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Simple crystallization approach for enhancing function of plant-based madder dye and performance of dyed fabric

Haijuan Du *, Qing Wang, Mengchao Tian, Xiaoming Yang

College of Textiles, Zhongyuan University of Technology, Zhengzhou 451191, PR China

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ABSTRACT

In the present study, the natural madder dye was investigated to the simultaneous extraction and dyeing of cotton (natural fiber) and nylon (synthetic fiber). The optimum dye extraction conditions were found to be 80 °C, 60 min, and 1:6 with ethyl alcohol after madder had been fermenting for 24 hours with water as solvent. Interestingly, crystallization can be done to separate crystal mollugin from dyed solution. And then, dyed fabrics exhibited improved color strength and ultraviolet protection factor. Meanwhile, the mollugin showed a strong fluorescence emission with maximum emission band at 464 nm with 372 nm excitation in the solid state, which may provide potential molecular system for bio-based optoelectronics and chemical sensors.

1. Introduction

A renewed international interest has arisen in natural dyes due to they were among the promising options for developing a greener textile dyeing process. In comparison between natural dyes and synthetic dyes, natural dyes are non-allergic, non-toxic, biodegradable, and do not cause environmental pollution [1, 2, 3, 4]. The use of madder (red dye) has been flourishing for centuries and ranging from Europe, Asia to Africa [5, 6, 7]. The dried roots of this plant are used as a component in herbal medicines for its anticancer, antifungal, anti-inflammatory and antioxidant activities. To date, colorants and other components extracted from the roots of various plant species of the genus Rubia have been reported and used as dyestuff. These components of the roots involved anthraquinones and naphthoquinone derivatives, which have been widely used as dyes, drugs, cosmetics and so on [8, 9, 10, 11].

Crystallization is an important method to obtain the desired properties or structures in crystal engineering. Crystal engineering is a branch of supramolecular chemistry that deals with the design, synthesis and use of molecular crystals. This branch of solid-state chemistry is aimed to select appropriate synthons and technologies to obtain crystal structure, which had intellectual challenge in constructing new structures similar to that in organic synthesis. And then, from the viewpoint of preparation of molecular crystals targeting property, the designated crystal structure was obtained by the conventional evaporation technique [12, 13]. Luminescent molecular crystals have been paid much attention due to their applications in optoelectronics, biological imaging and chemical sensors. Fluorophores having emission that is enhanced when they are either aggregated or in the solid state [14, 15, 16, 17, 18].

Based on the above facts, in this work, the madder dye solution was of interest from a crystallization point of view to volatilize slowly under low temperature. Interestingly, the yellow bulk crystals were obtained from dye solution, which were confirmed to be mollugin by single crystal X-ray diffraction. On one hand, the mollugin was used as medicine with antitumor, antiviral and other activities, however, its crystal structure and fluorescence property were not well studied [19, 20, 21, 22]. Here, the cotton (natural fiber) and nylon (synthetic fiber) samples were chose to dye with the extracted solution before and after crystallization [23]. The dyed fabrics of color strength and ultraviolet (UV) protection ability were tested. And then, the crystal structure of mollugin was characterized by single crystal X-ray diffraction, and its solid-state fluorescence property was also investigated.

2. Experimental

2.1. Materials and methods

The madder roots were purchased from China, grown in luanchuan region of henan province and received as dried roots, and were used for preparative isolation of mollugin. Other chemicals were of reagent grade and used as purchased without further purification. The purity of the bulk microcrystalline materials obtained from the syntheses was checked by Powder X-ray diffraction analysis. Powder X-ray diffraction (PXRD)

* Corresponding author.
E-mail address: duhaijuan2009@126.com (H. Du).

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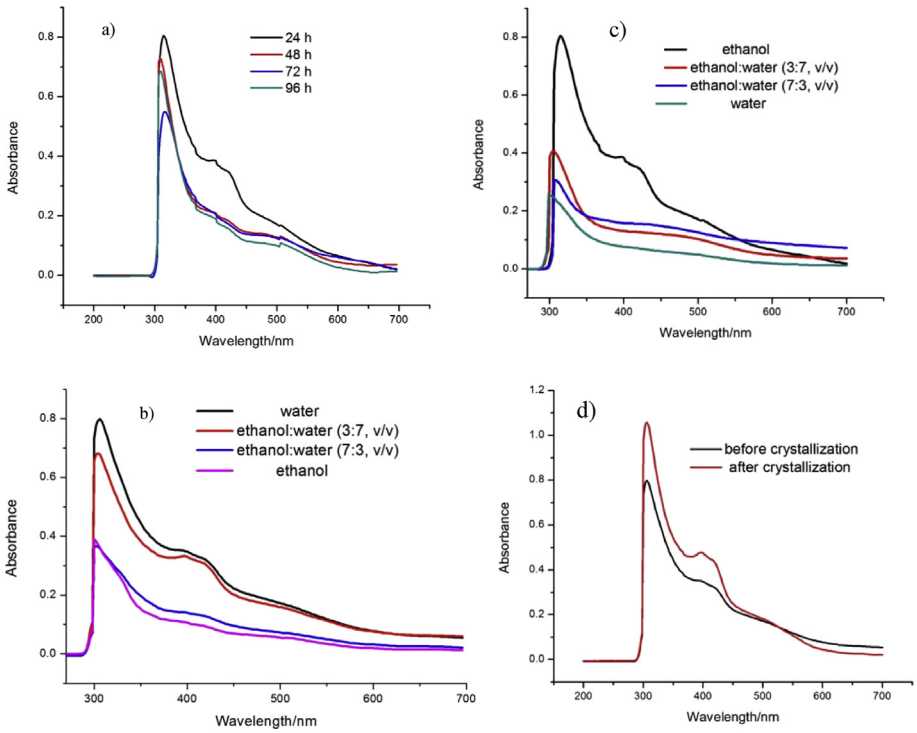

Fig. 1. (a) UV-visible spectrum of the extracted dye solutions under different fermentation times. (b) UV-visible spectrum of the extracted dye solutions under different fermentation solvents; (c) UV-visible spectrum of the extracted dye solutions under different extracted solvents; (d) UV-visible spectrum of the extracted dye solutions before and after crystallization (Taking 1mLthe concentrated dye solution dilution and constant volume to 100mL volumetric flask).

patterns were recorded using Cu Kα1 radiation on a PAN analytical X'Pert PRO diffractometer. UV-Vis absorption spectra were obtained using TU-1810 spectrophotometer. Fluorescence spectrum was carried out with a FL-4600 spectrometer. High Performance Liquid Chromatography (HPLC) analyses were using an Agilent C18 column (250 mm × 4.66 mm, particle diameter 5μm) kept at 35 °C. Methyl alcohol and water were used as mobile phase and the elution gradient was performed at 0.5 mL/min flow rate and 10 μL injection volume. Chromatographic peaks and data were analyzed using Analyst software.

2.2. X-ray crystallography study

Crystallographic data for the compound **mollugin** was collected at 100 (2)K on a Bruker APEX-II area-detector diffractometer equipped with graphite-monochromatized Mo-Ka radiation (λ = 0.71073Å). Its structure was solved by direct method and expanded using Fourier techniques.

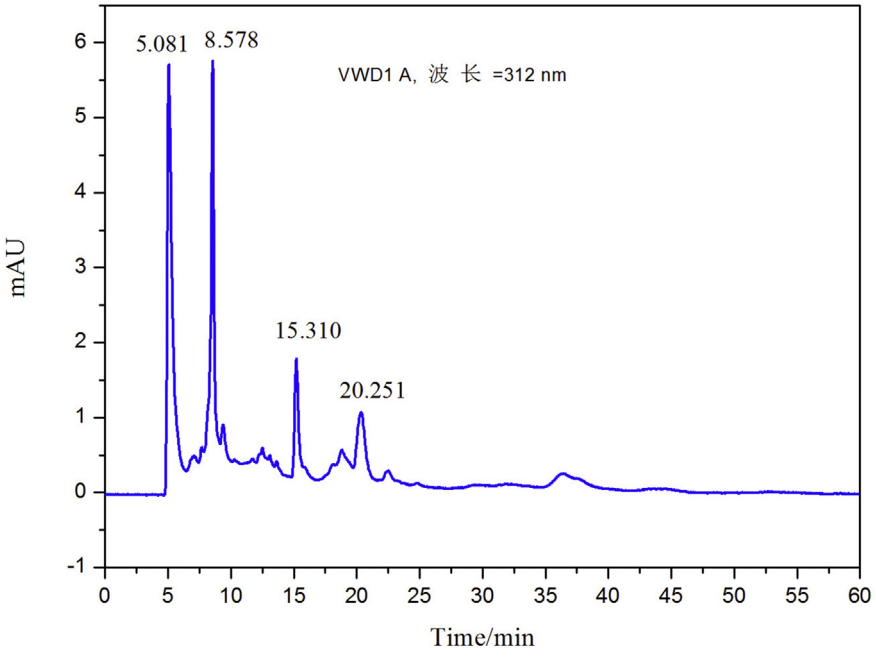

Fig. 2. (a) HPLC chromatogram of the extracted dye solutions.

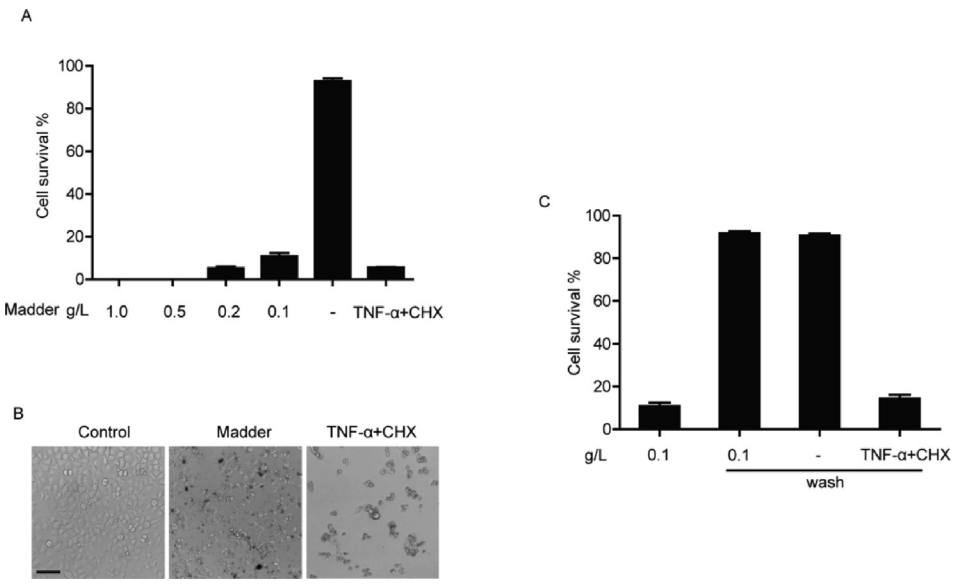

Fig. 3. (A) HeLa cells were stimulated with madder at the indicated concentrate and cell viability was determined by measuring ATP levels at 12 h post treatment. TNF-α+CHX, the cell death inducer, was added as the positivie control. (B) Hela cells treated with madder, TNF-α+CHX or DMSO. Photographs of were taken under microscope at 12 h post treatment. (Scale bar indicated 50 μm). (C) Hela cells were treated with madder, TNF-α+CHX or DMSO. At 3 h post treatment, cells were washed with PBS twice, and replaced with fresh DMEM medium. Cell viability was determined by measuring ATP levels at 12 h post treatment.

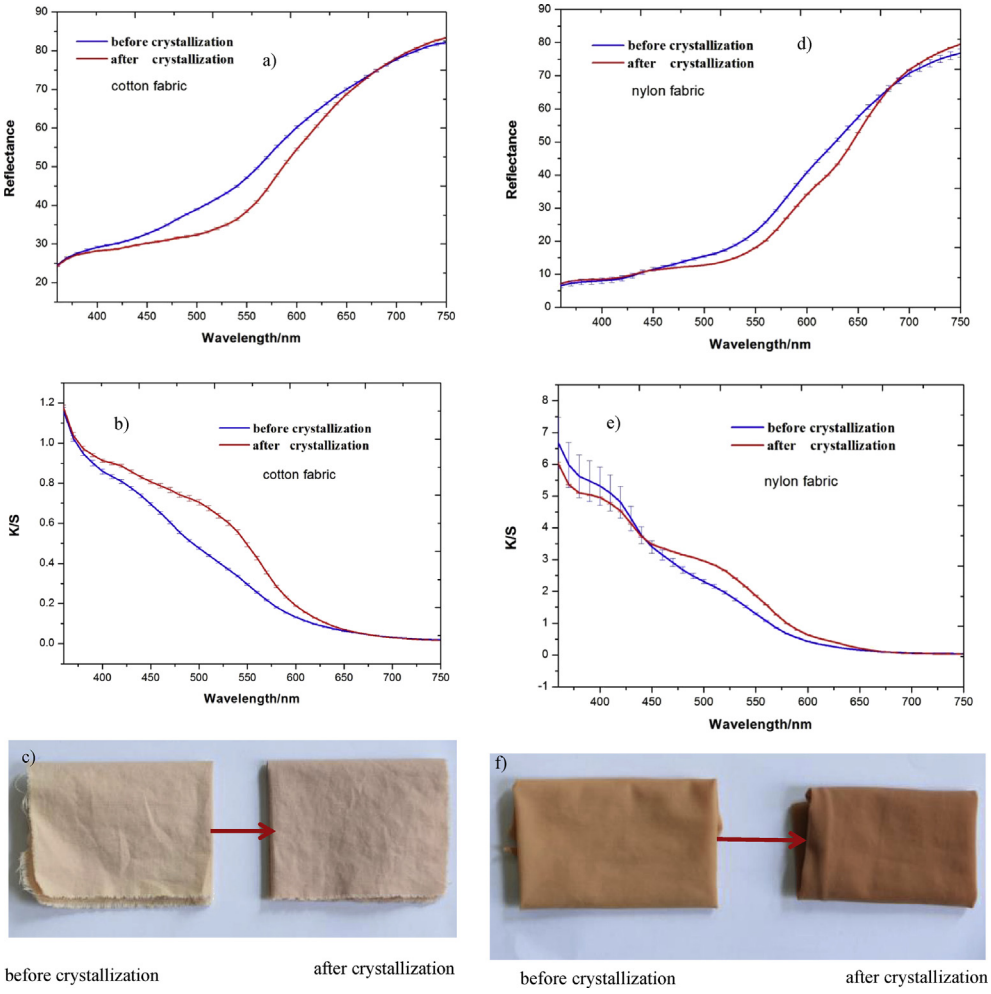

Fig. 4. Error bars: (a) Spectral reflectance of the dyed cotton fabric before and after crystallization; (b) K/S of the dyed cotton fabric before and after crystallization; (c) the picture of the dyed cotton fabric before and after crystallization; (d) Spectral reflectance of the dyed nylon fabric before and after crystallization; (e) K/S of the dyed nylon fabric before and after crystallization; (f) the picture of the dyed nylon fabric before and after crystallization.

Table 1
Results for ultraviolet protection factor (UPF).

Sample	UPF			
	Undyed fabric	Mordant fabric	Dyed fabric Before crystallization	Dyed fabric After crystallization
Cotton	7.5	34.4	35	44.8
Nylon	5.3	7.4	17.4	18.4

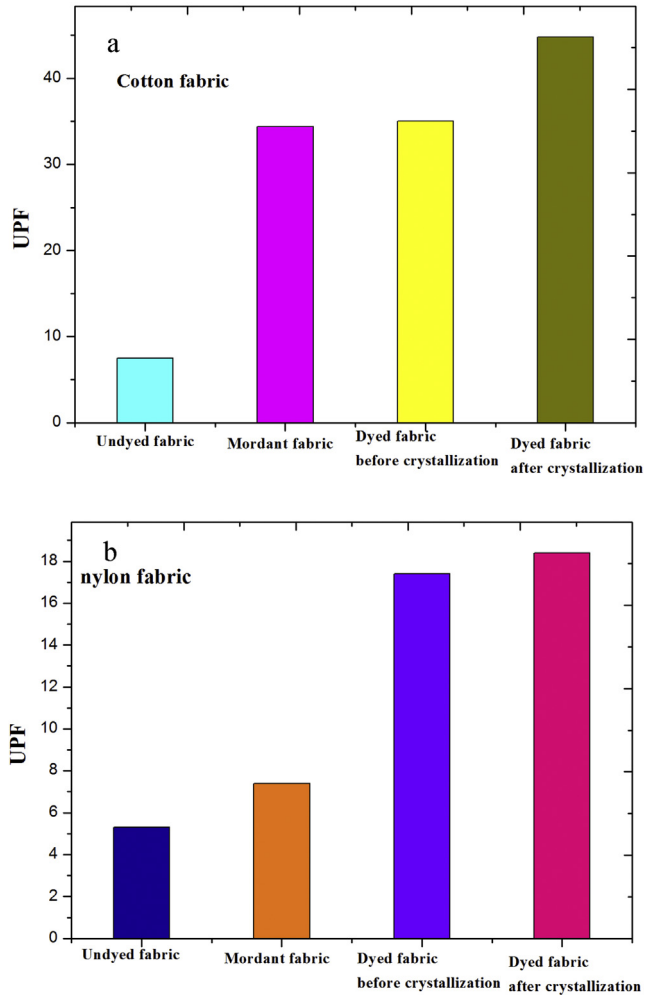

Fig. 5. (a) UPF of the dyed cotton fabric before and after crystallization; (b) UPF of the dyed nylon fabric before and after crystallization.

The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical constraint. The structures were refined with full-matrix least-squares techniques on F^2 using the SHELXTL-97 program package. Crystal data for **mollugin** was summarized in detail in Table S1 (CCDC number 184039), Selected bond lengths and bond angles were put in Table S2 (see the Supporting Information). In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (PXRD) experiments were carried out for **mollugin**. The experimental PXRD patterns of **mollugin** correspond well to the simulated PXRD patterns, indicating that the bulk phase materials are isomorphous (Fig. S1).

2.3. Extraction and crystallization

To extract the madder colorant, madder roots were first washed with tap-water in test sieve and air-dried at room temperature, and then chopped and powdered. And then, we selected different fermentation times (24h, 48h, 72h, 96h), fermentation solvents and extraction solvents (ethanol, ethanol:water (3:7, v/v), ethanol:water (7:3, v/v), water) to extract plant dyestuff and chose the best method of extraction according to the absorbance value. The extracting solution was filtration and concentrated in a rotary evaporator flask to 1/3 of the original volume. The concentrated dye solution was evaporated under low temperature and several days later yellow crystals suitable to X-ray diffraction, mollugin crystals were obtained by repeated crystallization.

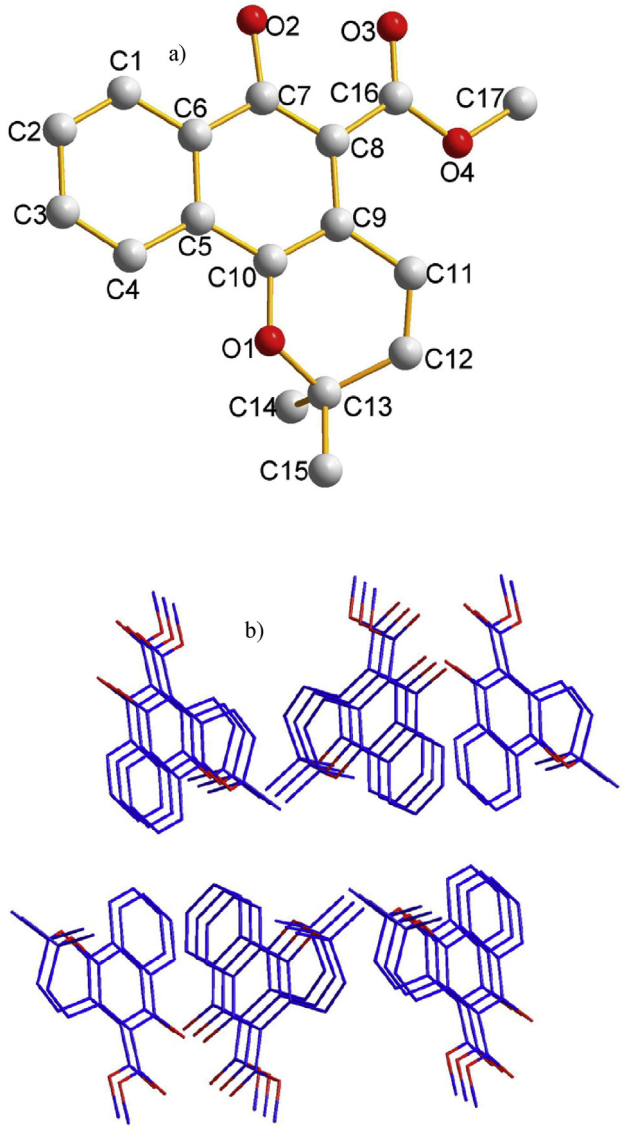

Fig. 6. (a) The unit diagram of mollugin with atom numbering scheme; (b) the packing diagram of mollugin.

2.4. Mordanting and dyeing

Mordanting was carried out using the pre-mordanting method. This was performed on cotton and nylon fabric using 1 g/L zinc sulfate, and at 50 °C for 45 min in a liquor ratio of 50:1. Samples were then squeezed and transferred into the dyebath. Then, the mordanted samples were heated in a liquor ratio of 50:1 (10 mL of extract) at 80 °C for 60 min. No adjustment of pH was made. The samples were then rinsed, squeezed and air-dried.

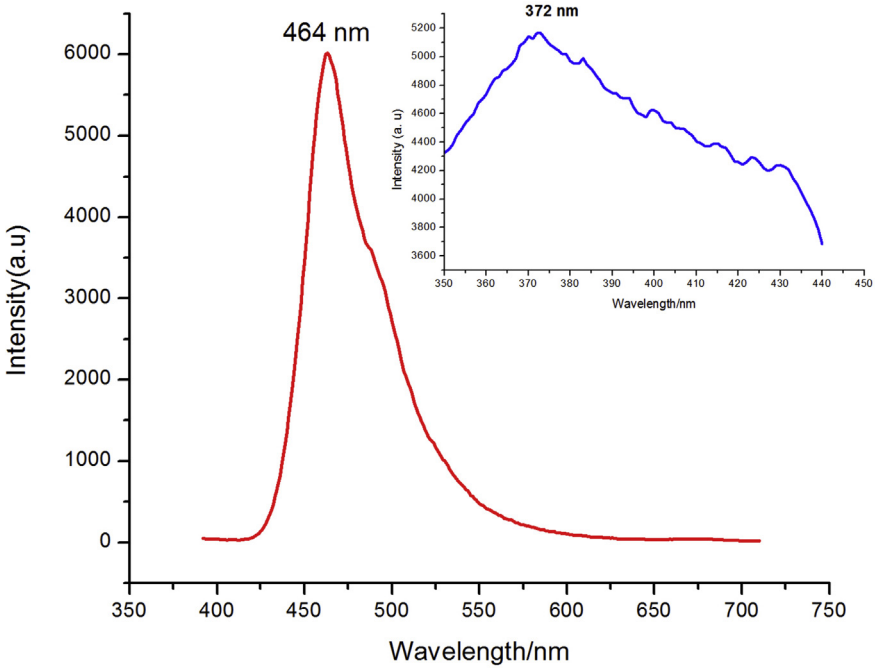

Fig. 7. (a) Solid state excitation (blue, λ_{em} = 464 nm) and emission (red, λ_{ex} = 372 nm) spectra of mollugin.

2.5. Color measurements

Dyed samples were analyzed by measuring the reflectance curve between 350 and 750 nm with the spectrophotometer with illuminant D_{65} at 10° observer. For each sample, three measurements at three different places were made, and the average values were reported. Color strengths (K/S) of dyed samples were calculated using the Kubelka-Munk equation:

$$K/S = (1-R)^2/2R \quad (1)$$

where R is the observed reflectance, K is the absorption coefficient, and S is the light scattering coefficient. In general, the higher the K/S value, the higher the depth of the color on the fabric [2, 3, 24, 25].

2.6. Evaluation of UV protection factor

UV protection provided by a textile material is measured in terms of its ultraviolet protection factor (UPF). It is defined as a ratio of average effective UV irradiance calculated for unprotected skin to the average UV irradiance calculated for skin protected by the test fabric. UPF of the original and dyed samples were measured using AS/NZ 4399:1996 method by Zancheng HB-902 instrument [3, 26].

3. Results and discussion

3.1. Optimization of extraction conditions

The results show that the dye solution of madder, which is extracted from madder with ethyl alcohol after madder had been fermenting for 24 hours with water as solvent. The best extraction of madder is choosing ethanol as solvent, which was ascribed to the cleanability and safety of ethanol comparing with the other organic solvents. The bath ratio is 1:6, extracting 3 times, the extracting temperature is 80 °C and the extracting time is 60 min (Fig. 1a-c). After crystallization, the dyed solution exhibited an enhanced absorption in the UV-visible spectrum at around 314 nm, and is shown in Fig. 1d.

3.2. Instrumental analysis (HPLC)

The HPLC of madder extracted solution exhibited at least four chromatographic peaks with preferable separation and major peak area, which indicated there were more than four chemical components (Fig. 2).

3.3. Test for cytotoxicity of madder dye

The safety of the extracted dye from madder was investigated in Hela cells. And they were reared in laboratory and were maintained at 37 °C at Dulbecco's Modified Eagle Medium (DMEM) (Hyclone) supplemented with 10% (v/v) heat inactivated fetal bovine serum (FBS) (Gibco) in 5% CO_2 atmosphere. Hela cells were seeded in a 96-well plate and treated as indicated. ATP level was determined using the CellTiter-Glo assay (Promega) according to the manufacturer's instructions (ATP Assay). The experimental results were shown in Fig. 3, which induced the cell death of epithelial cells. Although the madder revealed cytotoxicity similar to the reported paper [25b], the harm to skin cell could relieve via washing (Fig. 3C). Based on the experimental facts, the madder dye still need to purification and separation to improve its performance, and provide the opportunity for biofunctional textiles.

3.4. Dyeing studies

The color strength of cotton (natural fiber) and nylon (synthetic fiber) samples dyed with the extracted solution before and after crystallization are shown in Fig. 4. The spectral reflectance of samples dyed with different solutions is qualitatively very similar, and they haven't any distinguishable peak. The samples dyed with the extracted solution after crystallization showed higher color strength, which may be due to the extracted solution was further concentrated via crystallization. In addition, the crystal mollugin was separated from the solution, and could weaken the influence on dyeing process and colored light.

3.5. The improved ultraviolet protection factor (UPF)

Textile clothing can protect the skin from harmful UV radiations because the fabric can reflect, absorb and scatter these rays and reduce the amount of radiation transmitted through it [26]. As shown in Table 1 and Fig. 5, it is clear that in comparison with the undyed fabrics and dyed fabrics before crystallization, the dyed fabrics after crystallization give improved UPF rating. In addition, we also investigated the mordant fabric without dyeing to prove that the UV protective activity is really ascribable to the dye and not to the mordant.

3.6. Structural characterization of mollugin

The single crystal X-ray diffraction analysis shows that mollugin crystallizes in the triclinic space group *P-1*. The unit and packing diagram of mollugin were shown in Fig. 6, which was reported by the paper [21].

3.7. Solid-state fluorescence

The photoluminescent property of mollugin in the solid state at room temperature was investigated (Fig. 7). It shows a strong emission with maximum emission band at 464 nm with 372 nm excitation in the solid state, which may be assigned to its overall degree of conjugation in favor of to the π-π* transition in the crystal phase [14, 15, 16, 27].

4. Conclusions

In summary, this work has demonstrated crystallization can be done to separate crystal mollugin from dyed solution. The results indicated that madder may serve as a multifunctional species. Dyed fabrics exhibited improved color strength and ultraviolet protection factor. Meanwhile, the mollugin showed a strong emission with maximum emission band at 464 nm with 372 nm excitation in the solid state. Moreover, the use of madder dye is an interesting route and offers opportunities, in terms of functional performance, for environmentally friendly and minimum pollution.

Declarations

Author contribution statement

Haijuan Du: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Qing Wang, Mengchao Tian, Xiaoming Yang: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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