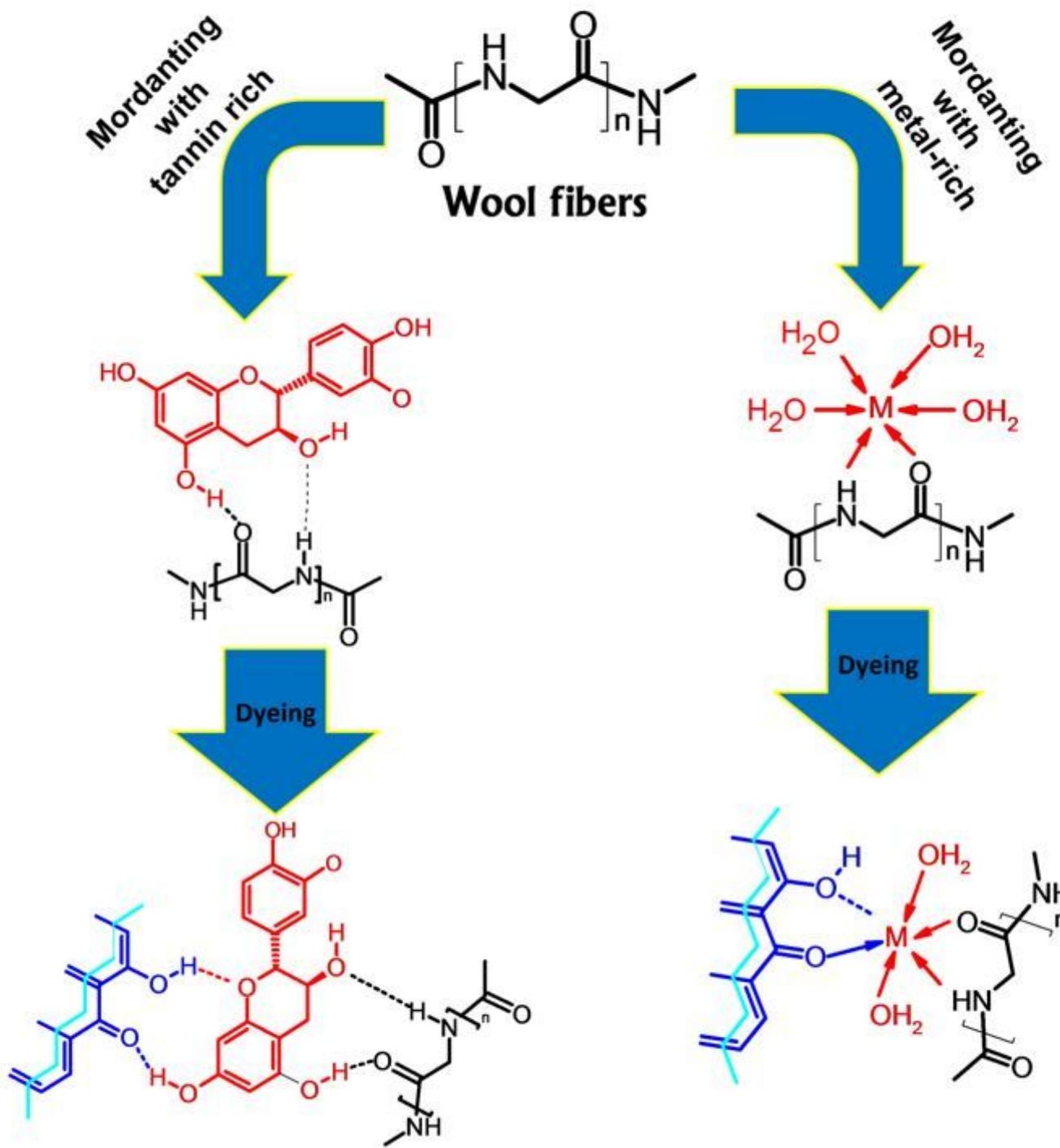


Figure 5

Schematic of mordanting and dyeing processes based on first- and second-generation biomordants

Supplementary Files

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