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Research Article

Improving Printability of Silk and Polyamide Substrates with Madder Nano-Sized Particles

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Abstract

The possibility of using madder nanoscaled particles, as a natural dye for printing silk and polyamide 6 fabrics, has been investigated. The dried plant is both milled and exposed to ultrasound waves (for a specific period of time), incorporated with urea in the printing paste at an acidic pH value, printed on the pretreated fabrics and eventually the prints are steamed and washed off. The influence of several parameters and measurements affecting K/S values as well as fastness levels of the prints are studied in detail i.e. mordant and urea concentrations, printing paste pH, SEM, TEM and FT-IR analysis and fastness properties. Results show that, printing using nano-scaled particles of the natural dye greatly enhances both: K/S values and fastness levels of the prints. SEM, FT-IR and UV-visible spectroscopes are employed to show particle changes after milling as well as sonication.

Keywords: Ball miller; Fastness properties; Printing; Madder nano-scaled particles; Sonication

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1. Introduction

The roll of dyestuffs industry in introducing contamination to the environment is increasingly being criticized. Many synthetic dyes may lead to various harmful by-products during their manufacturing [1]. In recent years, people realized the utility of natural dyes and moved towards them with a scientific background [2]. Natural dyes exhibit better biodegradability and generally have a higher compatibility with the environment [3].

The majority of natural dyes need a mordant in the form of a metallic salt [4]. The effect of the mordant is to assist the adsorption and fixation of the colour and promote good bonding of colour with fibre [5]. An almost complete range of colours can be obtained by appropriate combination of various natural dyes and mordants [6]. The main problem with natural dyes is that, whilst they are themselves harmless, most mordants are generally not eco-friendly [7].

Since silk and nylon have both amino and carboxylic end groups, these fibres can be dyed with natural acid dyes under acidic pH in the same manner as synthetic acid dyes [8]. Nylon being hydrophobic in nature, it can also be dyed with the non polar disperse dyes. The chemical structures of many natural dyes are similar to those of synthetic disperse dyes in the sense that they do not have solublizing groups and are sparingly soluble in water. Hence, they can be applied on hydrophobic fibres such as polyester and nylon. Further, these dyes can directly dye wool and silk since they have some limited affinity for these fibres [9].

Nanotechnology has been intensively developed and widely applied in many areas today, insoluble dye particles can be made into nanosize easily. Nanoparticles can be generated in aqueous environment through milling of bulk powders in the presence of dispersing agents, including anionic, cationic and polymeric electrolytes. The nanoparticles formed are immediately adsorbed by the surfactant molecules on their surfaces and stabilized as individual particles [10].

Ultrasound is a well-established method for particle size reduction in dispersions and emulsions. Ultrasonic processors are used in the generation of nano-size material slurries, dispersions and emulsions because of the potential of the deagglomeration and the reduction of primaries. These are the mechanical effects of ultrasonic cavitation. Ultrasound can also be used to influence chemical reactions by the cavitation energy. This is sonochemistry [11].

In the present study, an attempt has been made to optimize the conditions of printing silk and polyamide 6 fabrics with madder natural dye in the form of nanoscaled powder form, besides incorporating urea in the printing paste using mild acidic values. Results of colour strength and various measurements are investigated. Dye particles are milled and sonicated besides, fabrics are premordanted via two mordants (ferric chloride and ferrous sulphate separately) prior to printing stage.

2. Experimental

2.1. Materials

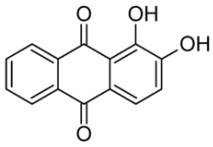
2.1.1. Substrates: Both used substrates in the present work are of the following specifications:

Natural silk fabric: mill scoured natural silk fabric, having a weight of 77 g/m^2 supplied by El-Khatib Sons Suhag, Egypt.

Polyamide 6 fabric: mill scoured nylon 6 knitted fabric, warp knitting, open width, having a weight of 108 g/m^2, supplied by Watanya Weaving Co., Cairo, Egypt.

2.1.2. Natural dye: Clean, dry, grinded madder plant, having the following specifications, is used throughout the present study:

Table 1. Technical information of madder natural dye

English Name	Latin Name	Coloured Component	Colour Index	Chemical Structure
Indian Madder [4]	Rubia Cardifolia	Munjistin (Acid/Mordant/Disperse) Red	Natural Red 8,16	

2.1.3. Mordants and other chemicals: All the used chemicals are of analytical grade:

Ferric chloride: $FeCl_3$

Ferrous sulphate: $FeSO_4$

Mypro gum NP-16 (Meyhall): which is a non-ionic thickening agent based on modified plant seeds gum that is capable of withstanding the high acidity required in printing.

2.2. Methodology

2.2.1. Fabric mordanting

Both substrates (silk and polyamide 6) are mordanted prior to printing process. The mordanting bath is set with different concentrations of both mordants, ferric chloride or ferrous sulphate, separately on weight of fabric at L.R. 1:40. Mordanting is carried out at 50 ^{o}C for 30 min. after which the samples are washed with distilled water and air-dried.

2.2.2. Preparation of dye nanoparticles

Madder natural dye was ground using an energy Ball Mill with a speed of 50 cycles/min. The dye powder was sealed in a hardened steel vial (AISI 44 ℃ stainless steel) using hardened steel balls of 6 mm diameter. Milling was performed using a ball : powder mass ratio of 4:1. The dye was milled at different intervals, after each milling interval the particle size of the resulted dye powder was measured. The smallest particle diameter of 34 nm chosen to be used in the present study was obtained from milling the dye powder for 30 days.

A stock solution was prepared using the milled dye particles of a concentration of 3% where 3g dye powder was dispersed in 97 cm^3 of distilled water. The suspension was irradiated afterwards with ultrasound waves (720 kHz) and stirred at 80 ^{o}C for different periods of time (4, 6 and 8 hours.) from which the ultrasound treatment of 8hrs. was chosen to proceed with since it gave best K/S values.

2.2.3. Printing procedures

To investigate each factor of the present work, a printing paste having the following formula was applied on all substrates:

20	g	Stock dye mixture
80	g	Mypro Gum thickener
10	g	Urea
X	ml	Water
1000	g	Total weight of paste

The pH is adjusted according to each required value using acetic acid solution. The printing paste is applied to fabric through flat screen printing technique then, the prints are left to dry at room temperature. Fixation of the dye is carried out via steaming at 120 ℃ for 20 min. for both substrates. The samples are finally washed off using 2g/l non-ionic detergent: Sera-Wash M-RK (manufactured by Dystar Textilfarben, Germany) at a liquor ratio of 1:50. Washing is carried out at 60 ℃ for 10 min.

2.3. Measuements

2.3.1. Colour Strength

The colour strength of the printed specimens expressed as K/S is evaluated by a light reflectance technique at maximum. The spectrophotometer used is of the model ICS-Texicon Ltd., England [12].

2.3.2. Scanning Electron Microscope (SEM)

The untreated and treated samples of dye particles with ultrasound waves are investigated by a Scanning Electron Microscope (SEM) Philips XL 30 attached with an EDX unit; with an accelerating voltage of 30 K.V., magnifications range 1500-2000x and a resolution of 200 A. Before examinations, the fabric surface was prepared on an appropriate disk and coated randomly by a spray of gold.

2.3.3. Transmission Electron Microscopic analysis (TEM)

The observation of the dye particle shape and the measurement of the particle size distribution of the precipitate were performed using a JSM-5200 Scanning Electron Microscope (JEOL) using conductive carbon paint. Transmission Electron Microscope (TEM) is a good tool to study the particle size and morphology of dyes. TEM gives a good resolution down to a nanometer scale. Photographs were taken using JEOL-2010.

2.3.4. Fourier Transform Infrared spectroscopy (FT-IR)

Fourier Transform Infrared spectroscopy (FT-IR) of the samples was recorded using a Brucker-FTIR. The method includes mixing few mgs. of a fine powder of the sample with KBr powder in a gate mortar. The mixture was then pressed by means of hydraulic press. The absorbance was automatically registered against wave number (cm^{-1}).

2.3.5. Optical properties (UV-Visible spectroscope)

The optical absorption of dye particles dissolved in distilled water was recorded in the wavelength range of 400-800 nm employed using a Shimadzu spectrophotometer, at room temperature.

2.3.6. Fastness properties

Fastness properties of silk and polyamide prints to washing, perspiration and rubbing are assessed according to standard methods [13].

2.3.7. Tensile mechanical testing

The samples are cut into strips of dimensions – x – cm and every data point is the average of 3 tests. Tensile strength measurement is carried out using a Textile Tensile Strength tester No: 6202, 1987, type: Asano Machine MFG, Japan.

3. Results and Discussion

3.1 Mordanting of substrates

Mordants are water-soluble salts of metals, which help bond fibre and dye at the molecular level. While not all natural dyes require the use of mordants, the majority of dyes will benefit from their use, they can provide fastness to light and washing as well as brilliance of colour [14]. By using different mordants, a variety of shades

and sometimes even different colours may be obtained from a single dyestuff [15]. To investigate the effect of fabric premordanting on colour development of the used natural dye nanoparticles, several concentrations (0, 20, 40, 60 and 80 g/l) of two mordants (ferric chloride and ferrous sulphate) are used in silk and polyamide fabrics' treatment, separately, prior to printing process and the results are illustrated in Fig. 1.

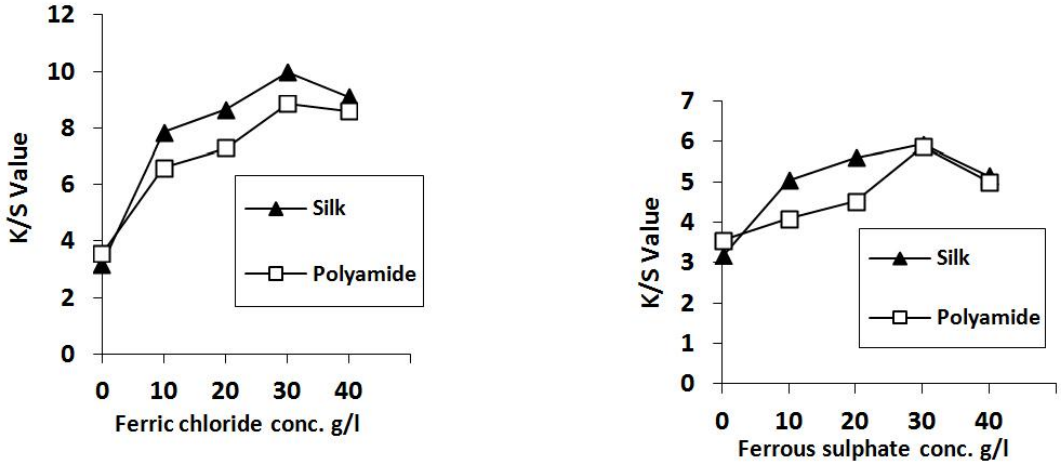


Figure 1 Effect of mordant type and concentration on K/S values of silk and polyamide 6 fabrics printed with madder nanoparticles

It is obvious from the figure that, best K/S values are accomplished on pretreating both used fabrics with 30 g/l mordant, separately. This is due to achieving huge improvements in colour yields by 214.8 and 149% for silk and polyamide prints pretreated with ferric chloride respectively, compared with the unmordanted prints. Less K/S enhancements can be observed (87.1 and 66.2% for silk and polyamide prints respectively) on comparing similar prints, pretreated with ferrous sulphate, with unmordanted prints.

It is established that, treating substrates by different mordants results in imparting fabrics a full range of colours of the same natural dye. Both mordants used in this study are iron salts which is a transition metal having two valences. Both metallic salts are known for their ability to form co-ordination complexes that are readily chelated with the dye. As the co-ordination numbers of ferrous sulphate and ferric chloride are 2 and 3 respectively, some co-ordination sites remained unoccupied when they interact with the fibre. Functional groups such as amino and carboxylic acid groups on the fibre can occupy these sites. Thus, these metals can form a ternary complex on one site with the fibre and on the other site with the dye. Such a strong co-ordination tendency can enhance the interaction between the fibre and the dye, resulting in high dye uptake. Furthermore, ferrous sulphate tends to shift the resuled colour towards red while ferric chloride shifts the colour towards blue which explains the increase in colour intensity for the printed substrates premordanted by ferric chloride compared with similar substrates premordanted using ferrous sulphate.

Meanwhile, grinding and sonication of the

used natural dye particles have a positive impact on colour yield of both printed substrates regardless of the mordant used in pretreatments. This trend can be clearly observed on comparing printed substrates using regular dye particles with others printed by nano-scaled dye particles, using constant concentrations of dye as well as other recipe ingredients. It is found that, K/S developments by 38.6 and 70% can be achieved for silk and polyamide prints pretreated with ferric chloride, respectively while developments by 63.4 and 85% in K/S can be obtained for the same prints pretreated with ferrous sulphate. The previous results can be explained by the facts that, grinding increases the specific surface area (ssa) of the ground particles due to particle size reduction [16]. Besides, a feasible technique for particle-size reduction is ultrasound. Cavitational collapse sonication in solids leads to microjet and shock-wave-impacts on the surface, together with interparticle collisions, which can result in particle-size reduction [17].

3.2. Urea concentration

Urea is an essential auxiliary in printing pastes because during the steaming process it swells the fibres so that the dye can rapidly penetrate them [18,19]. Urea acts as a solvent for the dye as it performs as a moisture-absorbing agent to increase the moisture regain during the steaming process. Thus, urea accelerates the migration of dye from the thickener film into the fibres. The effect of urea concentration on colour intensity of silk as well as polyamide printed fabrics with madder nano-particles is studied through adding different concentrations (0, 5, 10, 20 and 30 g/kg) and the results are illustrated in Fig. 2.

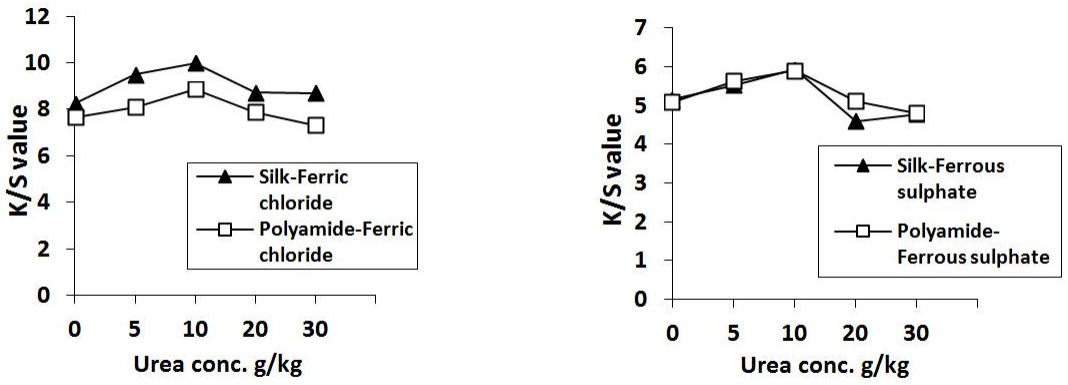


Figure 2 Effect of urea concentration on K/S values of silk and polyamide 6 fabrics pretreated with ferric chloride as well as ferrous sulphate, separately, and printed with madder nanoparticles

It is obvious from the previous figure that, best K/S enhancements can be achieved by adding a small urea concentration (10 g/kg) to the printing pastes regardless of both: kind of substrate or the mordant used in pretreatment. This result is due to accomplishing improvements in colour intensities by 21.2 and 15.6 % for silk and polyamide substrates respectively, pretreated with ferric chloride prior to printing process while improvements by 15.2 and 16.1 % for silk and polyamide substrates for ferrous sulphate respectively are obtained, all compared

with printed substrates without incorporating urea in their recipes.

The previous results are explained by the fact that, urea enhances the solubility of dyes in the printing paste due to its salvation and disaggregating action on dye molecules [20]. This action varies from one dye to another according to its ability to dissolve in the printing paste. Therefore, the hydrophobic/hydrophilic balance of the dye molecule will determine its ability to dissolve under the action of urea. Hydrophobic dyes such as disperse dyes are not affected by urea addition as the more hydrophilic dyes. Therefore, increasing the hydrophobic character of the used natural dyes may diminish the solvolysis effect of urea and reduces its role in the printing paste.

3.3. pH of printing pastes

Printing process is greatly influenced by variation of printing paste pH especially in the case of substrates that have ionizable functional groups such as silk and nylon. For high colour yield, it is essential to include an acid or acid donor in printing pastes of protein fabrics to be close to the isoelectric region of fibres which minimizes damage of substrates [21]. Meanwhile coloration of synthetic substrates is carried out at acidic pH (pH 5). A number of commercial dye ranges for protein substrates are available in which the member dyes have a wide colour gamut and good compatibility. All the dyes have very similar coloration methods and fastness properties despite being of several different types [22]. Fig. 3 shows the influence of pH value on colour intensity of printed silk as well as polyamide substrates with madder sonicated nanoparticles as a natural dye, through using different values (4.5, 5, 5.5, 6 and 7). Both substrates are premordanted with 30 g/l ferric chloride and ferrous sulphate separately besides, urea is the only ingredient incorporated in printing recipes.

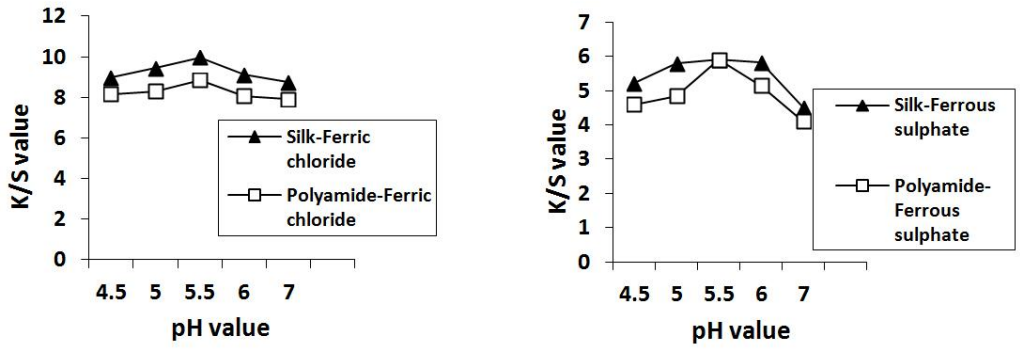


Figure 3 Effect of printing paste pH on K/S values of silk and polyamide 6 fabrics pretreated with ferric chloride as well as ferrous sulphate separately, and printed with madder nanoparticles

The previous figure reveals that, optimum K/S values can be achieved at pH 5.5 regardless of either the kind of mordant or substrate. This result can be referred to that, madder follows physical effects in a similar manner with disperse dyes towards synthetic fibres that are printed under weakly acidic conditions [23,24].

3.4. Scanning Electron Microscopic (SEM) and Transmission Electron Microscopic (TEM) studies

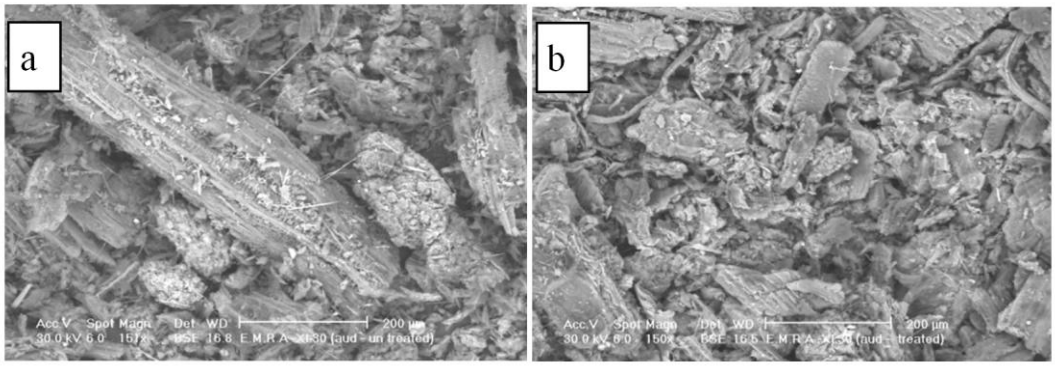


Figure 4 SEM images of madder dye particles: a) before milling b) after 30 days of milling

The surface morphology, structure and particle size of unmilled and milled dye samples for 30 days are shown in Fig. 4 (a & b) respectively. Fig. 4a shows the SEM images of dye particles which indicate that, they have different shapes like breaking dishes shape, spherical shape and tiny sprinkled dots. The micrographs in Fig. 4b indicate uniform spherical dye nanoparticles, with a size lying in the range of 34 nm in diameter. The difference in particle size after grinding is referred to their dissociation due to the impact of shear forces that act on dye particles in the ball miller which converted the particle size gradually from 80 nm (before milling) to 34 nm (after 30 days of milling).

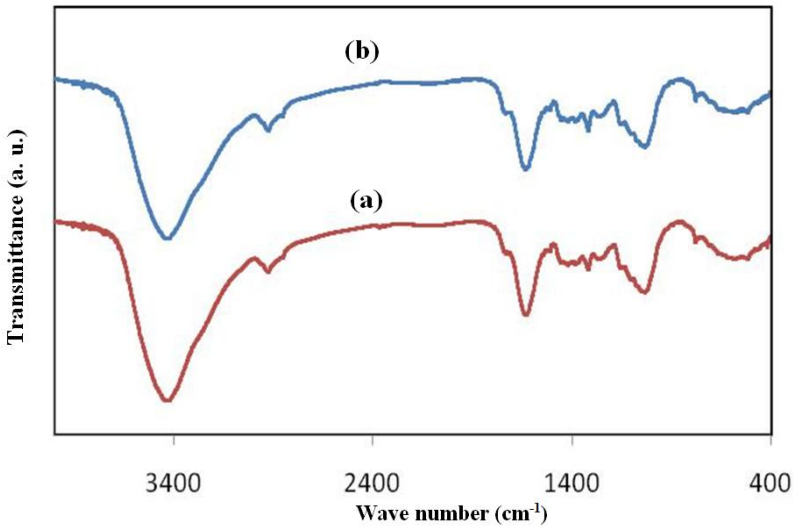


Figure 5 FT-IR spectra: a) ground madder; b) unground madder

3.5. Fourier Transition Infrared spectroscopy (FT-IR)

FT-IR spectra of the unground and ground madder particles were measured to investigate the effect of milling on the functional groups of materials as it is shown in (Fig. 5). FT-IR spectrum of the unground madder particles shows absorption peaks at 3450, 2925, 1634, 1318, 1035 and 518 cm^{-1}. The bands at 1636, 1035 and 518 cm^{-1} can be attributed to the carbonyl groups, the in-plane and out-of-plane C–H bending, respectively. The bands at 3450, 2927 cm^{-1} are attributed to OH groups of polyphenols in the dye. Furthermore, the spectrum of the ground particles exhibits a very slight shift in the peaks at 1636 cm^{-1} which is may be attributed to reducing the particle size.

3.6. UV–Visible spectroscope

UV–Visible spectroscopy was employed to characterize the optical properties of the unground and ground madder particles. Fig. 6 shows the results of optical absorption spectra of madder particles in the visible region. It can be seen that, the unground madder particles show absorption band in the range from 400 to 490 nm characteristics of red colour. The red color is due to that, madder contains polyphenols, compounds like 1,3-Dihydroxy-anthraquinone (purpuroxanthin), 1,4-Dihydroxyanthraquinone (quinizarin), 1,2,4-Trihydroxyanthraquinone (purpurin) and 1,2-dihydroxyanthraquinone (alizarin). On the other hand, madder particles reveal a strong change in their optical absorption when their size is reduced. The spectra of the ground madder particles show red shift of absorption (to higher wave length) and appear at 501-592 nm. This is may be attributed to the lowering of the particle size due to milling.

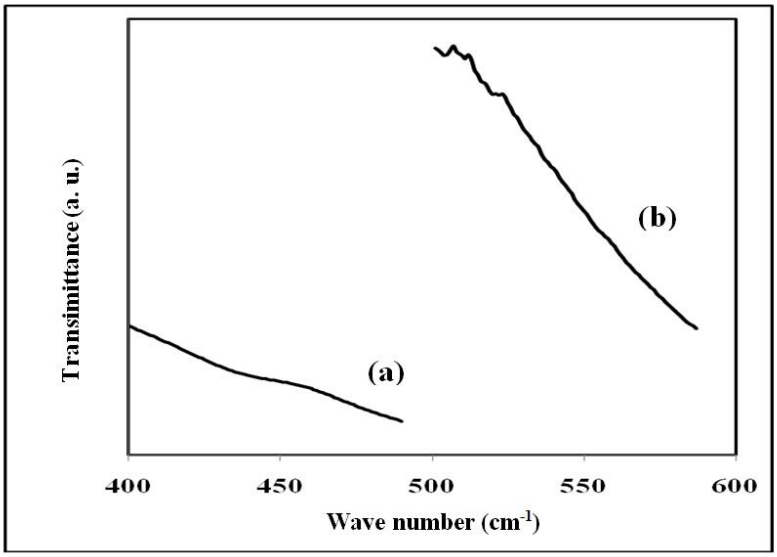


Figure 6 UV-Visible spectra: a) Unground madder; b) Ground madder

3.7. Fastness properties

Table 2 comprises the overall fastness properties in terms of washing, perspiration, rubbing and tensile strength of silk and polyamide 6 substrates pretreated with ferric chloride and ferrous sulphate separately, printed with madder nanoparticles using optimum pretreatment as well as recipe conditions, as it was previously mentioned in the experimental part. In the table, fastness levels of printed substrates using madder nano-scaled particles can be compared with typical printed substrates with regular dye particles (blank prints), all premordanted and printed at optimum conditions.

Table 2 Fastness properties of silk and polyamide 6 substrates printed with madder regular dye (blank) as well as madder nanoparticles using optimum pretreatment as well as paste conditions

Printed substrates condition	K/S Value	Washing fastness		Perspiration				Rubbing fastness		Tensile strength	
				Acidic		Alkaline					
		St.	Alt.	St.	Alt.	St.	Alt.	Dry	Wet	Tenacity kg	Elongation %
Blank pretreated silk with ferric chloride	7.20	4	4	4	4	3-4	3-4	3-4	3	19.30	0.073
Pretreated silk with ferric chloride	8.84	4-5	4-5	4-5	4-5	4-5	4-5	4	4	19.30	0.073
Blank pretreated polyamide with ferric chloride	5.20	4	4	4	4	3-4	4	3	2-3	27.82	1.150
Pretreated polyamide with ferric chloride	9.98	4-5	4-5	4-5	4-5	4-5	4-5	3-4	3	27.82	1.150
Blank pretreated silk with ferrous sulphate	3.63	4	4	4	4	3-4	4	3	2-3	33.10	0.117
Pretreated silk with ferrous sulphate	5.92	4-5	4-5	4-5	4-5	4-5	4-5	4	3-4	33.10	0.117
Blank pretreated polyamide with ferrous sulphate	3.19	4	3	4	3-4	3	4	3-4	3	25.20	1.273
Pretreated polyamide with ferrous sulphate	5.90	4-5	4-5	4-5	4-5	4-5	4-5	4	3-4	25.20	1.273

St. = Staining on cotton Alt. = Alteration

As shown in the table, colour fastness ratings of all prints indicate good to very good fastness levels which ensures the existence of strong bonds between dye molecules and the fibres. On the other hand, noticeable improvements in fastness levels are observed comparing printing with dye nanoparticles to printing with the regular dye. Concerning the influence of premordanting on tensile strength of both substrates it should be noted that, a slight reduction is detected in silk fabric due its treatment with ferric chloride compared with the unmordanted substrate.

4. Conclusion

The present work studies printing silk and polyamide 6 substrates with madder sonicated nanoparticles as a natural colorant. Meanwhile, two mordants are used separately in pretreating both substrates (ferric chloride and ferrous sulphate) through padding prior to printing stage and urea is the only ingredient incorporated in printing recipes. All parameters investigated (mordant and urea concentrations as well as pastes pH values) confirm that, dye milling as well as exposure to ultrasonic waves affect positively colour intensity and fastness levels of both printed substrates. SEM, FT-IR and UV visible spectroscopes are employed to illustrate dye-particle changes after their milling and sonication.

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