Eco-Friendly Printing of Textile Substrates with Rhubarb Natural Dye Nanoparticles

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Abstract: Wool, wool/polyester and polyester fabrics are printed with rhubarb natural dye. The dried plant is milled after which it is exposed to ultrasound waves (for a specific period of time). Both wool and wool/polyester fabrics are mordanted via padding in tartaric acid and potassium dichromate separately, prior to printing process. Dye nanoparticles are incorporated with urea in printing pastes at an acidic pH value and eventually the prints are steamed and washed off. All factors and measurements that are found to affect colour yield as well as fastness levels of the prints are investigated in detail. Results show that, printing with rhubarb nanoscaled particles enhances K/S values as well as fastness properties of the prints. SEM, FT-IR and UV visible spectrometers are employed to show dye-particle changes after milling as well as sonication.

Key words: Ball miller · Fastness properties · Printing · Rhubarb nanoparticles · Ultrasound waves

INTRODUCTION

In recent years, a lot of awareness and concern has developed over the environmental issues of textile wet processing [1]. Many attempts are being made to revive the old art of dyeing with natural vegetable dyes due to the carcinogenic nature of synthetic dyes and their intermediates [2]. Compared to synthetic dyes, natural dyes are less toxic, least pollutant and less hazardous. There is a great potential for revival of the use of natural dyes in Asia to substitute synthetic colours in certain areas [3]. Natural dyes are a class of colorants extracted from vegetable matters and animal residues. These are considered as mordant dyes, as they require the inclusion of one or more metallic salts of aluminum, iron, chromium, copper, tin and others for ensuring reasonable fastness of the colour to sunlight and washing. These metallic salts combine with the dyestuff to produce an insoluble complex compound inside the fibre, which cannot be removed from the cloth easily [4, 5]. These natural dyes are considered eco-friendly, provided metallic salts used are the safer ones and not copper or chromium of dyeing. Since wool structure has 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 [6]. It is evident that, the dyes present in materials such as rhubarb have molecules which have all the characteristics of a typical disperse dye, i.e. they are based on a quinone molecule. The molecules are very small and hydrophobic in nature which should make them substantive to hydrophobic fibres [7]. A lot of studies have been made for optimizing the extraction and application of natural dyes on natural fibres [7-10]. A great interest to apply natural dyes for dyeing and printing of synthetic fibres was also found during many previous studies [11-13]. Nanotechnology has real commercial potential for the textile industry. This is mainly due to the fact that, conventional methods used to impart different properties to fabrics often do not lead to permanent effects and will lose their functions after laundering or wearing. Nanotechnology can provide high durability for fabrics, because nanoparticles have a large surface area-to-volume ratio and high surface energy, thus presenting better affinity for fabrics and leading to an increase in durability of the function [14]. Ultrasound is a very effective processing method in the generation and application of nano-size materials. In general, ultrasonic cavitation in liquids may cause fast and...
complete degassing: initiate various chemical reactions by generating free chemical ions (radicals); accelerate chemical reactions by facilitating the mixing of reactants, enhance polymerization and depolymerization reactions by temporarily dispersing aggregates or by permanently breaking chemical bonds in polymeric chains; increase emulsification rates; improve diffusion rates; produce highly concentrated emulsions or uniform dispersions of micron-size or nano-size materials; assist the extraction of substances such as enzymes from animal, plant, yeast, or bacterial cells; remove viruses from infected tissue; and erode and break down susceptible particles, including micro-organisms [15]. In the present work, three substrates (wool, 45/55 wool/polyester and polyester) are selected to be printed with a plant species (rhubarb) in the form of nano-scaled powder form, as a natural dye, besides employing tartaric acid and potassium dichromate as mordants on wool and wool/polyester fabrics through fabric pretreatment. Furthermore, all factors and measurements that may optimize the printing properties are investigated in detail.

MATERIALS AND METHODS

Experimental

Substrates: All used substrates in the present work are kindly supplied by Misr Co. for Spinning and Weaving, Mehalla El-Kobra, Egypt:

Wool Fabric: Scoured, felted, steamed and chlorinated wool fabric having a weight of 245 g/m² and a twill weaving structure 1/2.

Wool/polyester 45/55 Blended Fabric: Scoured, steamed and chlorinated fabric having a weight of 170 g/m² and a plain structure 1/1.

Polyester Fabric: Plain weave fabric 1/1 having a weight of 185 g/m².

Natural Dye: Clean, dry, ground rhubarb plant, having the following specifications is used throughout the present study:

<table>
<thead>
<tr>
<th>English name</th>
<th>Latin name</th>
<th>Colour index</th>
<th>Coloured component</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhubarb [16] (Dolu)</td>
<td>Rheum emodi</td>
<td>Natural Yellow 23</td>
<td>1-Chryosophanic Quinone</td>
<td></td>
</tr>
</tbody>
</table>

Mordants and Other Chemicals: All the used chemicals are of an analytical grade:

Tartaric Acid: C₄H₆O₆

Potassium Dichromate: K₂Cr₂O₇

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 wool printing.

Avolan IW: A dispersing agent added to printing pastes on printing wool/polyester and polyester fabrics and is kindly supplied by Bayer AG Co. Germany.

Methodology:

Fabric Mordanting: Both substrates (wool and wool/polyester) are mordanted prior to printing process. The mordanting bath is set with different concentrations of both mordants, tartaric acid and potassium dichromate, separately on weight of fabric at L.R. 1:40. Mordanting is carried out at 60-70°C for 30 min after which the samples are washed with distilled water and air-dried.

Preparation of Dye Nanoparticles: Rhubarb natural dye was ground using energy Ball Miller with a speed of 50 cycles/min. The dye powder is sealed in a hardened steel vial (AISI 44°C stainless steel) using hardened steel balls of 6 mm diameter. Milling is performed using a ball: powder mass ratio of 4:1. The dye is milled at different intervals, after each milling interval the particle size of the resulted dye powder was measured. The smallest particle diameter of 48 nm chosen to be used in the present study is obtained from milling the dye powder for 30 days. A stock solution is prepared using the milled dye particles of a concentration of 3% where 3g dye powder is dispersed in 97 cm³ of distilled water. The suspension is irradiated afterwards with ultrasound waves (720 kHz) and stirred at 80°C for different periods of time (4, 6 and 8 hours) from which the ultrasound treatment of 8hrs. is chosen to proceed with since it gave best K/S values.
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
- 20 g Avolan IW (added on printing polyester/wool and polyester fabrics)
- 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°C for 20 min. for all 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°C for 10 min.

Smeasurements

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 [17].

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 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.

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.

Fourier Transition Infrared Spectroscopy (FT-IR): Fourier Transition Infrared spectroscopy (FT-IR) of the samples was recorded using a Brucker FT-IR. 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).

Optical Properties (UV-Visible Spectra): The optical absorption of dye particles dissolved in distilled water was recorded in the wave length range of 400-800 nm employed using a Shimadzu spectrophotometer, at room temperature.

Fastness Properties: Fastness properties of the three printed substrates to rubbing, washing and perspiration are assessed according to standard methods [18].

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.

RESULTS AND DISCUSSION

Mordanting of Substrates: Mordanting is the treatment of textile fabric with metallic salts or other complex forming agents which bind the natural mordantable dyes onto the textile fibres. Mordanting can be achieved by either premordanting, simultaneous mordanting or post-mordanting [19]. The metal ions of these mordants can act as electron donors to form coordination bonds with the dye molecules, making them insoluble in water. 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, i.e. tartaric acid and potassium dichromate, are used in wool and wool/polyester fabrics’ treatment, separately, prior to printing process and the results are illustrated in Fig. 1. It is established that, mordants improve the fixation and fastness properties of dyes lacking substantivity for natural fibres [20] and subsequently, mordanting is not applied on polyester substrate.

It is obvious from the Fig. 1 that, increasing mordant concentration results in increasing K/S values until they reach their maximum using 60 g/l of both mordants since K/S values increase by 46.8 and 45.3% for wool and wool/polyester prints, respectively, pretreated with tartaric acid compared with the untreated prints. While for prints pretreated with potassium dichromate, enormous K/S developments can be observed using the same mordant concentration, which are 136.8 and 99.3% for
Fig. 1: Effect of mordant type and concentration on K/S values of wool and wool/polyester fabrics printed with rhubarb nanoparticles.

Fig. 2: Effect of urea concentration on K/S values of wool and wool/polyester fabrics pretreated with tartaric acid and potassium dichromate, separately as well as polyester fabric, all printed with rhubarb nanoparticles.

wool and wool/polyester prints, respectively, compared with the untreated prints. These results are referred to grinding and sonication effect of rhubarb natural dye particles. Grinding increases the specific surface area (ssa) of the grinded particles due to particle size reduction [21]. Grind increase the specific surface area (ssa) of the grinded particles due to particle size reduction [21]. A feasible technique for particle-size reduction is ultrasound. Cavitation 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 [22]. Besides, comparing the results obtained from pretreating both substrates using both mordants it is observed that, improved K/S values are achieved on using potassium dichromate than those resulted from using tartaric acid. This trend can be explained by that, mordants are more capable of fixing natural dyes directly onto fibres by metal ions (when the mordant dissolves) and thereby producing various permanent substantive colours. These enhancements in K/S values obtained by mordanting using potassium dichromate can be ignored since tartaric acid is a green mordant.

Urea Concentration: The influence of urea concentration on the K/S values of printed wool, wool/polyester (pretreated with both mordants separately) and (unmordanted) polyester substrates with rhubarb nanoparticles is studied, through incorporating it into recipes with different concentrations (0, 5, 10, 20 and 30 g/kg) and the results are plotted in Fig. 2.

The previous Fig. 2 indicates that, 10g/kg can be considered as best urea concentration to be added to printing pastes with rhubarb nanoparticles regardless of both, kind of printed substrate as well as kind of mordant. Enhancements in colour yields by 8.4, 28.7 and 1.6% occurred in wool, wool/polyester (both pretreated with tartaric acid) and polyester prints respectively, compared with the same printed fabrics without urea addition to their recipes. Meanwhile, colour yields of wool and wool/polyester prints premordanted with potassium dichromate have colour yield enhancements by 5.8 and 6.8% respectively, compared also with the same printed fabrics without urea addition to their recipes. It should also be noted that, huge differences in K/S values are
accomplished on comparing printing with conventional to nano-size dye particles regardless of either the kind of fabric or the mordant used (260 and 319% for wool and wool/polyester fabrics pretreated with tartaric acid, respectively and 96 and 164% for both fabrics pretreated with potassium dichromate) while an improvement by 534% is achieved with polyester substrate. Urea enhances the solubility of dyes in the printing paste due to its salvation and disaggregating action on dye molecules [23]. 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. On the other hand, it is postulated that, urea increases the swelling of wool fibres especially at low concentrations due to the reduction of protein - protein interactions which facilitates the diffusion of dyes inside wool fibres [24]. It is suggested also that, urea facilitates the diffusion of dyes whose molecules are small enough through the unswollen fibres when the dye is disaggregated [25]. With high molecular weight dyes, the diffusion will be assisted only if the fibre is swollen to allow the disaggregated large dye molecule to enter [26]. Therefore, it may be concluded that, the efficiency of dye diffusion inside wool fibres and hence the realized colour strength under the action of urea, is greatly dependent on the degree of fibre swelling, the nature of the used natural dyes and their molecular weight as well as on the degree of aggregation/disaggregation of natural dyes in the printing paste.

Printing Paste pH: It is established that, the rate of dye fixation into wool fibres increases by decreasing the pH value since at lower pH values, dye concentration increases on the available wool fibre surfaces by increasing the number of ammonium ion sites [20]. On the other hand, disperse dyes are sensitive to alkalis and so polyester is generally printed under weakly acidic conditions with the incorporation of the proper dispersing agent in the printing paste [27]. The influence of printing paste pH on the K/S values of printed wool, wool/polyester (pretreated with both mordants separately) and polyester substrates with rhubarb nanoparticles is studied, through using different values (4.5, 5, 5.5, 6 and 7) and the results are plotted in Fig. 3. The data of the figure reveal that, optimum K/S values can be achieved at pH 5 and 5.5 for wool and wool/polyester prints respectively, regardless of the kind of mordant used in their pretreatment prior to printing. Meanwhile, pH 6 can be considered as an optimum value for printing polyester substrate. The previous results confirm well with literature.

Scanning Electron Microscopic (SEM) and Transmission Electron Microscopic Analysis (TEM): The surface morphology, structure and particle size of dye samples without milling and milled for 30 days are shown in Fig. 4a and b, respectively. Fig. 4a shows the SEM images of dye which indicates that, the dye particles 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 48 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 113 nm (before milling) to 48 nm (after 30 days of milling).
Fourier Transition Infrared Spectroscopy (FT-IR):

FT-IR spectra of the unground and ground rhubarb particles are 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 rhubarb shows absorption in the peaks 3450, 2927, 1633, 1384, 1050 and 578 cm\(^{-1}\). The bands at 1633, 1050 and 578 cm\(^{-1}\) can be attributed to the carbonyl groups, the in-plane and out-of-plane C-H bonding, respectively. The bands at 3450, 2927 cm\(^{-1}\) are attributed to OH groups of polyphenols in dye. While, the spectrum of the ground rhubarb exhibits shifts in the peaks 1633, 1448 cm\(^{-1}\) which is may be attributed to the decrease occurred in particle size.

UV-Visible Spectroscope: UV-Visible spectroscopy was employed to characterize the optical properties of the unground and ground natural dye. It is established that, rhubarb contains glycosides-especially rhein, glucorhein and emodin, which impart cathartic and laxative properties. It is hence useful as a cathartic in case of constipation [28]. Fig. 6 shows the results of optical absorption spectra of rhubarb in visible region. It can be

<table>
<thead>
<tr>
<th>Printed substrates condition</th>
<th>K/S value</th>
<th>Washing</th>
<th>Acidic</th>
<th>Alkaline</th>
<th>Rubbing</th>
<th>Tensile strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank pretreated wool with tartaric acid</td>
<td>1.55</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>4-5</td>
<td>40.50 59.50</td>
</tr>
<tr>
<td>Pretreated wool with tartaric acid</td>
<td>5.58</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>40.50 59.50</td>
</tr>
<tr>
<td>Blank pretreated wool with potassium dichromate</td>
<td>4.59</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>38.85 41.50</td>
</tr>
<tr>
<td>Pretreated wool with potassium dichromate</td>
<td>9.10</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>38.85 41.50</td>
</tr>
<tr>
<td>Blank pretreated wool/polyester with tartaric acid</td>
<td>1.04</td>
<td>3-4</td>
<td>3-4</td>
<td>4</td>
<td>4-5</td>
<td>51.84 61.00</td>
</tr>
<tr>
<td>Pretreated wool/polyester with tartaric acid</td>
<td>4.36</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>51.84 61.00</td>
</tr>
<tr>
<td>Blank pretreated wool/polyester with potassium dichromate</td>
<td>2.26</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4-5</td>
<td>52.73 60.50</td>
</tr>
<tr>
<td>Pretreated wool/polyester with potassium dichromate</td>
<td>5.98</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>52.73 60.50</td>
</tr>
<tr>
<td>Blank polyester</td>
<td>0.50</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4-5</td>
<td>115.00 49.00</td>
</tr>
<tr>
<td>Polyester</td>
<td>3.17</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>4-5</td>
<td>115.00 49.00</td>
</tr>
</tbody>
</table>

St. = Staining on cotton  Alt. = Alteration
seen that, the unground rhubarb particles show two main absorption bands around 444 and 411 nm that are characterized by a red brown color. The red color is due to rhubarb that contains polyphenols, compounds such as lycopene and anthocyanin. Rhubarb also contains glycosides especially rhein, glucorhein and emodin, which impart cathartic and laxative properties. On the other hand, rhubarb particles reveal a strong change of their optical absorption when their size is reduced. The spectra of ground rhubarb particles show blue shift of the main bands (to lower wave length) and appear at 440 and around 400 nm. This is may be attributed to particle size reduction due to milling because of quantum confinement effect.

**Fastness Properties:** The following Table 1 comprises the overall fastness properties in terms of washing, perspiration, rubbing and tensile strength of wool and wool/polyester substrates pretreated with tartaric acid and potassium dichromate separately, as well as polyester fabric all printed with rhubarb nanoparticles using optimum paste conditions. In the table, fastness levels of printed substrates using rhubarb nano-scaled particles can be compared with typical printed substrates with regular dye particles (blank prints), all premordanted and printed at optimum conditions. It is clear from the data in the Table 1 that, in all cases the colour fastness levels are quite satisfactory for practical application purposes where, they range between good and very good. On the other hand, noticeable improvements in fastness levels are observed comparing printing with dye nanoparticles to printing with regular dye particles (blank). Concerning the effect of mordant pretreatment on tensile strength of wool and wool/polyester substrates it should be noted that, limited reduction in tensile strength can be detected regardless of mordant type.

**CONCLUSION**

The present study confirms the possibility of printing wool, wool/polyester and polyester fabrics with rhubarb nanoparticles incorporating a slight concentration of urea in printing pastes at mild acidic pH values. Rhubarb natural dye particles are ground in a ball miller for 30 days after which they are exposed to ultrasound for 6 hours in order to obtain a reduced dye particle size from 113nm to 48nm. Wool and wool/polyester substrates are premordanted with a green mordant (tartaric acid) and a metal mordant (potassium dichromate), separately prior to printing process. It is proved from the obtained data that, enormous improvements in K/S values can be accomplished on comparing printing with traditional to nano-scaled dye particles which can be referred to particle size reduction due to both grinding and sonication effects. On the other hand, this effect can be observed in SEM, FT-IR as well as UV-Visible spectrosopes, besides achieving satisfactory fastness levels of all printed substrates.

**REFERENCES**


