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Novel green printing of cotton, wool and polyester fabrics with natural madder dye nanoparticles

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In this study, madder dye nanoparticles have been successfully prepared by using a simple ball milling technique. Madder dye nanoparticles are characterized by using UV-vis. absorption, XRD, TEM, FTIR spectroscopy and SEM. The prepared madder dye nanoparticles are used as an active ingredient for printing cotton, wool, and polyester fabrics via dye printing technique and pigment printing technique. Factors of printing process, such as substrates mordanting, thickeners type, urea concentration and *p*H of printing paste, urea concentration of first paste and binder concentration of second paste, are studied. Results show that fabrics printed with madder dye nanoparticles via mentioned two methods show very good to excellent fastness properties with a full green method. These data indicate that printed samples have high quality for colour strength without any environmental hazards as compared to other conventual and nanotechnological aspects.

Keywords: Ball milling, Cotton, Nanoparticles, Madder, Natural dye, Novel green printing, Polyester fabrics, Wool

1 Introduction

Textile industries are represented as the second source of pollution in the world after agriculture. Therefore, natural dyes could replace synthetic chemical pouting dyes by achieving green chemistry principles [1, 2]. Mostly, the natural dyes are vegetable dyes from plant sources [3, 4].

Madder dyes are considered a queen of natural dyes. It is a red colorant obtained from the roots of species belonging to the Rubiaceae family, which are producing a variety of anthraquinone dyes in its roots and rhizomes. The main components are di- and tri-hydroxy-anthraquinones, alizarin and purpurin and their derivatives; ruberythric acid (alizarin-primeveroside), pseudopurpurin, and lucidinprimeveroside. Rubiadin, munjisti, quinizarin (1,4 dihydroxyanthraquinone), lucidin, nordamnacanthal, xanthopurpurin, and 1,8-dihydroxyanthraquinone are also identified from plant tissues [5-8].

Mordants have an affinity for both textile fabrics and dyes, thus they are used to link the dyestuff to the fibre [9, 10]. Therefore, they can be used for improving dye uptake and fixation causing a change in color shade and fastness properties[9]. The metal ions of these mordants can act as electron donors to form coordination bonds with the dye molecules, making them insoluble in water [8, 9, 11-13].

Nanotechnology is a new field of research dealing with nanomaterials with particles size from 1nm to 100 nm. Nanoparticles impart new amazing physical and chemical properties in textiles [14-21].

Ball milling is a top-down technique used to prepare nanoparticles. Nowadays it is widely used for nanoparticles preparation, as it is simple, cheap, and used for all materials [22-25].

In the present work, nanoparticles are prepared from madder dye via ball milling technique for printing some selected natural and synthetic fabrics, such as wool, cotton, and polyester. The prepared nanoparticle dye is characterized by transmission electron microscopy, UV-vis., spectra, and X-ray diffraction. Several factors are studied to optimize the printing process, such as mordanting of substrates, thickeners type, urea concentration and printing paste *p*H for first paste; and urea concentration, printing paste *p*H, and binder concentration for second paste. The printed fabrics are characterized by colorimetric measurements.

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2 Materials and Methods

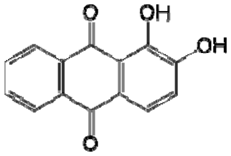
2.1 Materials

Mill-scoured wool fabric (1/1 plain weave and 239 g/m^2 weight) was supplied by EL-Nasr Company for Spinning, Weaving, and Dyeing, El-Mehalla Elkubra, Egypt. Mill desized, scoured, and bleached cotton fabric (plain weave, warp 36 yarns/cm, weft 30 yarns/cm, and fabric weight 150 g/m^2) was supplied by EL-Nasr Company for Spinning, Weaving, and Dyeing, El-Mehalla Elkubra, Egypt. Polyester (plain weave fabric1/1, weight 185 g/m^2) was kindly supplied by Artex Apparel, Egypt.

Clean, dry, and ground madder plant were purchased from the Agricultural Seeds Medicinal and Medical Plant Company (Harraz), Cairo, Egypt, having the following specifications:

Botanical name	:	*Rubia tinctorum L.*
Class	:	Di- and tri-hydroxy-anthraquinones
CI No.	:	C.I.Natural Red 8
Part used	:	Roots

Structure (Alizarin):



Sodium alginate (8%), Meypro gum (8%), carboxymethyl cellulose (CMC) (3%) and DEL Thickner P (3%) were used as thickening agents. Tartaric acid (2,3-dihydroxybutanedioic acid) was used as mordant. Urea [$(NH_2)_2CO$], sodium carbonate Na_2CO_3, diammonium phosphates $(NH_4)_2HPO_4$ and acrylate binder were also used in this study.

2.2 Methodology

2.2.1 Preparation of Dye Nanoparticles

The madder dye powders were milled for 15 h in a planetary ball mill type under the conditions as ball to powder weight ratio (BPR) 10:1, balls diameter 10 mm, and rotating speed 400 rpm. It is worth mentioning that the milling was done in a cycle of 3 h and paused for 2 min. A stock solution of madder dye nanoparticles was prepared by using the milled dye particles of 3% concentration (3g of dye powder was dispersed in 97 cm^3 of distilled water). The suspension was irradiated afterward with ultrasound waves (53 mega Hz) and stirred at 60 °C for 90 min (Scheme 1).

2.2.2 Fabric Mordanting

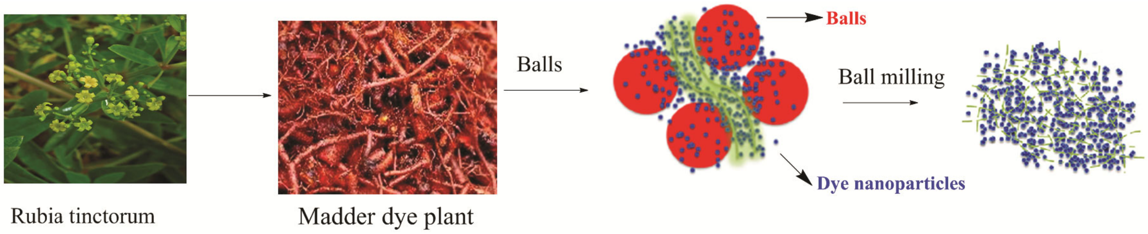
Wool is mordanted in two ways. The first way is before the printing process. The second way is after the printing and fixation process. The mordanting bath is set with tartaric acid, separately on the weight of fabric at M:L ratio 1:40. Mordanting is carried out for wool at 50-60°C for 30 min after which the samples were washed with distilled water and then air dried.

2.2.3 Printing Procedures

To investigate each factor of the present work, two printing pastes having the following formula were applied separately on all substrates:

First paste recipe (dye-printing)		Second paste recipe (pigment-printing)	
Natural dye	:50g	Natural dye	:50g
Thickener	:600 g	Thickener	:600 g (3%)
Urea	:Xg	Diammonium phosphate	:x g
pH adjusting	:y g	Acrylate binder	:y g
Water	:z g	Urea	:z g
		Balance	: G
Total	*:1000 g*	*Total*	*: 1000 g*

The pH was adjusted according to each required value using sodium carbonate and citric acid for the first paste and diammonium phosphate for the second paste. The printing paste was applied onto the fabric through a flat screen-printing technique, and then the prints were left to dry at 25°C. Fixation of the first paste was carried out via steaming at 105°C for 20 min for wool and 125°C for 45min for polyester.



Scheme 1 — Schematic diagram of madder dye nanoparticles production by ball milling

The second paste was applied using thermo-fixation at 160°C for 4 min.

2.2.4 Washing

After the fixation process, the samples were rinsed in cold water, washed with 2 g/L non-ionic detergents (Hostapal CV-ET) using M:L 1:50. for 15 min at 40°C for wool fabrics and 90°C for cotton and polyester fabrics.

2.3 Testing and Analysis

2.3.1 Color Measurements and Fastness Properties

The printed samples were tested according to AATCC and ISO standards [26, 27]. The colour strength values (*K*/*S*) were determined using CIE Lab: D-65 10 standard. The ISO-CO6 D1M was used to determine the colour fastness to laundering. The colour fastness to laundering, perspiration and rub were measured using AATCC-15, AATCC-8, and AATCC-16 standards respectively. The test specimen and the two adjacent fabrics (cotton and wool) were compared using a grayscale. The rating scale of wash fastness for color change was from 1 (very poor), 2 (poor), 3 (fair), 4 (good) to 5 (excellent). The rating scale of light[26-27] fastness was from 1 (very poor), 2 (poor), 3 (fair), 4 (moderate), 5 (good), 6 (very good), 7 (excellent), to 8 (outstanding).

2.3.2 Tensile Strength

The tensile strength of the fabric sample was determined using the ASTM Test Method D5035 on a Q-Test 1/5 tensile tester. Three specimens for each treated fabric were tested in the warp direction and the average value was recorded to represent the fabric breaking load (Lb).

2.3.3 FTIR, UV-Vis, TEM, SEM and X-Ray Study

The FTIR spectra of samples were recorded on FTIR spectrophotometer (JASCO FT-IR-6100) using the KBr pellet disk method for transmittance measurements, in the region of 4000 - 400 cm^{-1} with spectra resolution of 4 cm^{-1}. UV-Vis spectra have been used to confirm the formation of madder dye nanoparticles. The spectra were collected over a range of 250-800 nm. The shape and size of madder dye nanoparticles were practically obtained by using TEM (JEOL-JEM-1200, Japan). The average diameter of the prepared madder dye nanoparticles was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs. Microscopic investigation on madder dye powder before and after milling was carried out using a Philips XL30 scanning electron microscope (SEM) equipped with a LaB6 electron gun and a Philips-EDAX/DX4 energy-dispersive spectroscopy (EDS). Images were taken at different magnifications (from ×1509 to ×30009), using a scanning electron microscope (SEM) to the clarity of the images. X-ray diffraction patterns of samples were recorded on an STOE STADI P Transmission X-ray powder diffractometer system by monitoring the diffraction angle from 10^0 to 80^0 (2h) using monochromatized Cu Ka (k = 1.54051 Å) radiation.

3 Results and Discussion

3.1 Preparation and Characterization of Dye Nanoparticles

The colours before and after ball milling show no different change. Figure 1(a) shows that madder dye has broadband peaks in UV-vis absorption, while madder dye nanoparticles show a sharp band peak due to the nanostructure of madder dye nanoparticles.

Figure 1(b) shows that FTIR spectra of madder dye nanoparticles have the same band peaks as madder dye, but its band peaks decrease as compared to madder dye itself.

To compare the crystalline structure of unmilled and milled madder dye, XRD analysis was performed and its results are shown in Fig. 1(c). XRD of both milled and unmilled madder dye are found similar, except there are broader bands in madder dye nanoparticles than in unmilled madder dye.

Transmission electron microscopy (TEM) illustrates the shape and size of madder dye nanoparticles as shown in Fig. 1(d). Madder nanoparticles formed from madder powder via ball milling show well disperse and semi-spherical shapes. From the histograms (Fig. 1d), it is indicated that particles size ranges from (15 - 55nm) to a major diameter range (30-40 nm). These results data agree with UV-vis spectral data.

Figure 2 shows scanning electron microscopic images of madder dye before and after milling. SEM images show the conversion of particle size of the madder dye from microform to nanoform. In addition, SEM images show that surface particles size changes from 87-232 μm of madder dye to 36-60 nm of madder nanoparticles, which confirms the formation of nanoparticles via a green method. In addition, SEM images illustrate the madder morphology and its conversion to more uniform nanoparticles with a green method.

3.2 Printing of Wool and Polyester Fabrics

The main goal of the present study is printing wool and polyester fabrics with a green printing paste, consisting of green thickeners such as carboxymethyl-

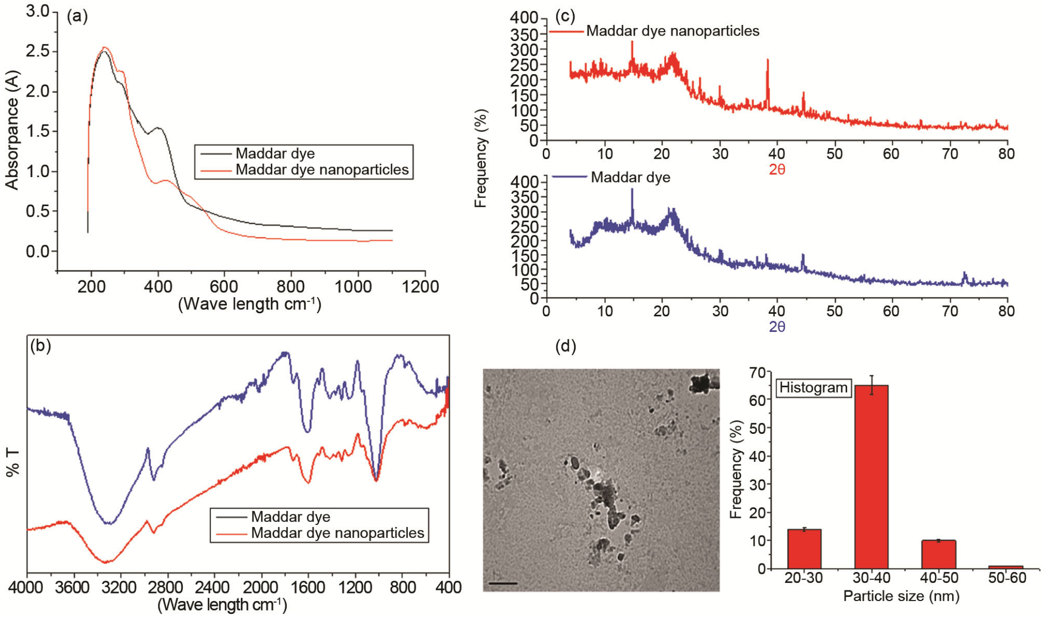


Fig. 1 — (a) UV-vis spectra, (b) FTIR, (c) x-ray diffraction and (d) TEM image/histogram of madder dye and madder dye nanoparticles

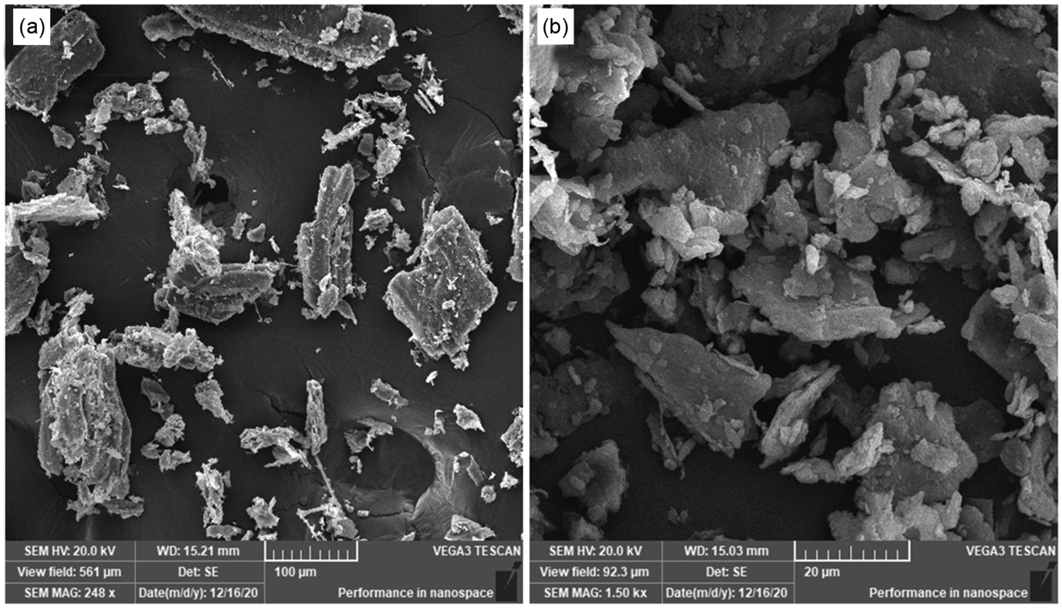
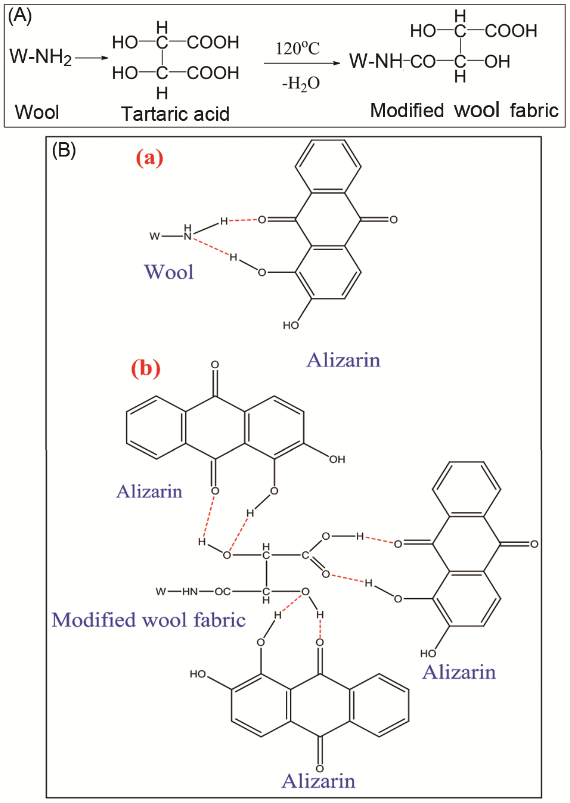


Fig. 2 — Scanning electron microscopic images of (a) madder dye nanoparticles and (b) madder dye

cellulose, sodium alginate, Meypro gum and DEL THICKNER P along with natural madder dye nanoparticles. Natural fabric, such as wool, is pretreated first with tartaric acid as a mordant to increase its dye accessibility (Scheme 2A).

Wool fabric can be modified through its reaction with tartaric acid (mordant) to form the corresponding ester and amide [28, 29] derivatives (Scheme 2A). The reaction will take place in physical absorption at 50-60 ^{0}C, then a chemical reaction takes place during the steam fixation process at 120 ^{0}C. This process creates a more reactive site (amine groups on wool fabrics).

Scheme 2B shows how mordant has a great effect on wool fabric as compared to unmodified fabric. The main difference is that unmodified fabrics have one accessible site from a strong H bond with one-mole madder dye [Scheme 2B (a)], whereas the mordanted fabrics that have three accessible sites can form stronger H bonds with three-moles madder



Scheme 2 — (A) Modification of wool fabric via reaction with tartaric acid; and (B) the reaction of madder dye with unmodified wool fabrics (a), and tartaric acid modified wool fabrics (b)

dyes[Scheme 2B (b)]. In addition, we can find that reaction fixation of wool fabrics comes from amide bond formation. This will reflect the difference in colour strength and fastness properties of the printed fabrics.

To investigate the effect of fabric mordanting on colour development of the used madder dye nanoparticles, different concentrations (0, 40, 60,80,100 and 120 g/L) of tartaric acid are used in wool fabrics' treatment separately, before the printing process (Fig. 3).

Figure 3 shows that an increase in mordant concentration results in increase in *K*/*S* values till 100 g/L concentration of tartaric acid for wool, whereas the value of *K*/*S* increases by 24.53 % for pretreated wool prints and 15.35% for post-treated wool respectively, as compared to untreated prints. On comparing the results of pretreated and post-treated fabrics, it is found that pretreated is better than post-treated.

The above results are due to the effect of both grinding and ultra-sonication of madder natural dye particles on colour strength of wool and polyester fabrics, expressed in *K*/*S* values. The grinding process increases the specific surface area of the madder dye nanoparticles due to particle size reduction [30]. A feasible technique for particle-size reduction is ultrasonic. Ultrasonication of solids leads to microjet and shock-wave-impacts on the surface, together with interparticle collisions, which can result in particle size reduction [31]. Therefore, wool fabric pretreated with 100 g/L tartaric acid as mordant shows improvement in printing with madder dye nanoparticles.

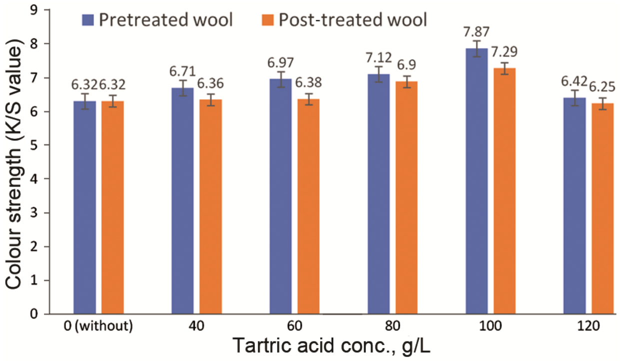


Fig. 3 — Effect of mordant concentration on *K*/*S* values of untreated, pretreated, and post-treated wool fabrics printed with madder nanoparticles

3.3 Factors Affecting Printing of Wool and Polyester Fabrics (First Recipe)

Several factors have been studied to observe role of madder dye nanoparticles prepared by the green method as compared to conventional dye. The factors, such as thickener type, urea concentration and *p*H, are discussed hereunder.

3.3.1 Effect of Thickener Type

Different thickeners, such as carboxymethyl cellulose (CMC), sodium alginate, Meypro gum, and DEL THICKNER P, have been used in the printing pastes to investigate the effect of thickener type. Colour changes of printed fabrics, express in *K*/*S* values, are shown in Fig. 4(a) for wool and polyester fabrics. It is clear from Fig.4 that the type of thickener has a remarkable effect on the *K*/*S* of the printed samples. In most of the cases, the highest *K*/*S* value is obtained by using DEL THICKNER P as a thickener, whereas the value of *K*/*S*increases by 685.71% and 252.87 % for wool and polyester prints respectively, with madder dye nanoparticles as compared to that with madder dye.

3.3.2 Effect of Urea Concentration

Urea is considered as an essential auxiliary in most printing pastes because of its ability to swell the

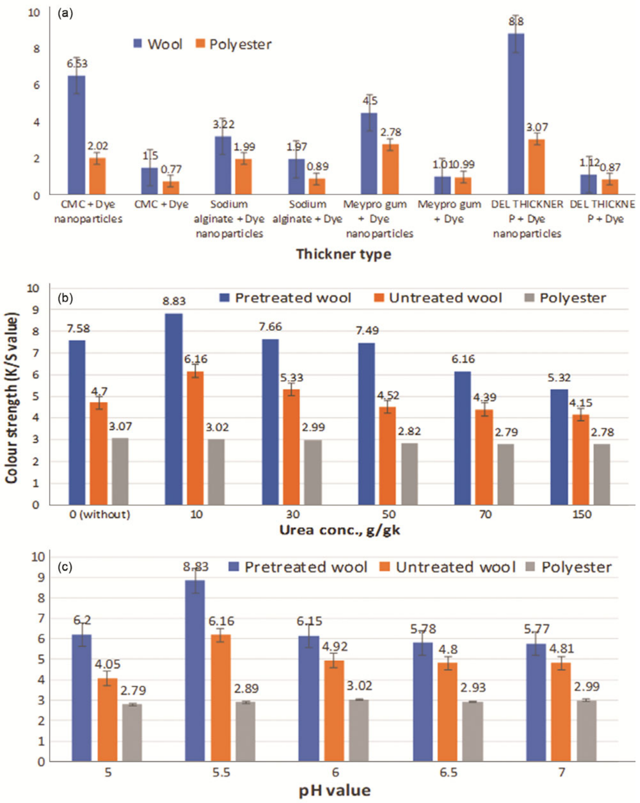


Fig. 4 — Effect of (a) thickener type, (b) urea concentration, and (c) *p*H on *K*/*S* values of wool and polyester fabrics printed with madder dye and madder dye nanoparticles

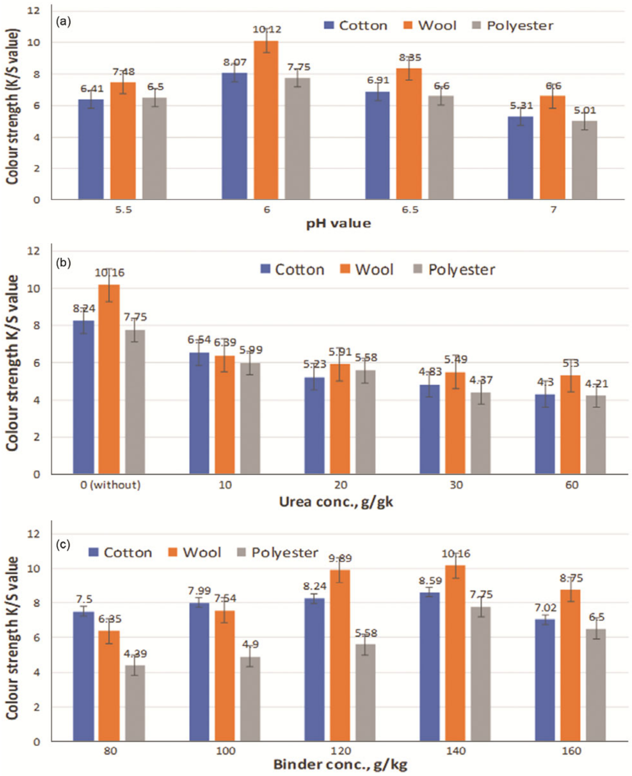


Fig. 5 — Effect of (a) *p*H value, (b) urea concentration, and (c) binder concentration on *K*/*S* values of cotton, wool, and polyester fabrics printed with madder dye nanoparticles

fabrics, that accelerates penetrating dye inside the fabrics [32]. In addition, it acts as a solvent for the dye, i.e used as a moisture-absorbing agent, and accelerates the migration of dye from the thickener film into the fabrics. The influence of urea concentration on colour strength of wool and polyester printed fabrics with madder dye nanoparticles has been studied by using different urea concentrations to the printing pastes (0, 10,30,50,70, and 150 g/kg) and the results are given in Fig. 4(b). In addition, Fig. 4(b) indicates that 0 g/kg (without urea) and 10 g/kg urea conc. can be considered as the best to be added to printing pastes with madder nanoparticles on polyester and wool, regardless of enhancements in colour yields by 16.49 % occurred in wool (pretreated with tartaric acid) print, as compared with the same printed fabrics without urea addition. In addition, colour strength of the treated fabric is higher than their corresponding untreated fabrics for wool, whereas the value of *K*/*S* is increased by 43.344% for treated wool print, pretreated with tartaric acid as compared to the untreated prints. This is due to the fact that the urea has solvation and disaggregation effects on the dye molecules in the printing paste and enhances the solubility of dyes in the printing paste.

3.3.3 Effect of pH on Printing Paste

The *p*H of printing paste has an important role in dye fixation rate. The rate of dye fixation has been increased as the *p*H of printing paste of wool decreased because of increased dye concentration and ammonium ion sites numbers at lower *p*H values[33]. The influence of printing paste *p*H on the *K*/*S* values of printed wool (pretreated with tartaric acid) and polyester substrates with madder nanoparticles is studied, by using different *p*H values (5, 5.5, 6, 6.5 and 7) as shown in Fig. 4(c). The optimum values of *K*/*S* are found at a *p*H value of 5.5 for wool, and *p*H value of 6 for polyester fabrics.

3.4 Factors Affecting Printing of Cotton, Wool, and Polyester Fabrics (Second Recipe)

3.4.1 Effect of Diammonium Phosphates Concentration

Printing paste *p*H is considered as an effective factor in colour variation and subsequently, the influence of printing paste *p*H on colour intensity of the prints is studied by applying *p*H values (5, 5.5, 6, 6.5, and 7) and the results are exhibited in Fig. 5(a).

It is clear from the figure that, maximum *K*/*S* values can be obtained at *p*H 6 for cotton, wool, and polyester substrates printed with madder nanoparticles respectively.

3.4.2 Effect of Urea Concentration

Different concentrations of urea (0, 10, 20, 40, 60, and 80 g/kg) are used to study its effect on the colour strength of cotton, wool and polyester printed fabrics with madder dye nanoparticles. Figure 5(b) shows that printed cotton, wool, and polyester fabrics without urea have the highest *K*/*S* values. This may be because of the swelling properties of urea that helps fixation of dye. So, the fixation here depends on a binder in the presence of diammonium phosphate as a catalyst. Diammonium phosphate catalyst can promote the crosslinking reaction, leading to the fixation of the binder to the fabric. Diammonium phosphate treatment at 160 °C for 4 min adjusts the *p*H of the medium at 6. At this value, binder can be chemically crosslinked on the fabrics and dye [17].

3.4.3 Effect of Binder Concentration

To investigate the effect of acrylate binder concentration on the *K*/*S* values of printing goods, using different amounts of binder concentrations (80,100, 120, 140, 160 g/kg) are used. It is clear from **Fig. 5(c),** that the concentration of binder has a remarkable effect on the *K*/*S* of the printed samples. In most cases, the highest *K*/*S* value is obtained by using 140 g/kg binder.

3.5 Fastness and Mechanical Properties of Printed Fabrics

Table 1 shows the fastness characteristics of the printed cotton, wool and polyester fabrics using madder dye nanoparticles for the first recipe (as a dye) and the second recipe (as pigment). The printed fabrics reveal very good to excellent fastness properties using madder dye nanoparticles as a dye (first recipe) and very good to excellent fastness properties using madder dye nanoparticles as a pigment (second recipe). Light fastness properties are found very good for all printed fabrics, indicating the suitability of madder dye nanoparticles for better fabrics printed (dye or pigment) as a result of chemical bonds between the fabrics and the madder dye nanoparticles molecules. Table 1 also shows that colour strength (expressed in *K*/*S* values) has higher values for all printed fabrics with the second recipe as pigment than those fabrics printed with the first recipe as a dye. In addition, mechanical properties (tensile

Table 1 — Colour strength (*K*/*S*), fastness properties, and mechanical properties of printed wool, cotton, and polyester fabrics at optimum values for both first (as a dye) and second (as a pigment) recipes

Parameter	*K*/*S*	Wash fastness			Rub fastness		Perspiration fastness						Light fastness	Mechanical properties	
		St.	St*	Alt.	Dry.	Wet.	Acidic			Alkaline				TS kgF	EB mm
							St.	St*	Alt.	St.	St*	Alt.			
Pretreated wool printed with madder dye	1.12	3-4	4	3-4	4	4	5	5	5	5	5	5	5	30	34
Pretreated wool printed with madder dye nanoparticles	8.83	4	4	4	4-5	4	5	5	5	5	5	5	5	30	35
Untreated wool printed with madder dye nanoparticles	6.16	5	4	5	4	2-3	5	5	5	5	5	5	4-5	37	42
Prostrated wool printed with madder dye nanoparticles	7.29	5	4	5	4	4	5	5	5	5	5	5	4-5	30	38
Polyester printed with madder	0.89	4-5	4-5	4-5	4	3	5	5	5	5	5	5	4-5	33	40
Polyester printed with madder dye nanoparticles	3.07	5	5	5	4	3	5	5	5	5	5	5	4-5	35	40
Wool printed with madder dye as pigment	2.55	5	5	5	4	2-3	5	5	5	5	4	4	6	39	40
Wool printed with madder dye nanoparticles as pigment	10.16	5	5	5	4-5	2-3	5	5	5	5	4-5	4-5	7	39	40
Polyester printed with madder dye as pigment	1.72	5	5	5	4-5	4	5	5	5	5	4	4	6	40	38
polyester printed with madder dye nanoparticles as pigment	7.75	5	5	5	5	4	5	5	5	5	4-5	4-5	6	40	38
cotton printed with madder dye as pigment	1.05	5	5	5	5	4	5	5	5	4	4-5	4-5	5	74	17
cotton printed with madder dye nanoparticles as pigment	8.24	5	5	5	5	4-5	5	5	5	4	4-5	4-5	5	75	20

TS─Tensile strength, EB─ Elongation-at- break, * Data are expressed as Mean ± S.D. for n=3.

strength and elongation-at-breaks show very good data compared with untreated and unprinted fabrics for all fabrics but the values of mechanical properties for fabrics printed with the first recipe as the dye is slightly higher than that for the fabrics printed with the second recipe as a pigment. Tensile strengths for untreated wool, cotton and polyester fabrics are 36.75 ± 0.750, 45.25 ± 1.750 and 34.75 ± 0.250 kgf respectively. Elongation-at-break for wool, cotton and polyester blank fabrics are 49.00 ±1.000, 23.50 ± 1.500 and 36.50 ± 0.500 mm respectively. Table 1 shows that the dye nanoparticles enhance the mechanical properties of printed fabrics due to the nanostructure.

4 Conclusion

A new green approach for the printing of cotton, wool, and polyester fabrics has been established using madder natural dye nanoparticles.The ball milling technique is used for producing madder dye nanoparticles in one step at normal temperatures and pressures. The prepared madder dye nanoparticles have been confirmed by UV-vis, XRD, TEM, and SEM. Madder dye nanoparticles are used to print cotton, wool, and polyester fabrics through two methods one as a dye and the second as a pigment. The first method (as a dye) shows satisfactory results for wool and polyester with madder dye nanoparticles, while it does not give satisfactory results with cotton. However, the second method gives satisfactory results with cotton, wool, and polyester fabrics. In the first method (as a dye), the best primary treatment is observed as, the use of 100 g/kg tartaric acid for treating cotton and wool fabrics; thickener DEL THICKNER P; *p*H level 8 for cotton, 5.5 for wool, and 6 for polyester; urea 150 g / kg with safflower, 10 g / kg with wool. Second method (as a pigment) shows best results using thickener: DEL THICKNER P; binder 140 g/kg; and *p*H 6 for the three fabrics. The use of madder dyes nanoparticles and tartaric acid as a natural fixative increase the colour fastness and reduces the pollution. Using madder as a dye gives a medium colour fastness with very good washing and rub fastness, while printing with madder as a pigment gives higher colour strength with low rub fastness (wet or dry). Thus, whoever wants high color depth and does not need high rub fastness, can choose printing with madder as a pigment; and those who want medium colour depth and rub and wash fastness can choose printing with madder as a dye.

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