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Bioactive and Multifunctional Textile Using Plant-based Madder Dye: Characterization of UV Protection Ability and Antibacterial Activity

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Abstract: In the present work the natural madder dye (*Rubia tinctorum L.*) was applied to the simultaneous dyeing and functionalization of polyester (PET) fabric. In the first part of the study the color performance and the durability were revealed for exhaustion dyed fabric. The dyed fabric was then characterized with respect to ultraviolet (UV) protection ability and antibacterial activity against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). CIELab color coordinates, namely the positive a^* and b^* values, confirmed a yellow/orange color of the dyed fabric. From durability tests, the color showed a moderate to good light fastness and good to excellent fastness to washing and rubbing. The madder dye improved both the UV protective performance and the antibacterial activity of the fabric. With 3 % on weight of fiber (owf) the UV protection factor increased up to 106, and the antibacterial activity up to 86 % against both types of bacteria tested.

Keywords: *Rubia tinctorum* L., Anthraquinone, Functional dyeing, Antibacterial activity, Ultraviolet protection ability

Introduction

Textiles today are mainly dyed with synthetic dyes. However, environmental issues such as resource shortage have led to a renaissance in research into the potential use of natural dyes as alternatives to existing synthetic ones [1]. Bio-sourced dyes are interesting for several reasons, and two motivations for using them are given here. Firstly, bio-sourced dyes can potentially impart several attributes to the textile through one single dyeing treatment and by doing so enable 'design for more consumer value using less material'. Currently, textiles are namely, to a great extent, expected to fulfill several functional properties; for example, not only have a certain color but also show antibacterial activity [2] or flame retardant properties [3]. Secondly, resource consumption can be replaced by the use of renewable materials.

One dye plant, which can be cultivated under European soil and climatic conditions, is the tinctorial plant madder (*Rubia tinctorum L.*) also known as European madder or the 'Queen of reds' [4]. The coloring species, so called the anthraquinone dyes, can be found in the root of the plant [5].

Anthraquinones constitute the largest group of natural coloring species, and around 200 different types can be found in flowering plants [6]. About 36 anthraquinones have been identified in the madder root whereof 14 are presented in Table 1. Alizarin **(1)** is well known as the main dye. Other species present are for example, purpurin **(2)**, xanthopurpurin **(3)**, rubiadin **(4)**, pseudopurpurin **(5)**, munjistin **(6)** and lucidin **(7)**.

In previous work we dealt with coloration [12] and eco-sustainability [13] related to PET fabric dyed with the madder dye. Madder dyeing of PET is not common. The fiber is generally dyed with synthetic disperse dyes, designed specially for hydrophobic fibers such as PET.

Nevertheless, when looking at some of the characteristics of alizarin, the main dye in madder, it can be hypothesized that this molecule has the potential to dye PET. For example, the molar volume is 155.9±3 cm^3, indicating a finer size than several commercial anthraquinone disperse dyes. This holds also for other dyes present in madder such as purpurin and quinizarin [14] and, shown in [12], the madder dye indeed has the potential to dye PET. However, the dyeing requires a temperature above the glass transition temperature (T_g) of the PET fiber and thus greater than 120 °C [15]. This induces segmental movements of the polymer chain. Once the polymer chains are mobile, a free volume will allow the madder coloring species to enter the center of the fiber.

Reasons for using PET include that this fiber type is the most produced and consumed fiber in the world, with a global production of 49.1 million tons in 2014 compared to 25.4 million tons for natural fibers (cotton, wool, linen and silk) [16]. Moreover, PET recycling is in development [17], as well as bio-based PET. The latter includes the use of sources of cellulose such as grasses and corn stover, instead of using crude oil [18]. It can thus be envisaged that recyclable and bio-based PET will be available in the future, and this motivates to research madder-functionalization of this fiber type.

There are various methods for applying the functional

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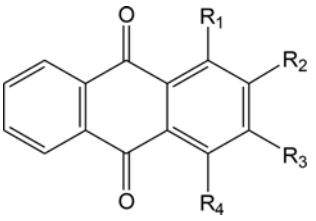
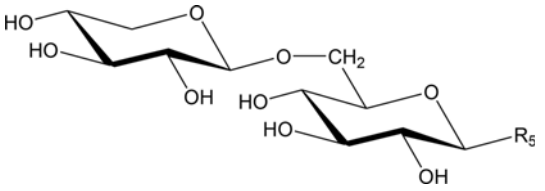
Table 1. Chemical composition of dyes in madder roots [7-11]



Anthraquinone (aglycone)



Primeveroside R_5 = O – aglycone

Common name	Structure
Alizarin **(1)**	R_1 = OH, R_2 = OH, R_3 = H, R_4 = H
Purpurin **(2)**	R_1 = OH, R_2 = OH, R_3 = H, R_4 = OH
Xanthopurpurin **(3)**	R_1 = OH, R_2 = H, R_3 = OH, R_4 = H
Rubiadin **(4)**	R_1 = OH, R_2 = CH_3, R_3 = OH, R_4 = H
Pseudopurpurin **(5)**	R_1 = OH, R_2 = COOH, R_3 = OH, R_4 = OH
Munjistin **(6)**	R_1 = OH, R_2 = COOH, R_3 = OH, R_4 = H
Lucidin **(7)**	R_1 = OH, R_2 = CH_2OH, R_3 = OH, R_4 = H
Anthragallol **(8)**	R_1 = OH, R_2 = OH, R_3 = OH, R_4 = H
Nordamnacanthal **(9)**	R_1 = OH, R_2 = COH, R_3 = OH, R_4 = H
Quinizarin **(10)**	R_1 = OH, R_2 = H, R_3 = H, R_4 = OH
Lucidin primeveroside **(11)**	R_1 = OH, R_2 = CH_2OH, R_3 = O – primeveroside, R_4 = H
Ruberythric acid **(12)**	R_1 = OH, R_2 = O – primeveroside, R_3 = H, R_4 = H
Galiosin **(13)**	R_1 = O – primeveroside, R_2 = OH, R_3 = COOH, R_4 = OH
Rubiadin primeveroside **(14)**	R_1 = OH, R_2 = CH_3, R_3 = O – primeveroside, R_4 = H

species to PET. It can be done either during fiber production [19], or in a fiber/fabric treatment [20]. The latter, more specifically combined exhaustion dyeing and functionalization, has been used in this study. Noteworthy, different from others [14] no mordants have been used.

Multifunctional PET through the madder dye has, to our knowledge, not been addressed in literature before this study. The present work is the first of its kind by characterizing not only color but also the UV protection ability and antibacterial activity of madder dyed PET fabric. By doing so, it presents a benchmarking study for madder dye applied to the simultaneous dyeing and functionalization of PET and augments the research arena dealing with bio-based functionalization of textiles.

Experimental

Materials and Chemicals

A polyester (polyethylene terephthalate-PET) plain woven fabric, of density 110 g/m^2, was dyed with madder dye (*Rubia tinctorum L.*) used as received from Couleurs de plantes (France). Nutrient agar for the antimicrobial tests was obtained from Sinopharm Chemical Reagent Co. Ltd., China. Nutrient broth was purchased from Shanghai Sincere Biotech Co. Ltd., China.

Dyeing

Pre-washed fabric samples (10 g) were dyed in beakers of 200 m*l*, housed in a high pressure and high temperature/ beaker dyeing machine (Labomat, Switzerland). The liquor: fabric ratio (LR) was 15:1. The dyebath was adjusted to proper pH using aqueous acetic acid (pH 5), and heated steadily (2 ^{o}C/min) until the dyeing temperature was reached (130 ^{o}C). The dyebath was then held at that temperature for 45 minutes. After dyeing, the fabrics were rinsed in soft water and left to dry at ambient temperature (around 20 ^{o}C). To assess the functional properties of madder dyed PET, the fabric was dyed with 3 % and/or 5 % on weight of fiber (owf).

Evaluation of Coloration

The color strength (*K/S*), L^*, a^*, b^*, C^* and h color coordinates (lightness [L^*], redness-greenness value [a^*], yellowness-blueness value [b^*], chroma [C^*] and hue [h]) of the dyed fabrics were evaluated using a HunterLab UltraScan PRO reflectance spectrophotometer (illuminant D65, 10 ^{o} standard observer). The *K/S* values were calculated from reflectance factors taken between 380 to 700 nm, using the Kubelka-Munk equation, equation (1):

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (1)$$

where R is the reflectance of the dyed fabric, K is the absorption coefficient and S is the scattering coefficient [21]. The color fastness to light was evaluated using an Atlas XenoTest Alpha (SDL Atlas, USA) light fastness tester according to GB/T 8427-2008 (eq. ISO1105 B02:1994). The dyed fabrics were exposed to the xenon arc lamp for 10 hours. Color fastness tests to washing and rubbing were carried out according to ISO 105:C10 and ISO 105-X12, respectively. The color change/fading and staining were assessed using gray scale, ranging between 1 (worst) and 5 (best).

FT-IR Analyses

The Fourier transform infrared (FT-IR) spectra of fabric samples were recorded using a Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA) from 32 scans at 4 cm^{-1} resolution.

UV Protection Performance

UV protection performance of dyed PET fabrics was measured and evaluated according to Australia/New Zealand Standard AS/NZS 4399:1996 (AS/NZS 4399). The UV protection factor (*UPF*) and the UV transmittance were determined using a Labsphere UV-1000F ultraviolet transmittance analyzer (Labsphere Inc., USA). Transmission measurements were performed in the 250-450 nm range. *UPF* was calculated according to equation (2):

$$UPF = \frac{\sum_{290}^{400} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{290}^{400} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda} \quad (2)$$

where E_λ is the relative erythemal spectral effectiveness, S_λ is the solar spectral irradiance, T_λ is the spectral transmittance of each fabric and $\Delta\lambda$ is the wavelength step in nm.

Antibacterial Activity

The antibacterial activity of dyed samples was evaluated according to GB/T 20944.3-2008 (eq. ISO 20743-2007). *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) were used. The former Gram-positive and the latter Gram-negative. Fabric specimens (0.37 g) were immersed in conical flasks with bacteria, placed into a water bath shaker and treated for 24 hours at proper temperature (*S. aureus* at 24 °C and *E. coli* solution at 30 °C). The bacteria solution was then diluted to 1000 times with sterilizing phosphoric buffer solution to obtain a test bacteria solution. The diluted bacteria solutions were inoculated onto agar plates and incubated at 37 °C, 48 hours for *S. aureus* solution and 24 hours for *E. coli* solution. The bacterial colonies on agar plates were counted and the antibacterial activity was evaluated based on equation (3):

$$\text{Antibacterial activity (\%)} = \frac{N_{ctrl} - N_{spl}}{N_{ctrl}} \times 100 \quad (3)$$

where N_{ctrl} and N_{spl} are the quantities of the visual bacterial colonies of control cotton fabric and sample polyester fabric, respectively [22].

Results and Discussion

Color Performance

In previous work it was revealed that the pH of the madder dyebath influenced the durability performance of the color and its hue and saturation. For example, with increased pH the wash fastness decreased and the color on the PET fabric shifted from yellow/orange to purple [12]. Based on additional experiments, which regarded dyeing temperature and dyeing duration, the same study found an optimized dyeing condition. This included an acidic dyebath (pH 5) with dyeing temperature of 130 °C, dyeing duration of 45 minutes and a LR of 15:1. The just described condition was used in this study, furthermore shown in Figure 1.

The color of the dyed samples appeared warm yellowish with a λ_{max} at 430 nm. Color coordinates are presented in Table 2. As seen, both a^* and b^* are positive. However, the b^* value is greater than a^* and thus the yellow color predominates over red. From the durability tests we could confirm that the fastness to light was moderate to good, and fastness to washing and rubbing were good to excellent. Gray scale data was 3-4 for the light fastness and 4-5 for the washing as well as rubbing tests, Table 3. From this, the study could proceed with a colored fabric with overall good

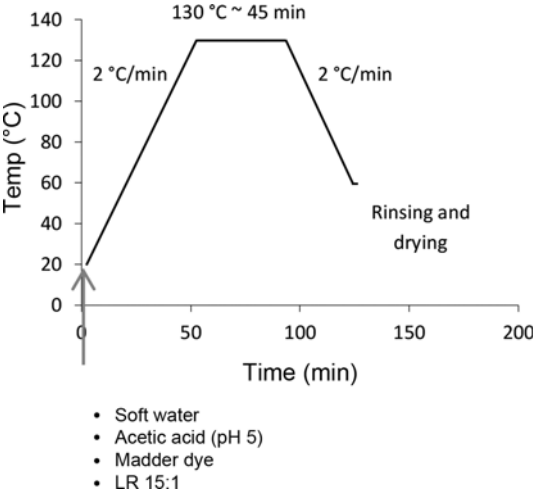


Figure 1. Experimental conditions for the dyeing process.

Table 2. Color coordinates of madder dyed PET fabrics

	L^*	a^*	b^*	C^*	h
Undyed	94	<1	3	3	80
Madder dyed 3 % owf	74	14	24	28	60
Madder dyed 5 % owf	70	14	28	31	63

Table 3. Durability characteristics

	Light fastness	Wash fastness	Rub fastness
Madder dyed 3 % owf	3-4	4-5	4-5

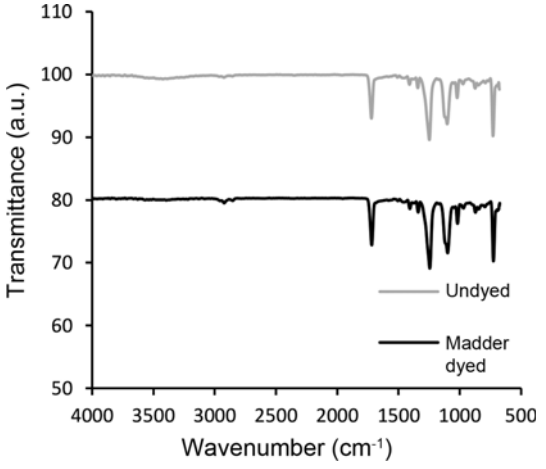


Figure 2. FT-IR spectra of undyed and 3 % owf madder dyed PET fabrics.

durability performance.

FT-IR Analyses

Before determining the functional properties other than color, the madder dyed PET fabric (3 % owf) was subjected to FT-IR analyses. This was done in order to see if the dyeing with madder dye had any impact on the functional groups of the PET fiber. It can be seen in Figure 2 that the spectrum of the dyed PET was in agreement with that of the undyed one. More specifically, both the dyed and undyed sample displayed four characteristic peaks distributed throughout 1714-723 cm^{-1}. The peak observed at 1714 cm^{-1} represents the C=O stretching vibration associated to the PET. The two distinct absorption bands at 1241 cm^{-1} and 1093 cm^{-1} can be assigned to -C-O-C stretching while the peak at 723 cm^{-1} can be attributed to aromatic ring out of plane bending [23]. The similarities between the two spectra indicate that the dyeing had no obvious impact on the functional groups of the PET fiber.

UV Protection Performance

Ultraviolet radiation ranges between 100 and 400 nm, and is subdivided into UV-C (100-280 nm) stopped in the stratosphere, UV-B (280-315 nm) and UV-A (315-400 nm) [24]. It is known that overexposure to UV-A and UV-B can cause harmful effects such as premature aging and skin cancers. In order to avoid these effects, the UV radiation exposure needs to be reduced, for example, with textile clothing [25,26].

The UV protection ability of textiles is influenced by several factors such as the fiber type, the fabric structure and its color. With respect to the madder dye, it has been shown that several species in the dye exhibit absorption not only in the visible region but also in the UV region. For example, alizarin presents an absorption maximum at 430 nm in the visible region and at 300 nm in the UV region [8,27]. Thus, as expected, the madder dye improved the UV protective effect of the PET fabric.

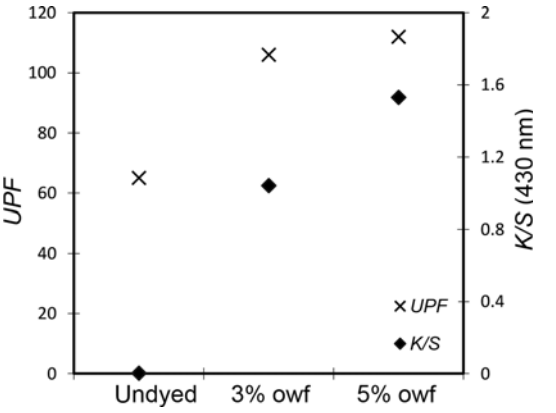


Figure 3. *UPF* and *K/S* of madder dyed PET fabrics.

The undyed PET fabric showed a *UPF* value of 65. This value is already high and, according to the standard, the fabric can be classified as 'excellent' UV protection. Nevertheless, when the fabric was dyed with madder dye the UV protection increased, see Figure 3. Specifically, *UPF* values of 106 and 112 were found for 3 % owf (*K/S*=1.0) and 5 % owf (*K/S*=1.5), respectively. These results encourage the use of the madder dye so as to simultaneously impart color and UV protective effect onto textiles.

Antibacterial Activity

Besides looking into the UV protection ability, this study also dealt with the antibacterial activity of the dyed fabric. The term 'antibacterial' refers to an agent that either destroys various bacteria or slows down their growth. More specifically, there are several ways antibacterial agents may inhibit bacterial growth; for example, by cell wall damage, inhibition of cell wall synthesis or inhibition of the synthesis of proteins and nucleic acids [28]. Antibacterial activity of madder dye extracts has been reported in [29]. Other researchers have shown that alizarin, purpurin and quinizarin present antioxidant and antibacterial activities [30-32]. The antibacterial effect may be related to the redox potential of these molecules, as for quinones in general, and their ability to form complexes with amino acids. This will inhibit the synthesis of proteins and the bacterial growth [33]. Moreover, it has been suggested that the anthraquinone backbone, which bear hydroxyl units on carbon-1 and carbon-2 such as alizarin, can affect the bacterial cell wall of *S. aureus* [31].

Figure 4 shows that the madder dye inhibited bacterial

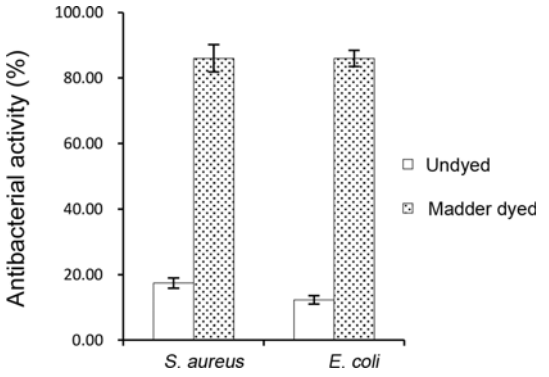


Figure 4. Antibacterial activities of undyed and 3 % owf madder dyed PET fabrics.

growth. Compared to the control cotton sample, the dyed fabric showed an antibacterial activity of 86 % against both types of bacteria tested while the undyed one showed an antibacterial activity less than 17 %. The antibacterial effect may potentially be the result of released alizarin molecules from the dyed fabric, which affect the bacterial cell wall and thus inhibit bacterial growth.

Conclusion

This paper has characterized the multifunctional performance; namely, color, UV protection ability and antibacterial activity of madder dyed PET fabrics. The results indicated that the madder dye may serve as a multifunctional species in the PET dyeing. The dyed fabric showed a yellow/orange color, improved the UV protective effect and inhibited growth of both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria. These results demonstrate that the use of madder dye is an interesting route and offers opportunities, in terms of functional performance, for potential bio-based value upgrading of textile dyeing.

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