

NOVEL GREEN PRINTING OF COTTON, WOOL AND POLYESTER FABRICS WITH NATURAL ALKANET DYE NANOPARTICLES

Mai M Bakr¹, Hassan M. Ibrahim^{2*}, Mohammed A. Taha³ and Hanan Osman¹

¹Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Banha University, Banha, Egypt

²Textile Research Division, National Research Centre, 33 El Bohouthst. (Former El Tahrir St.), Dokki, Giza, Egypt, P.O.12622

³Solid State physics Department, National Research Centre (NRC), El Bohouth St., 12622 Dokki, Giza, Egypt

Abstract - Hiren alkanet dye nanoparticles were successfully prepared by using simple ball milling technique at room temperature. UV-vis. absorption, XRD, TEM, FT-IR spectroscopy and SEM were used to characterize alkanet dye nanoparticles. The prepared alkanet dye nanoparticles were used as active ingredient for printing cotton, wool and polyester fabrics via dye printing technique and pigment printing technique. Factors of printing process were studied such as Mordanting of Substrates, thickeners type, urea concentration and Printing Paste pH for first paste and urea concentration, Printing Paste pH and binder concentration for second paste. Results shows fabrics printed with alkanet dye nanoparticles via mentioned two methods shows very good to excellent fastness properties with full green method. These data indicated that printed samples have high quality for colour strength without any environmental hazards compared with other conventual and nanotechnological aspects.

Keywords: Novel green printing, cotton, wool and polyester fabrics, ball milling, alkanet, natural dye, nanoparticles

1. INTRODUCTION

Nowadays, there is new trend to replace synthetic based products to nature-based materials via green process to obtain eco-friendly, non-toxic and hygienic textile materials [1, 2]. So that there is an interest of using natural dyes in textile coloration has been growing due to the environmental impact appearing in response to the toxic and allergic reactions associated with synthetic dyes. However, natural dyes are friendly to the environment and exhibit better biodegradability with higher environment compatibility [3-7].

Alkanet plant (*Anchusa officinalis* L.) from Boraginaceae family and indigenous to the Mediterranean region. Alkanet root is used as a natural red dye. It is appeared as dark red. Its dye powder is insoluble in water and soluble in organic solvents such as ether, alcohol, and oils [8-10].

Mordants have affinity for both textile fabrics and dyes, thus they used to link the dyestuff to the fiber [11-13]. Therefore, they can be used for improving dye uptake and fixation causing change in color shade and fastness properties. [1, 2, 11, 12, 14-16]. The metal ions of these mordants can act as electron donors to form coordination bonds with the dye molecules, making them insoluble in water [15-17].

Nanotechnology is a new field of research dealing with nanomaterials with particles size from 1-100 nm. Regarding the textile industry, nanotechnology becomes a new and promising tool to develop new textile materials for technical and smart use [18-20]. Nanoparticles have a high surface-to-volume ratio, which gives them new interesting physical and chemical properties in the textile field [2, 19-26].

Ball milling is a top-down technique to form micro to nano scale materials, by inducing heavy cyclic deformation in materials. Ball milling is nowadays widely used for the preparation of nanoparticles because of its simple operation, use of relatively inexpensive equipment and its applicability to essentially all classes of materials [27].

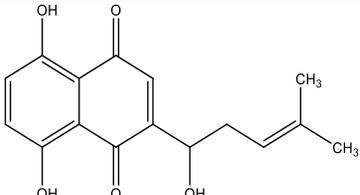
In the present work we prepare nanoparticles from alkanet dye via ball milling technique for printing some selected natural and synthetic fabrics such as wool, cotton and polyester. The prepared nanoparticle dye was characterized by using transmission electron microscopy, UV-vis., spectra and X-ray diffraction. Several factors were studied to optimized the printing process such as (Mordanting of Substrates, thickeners type, urea concentration and Printing Paste pH for first paste and urea concentration, Printing Paste pH and binder concentration for second paste). the printed fabrics were characterized by using colorimetric measurements.

2. MATERIALS AND METHODS

2.1 Materials

Fabrics: Mill-scoured wool fabric (100%) was supplied by EL-Nasr Company for Spinning, Weaving, and Dyeing, El-Mehalla Elkubra, Egypt. The fabric has the following specifications: Plain weave fabric1/1 having a weight of 239 g/m². Mill desized, scoured, and bleached 100% cotton fabric was supplied by EL-Nasr Company for Spinning, Weaving, and Dyeing, El-Mehalla Elkubra, Egypt. The fabric has the following specifications: plane weave, warp 36 yarn/cm, weft 30 yarn/cm, fabric weight, 150 g/m²., polyester 100%, Plain weave fabric1/1 having a weight of 185 g/m² kindly supplied from Artex Apparel, Egypt.

Natural dye: Clean, dry, ground Alkanna tinctoria plant, was purchased from the Agricultural seeds Medicinal and Medical plant company (Harraz), Cairo, Egypt, having the following specifications

Botanical name	Class	Colour index	Part used	Chemistry
Alkana tinctorial	Naphthoquinone	Natural red20	Root	

Thickening agents: Sodium alginate used at concentration 8%. Meypro gum used at concentration 8%. Carboxymethyl cellulose (CMC) used at concentration 3%. DEL THICKNER P used at concentration 3%.

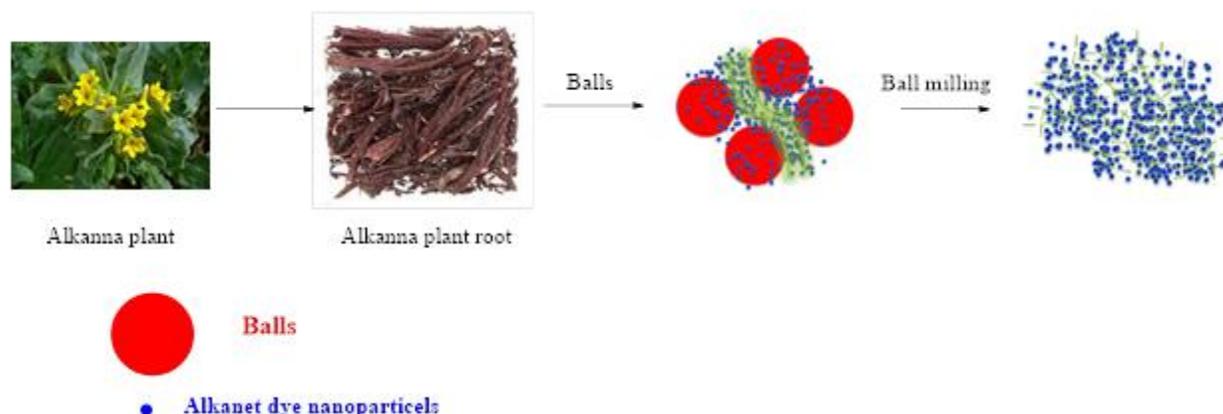
Mordant: Tartaric acid (2,3-dihydroxybutanedioic acid)

Other chemicals: Urea [(NH₂)₂CO]. Sodium carbonate Na₂CO₃. Diammonium phosphates (NH₄)₂HPO₄ Acrylate binder.

2.2. Methodology

2.2.1. Preparation of Dye Nanoparticles

The alkanet dye powders were milled for 15 h in a planetary ball mill type. The milling conditions were; a) ball to powder weight ratio (BPR) equal 10:1, (b) 10 mm balls diameter, and (c) 400 rpm rotating speed. It is worth to mention that the milling was done in a cycle of 3 h and paused for 2 min. A stock solution of alkanet dye nano particles was prepared by using the milled dye particles of a concentration of 3% (3g of dye powder was dispersed in 97 cm³ of distilled water). The suspension was irradiated afterwards with ultrasound waves (53 mega Hz) and stirred at 60 °C for 90 min (**Scheme. 1**).



Scheme 1. Schematic diagram of alkanet dye nanoparticles production by ball milling

2.2.2. Fabric Mordanting: substrates (cotton and wool) are mordanted prior to printing process. The mordanting bath is set with tartaric acid, separately on weight of fabric at L.R. 1:40. Mordanting is carried out cotton and wool at 50-60°C for 30 min after which the samples are washed with distilled water and air-dried.

2.2.3. Printing Procedures: To investigate each factor of the present work, two printing paste having the following formula was applied on all substrates:

The first Paste recipe (dye-printing)		The 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	Binder	y g
Water	z g	Urea	z g
		Balance	G
Total	1000 g	Total	1000 g

The pH is adjusted according to each required value using Sodium carbonate for first paste and Diammonium phosphate for second paste. 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 first paste is carried out via steaming at 105°C for 20 min. for wool ,115 for 15 min. for cotton and 120°C for 45min. for polyester. The second paste is carried out with thermofixation at 160°C for 4 min.

2.2.4. Washing

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

2.3. Testing and analysis

2.3.1. Color measurements and fastness properties

The printed samples were tested according to AATCC and ISO standards [28, 29]. The colour strength values (K/S) were determined using CIE Lab: D-65 10 standard. The ISO-CO6 DIM was used to determine the colour-fastness to laundering. The color fastness to laundering, color fastness to perspiration and color fastness to rubbing was 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 the gray scale. The rating scale of washing fastness for color change was from 1 (very poor), 2 (poor), 3 (fair), 4 (good) to 5 (excellent). The rating scale of light 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. FT-IR spectra

The FT-IR spectra of the samples were recorded by using an FT-IR 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} .

2.3.3. Tensile strength

The tensile strength of the fabric sample was determined by the ASTM Test Method D5035. 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).

2.3.4. Ultraviolet-visible (UV-vis) spectra

UV-Vis spectra have been used to confirm the formation of alkanet dye nanoparticles. The spectra were collected over a range of 250-800 nm.

2.3.5. Transmission Electron Microscopy (TEM)

The shape and size of alkanet dye nanoparticles were practically obtained by using TEM; JEOL-JEM-1200. Specimens for TEM measurements were prepared by placing a drop of colloidal solution on 400 mesh copper grids coated by an amorphous carbon film and evaporating the solvent in air at room temperature. The average diameter of the prepared alkanet dye nanoparticles was determined from the diameter of 100 nanoparticles found in several arbitrarily chosen areas in enlarged microphotographs.

2.3.6. Scanning Electron Microscopy (SEM)

Microscopic investigation on alkanet dye powder before and after milling were carried out by 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 scanning electron microscope (SEM) in accordance with the clarity of the images. Fabric samples were fixed with carbon glue and metalized by gold vapor deposition to record images.

2.3.7. X-ray diffraction

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 to 80 (2 θ) using monochromatized Cu K α ($k = 1.54051 \text{ \AA}$) radiation.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of Dye Nanoparticles

The colours before and after ball milling was no difference change. Fig.1a. shows that alkanet dye shows broad band peaks in UV-vis. absorption while, alkanet dye nanoparticles shows sharp band peak due to nanostructure of alkanet dye nanoparticles.

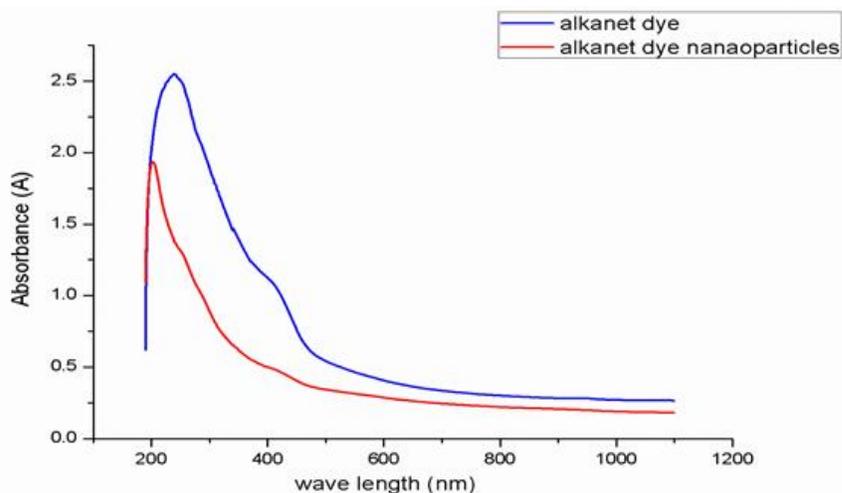


Fig. 1a. UV-vis. spectra of alkanet dye and alkanet dye nanoparticles

Fig. 1b., shows that FT-IR spectra of alkanet dye nanoparticles have the same band peaks of alkanet dye but its band peaks decreased compared with alkanet dye itself

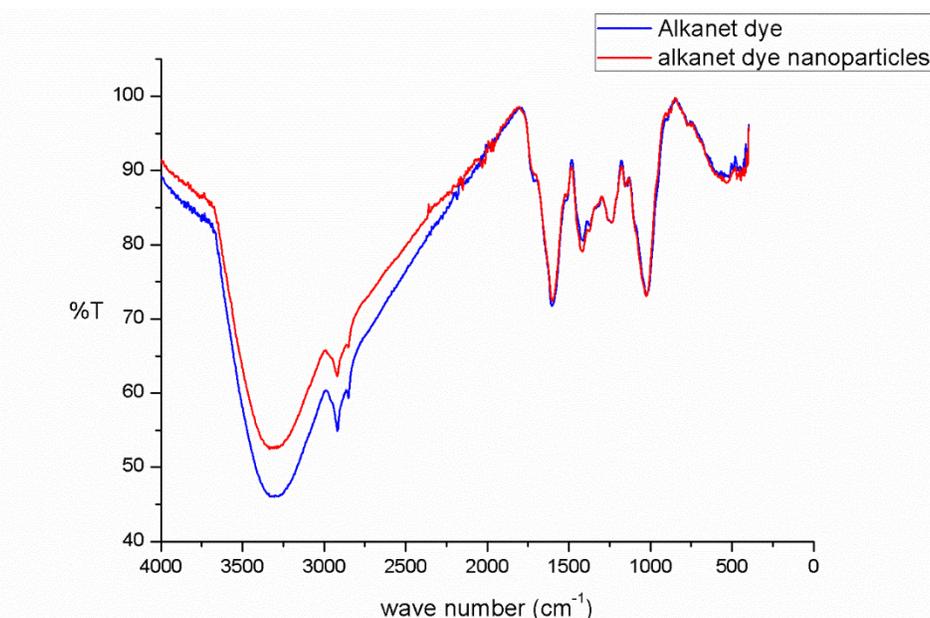


Fig. 1b. FT-IR of alkanet dye and alkanet dye nanoparticles

To compare crystalline structure of unmilled and milled alkanet dye, XRD analysis was performed and its results are shown in Fig. 1b. XRD of both milled and unmilled alkanet dye are similar except there is more broader bands in alkanet dye nanoparticles than unmilled alkanet dye. The alkanet dye shows four characteristic peaks of 2θ at 21.4, 22.9, 38.15 and 44.46 whereas, the alkanet dye nanoparticles shows the same peak at 21.4. the second peak was shifted to 26.56, and the third one shifted to disappeared with splitting into two adjacent peaks at 29.36 and 30.86. The fourth one appears at 44.62.

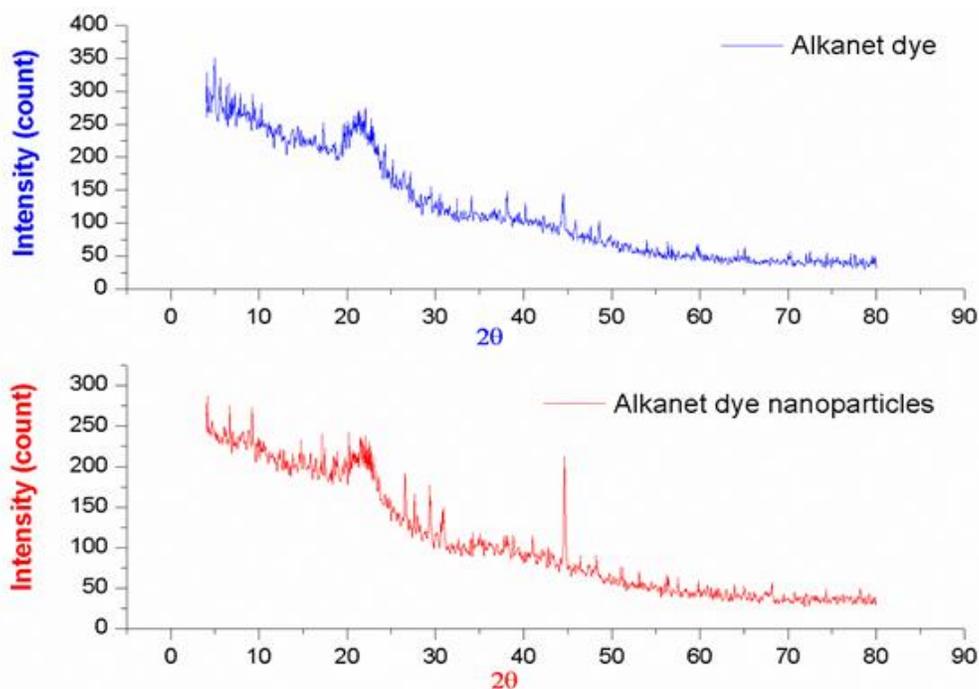


Fig. 1c. x-ray diffraction (XRD) of alkanet dye and alkanet dye nanoparticles

Transmission electron microscopy (TEM) illustrates the shape and size of alkanet dye nanoparticles as shown in Fig. 1d. alkanet nanoparticles formed from alkanet powder via ball milling show well disperse and semi spherical shapes. From the histograms in Fig. 1d, it was indicated that particles size ranged from (20 - 60nm) with a major diameter range (30-40 nm). These results data agreed with UV-vis spectral data.

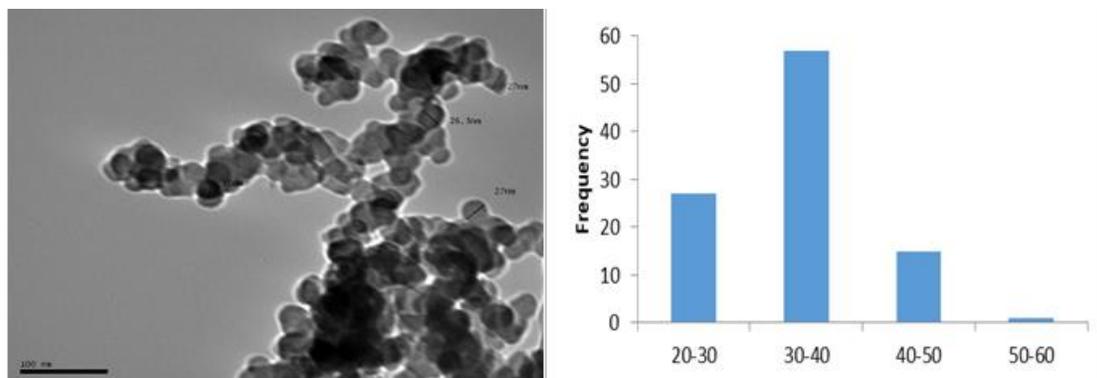


Fig. 1d. TEM image of alkanet dye nanoparticles prepared via ball milling and histogram of its nanoparticle size

Fig. 2. shows scanning electron microscopy of alkanet dye before and after milling. SEM images shows the conversion of particle size of the alkanet dye from microform to nanoform. In addition SEM images shows that surface particles size changed from 107-360 μm of alkanet dye to 85-100 nm of alkanet nanoparticles which confirm formation of nanoparticles via green method.

In addition, SEM images illustrate the alkanet morphology and its conversion to more uniform nanoparticles with green method.

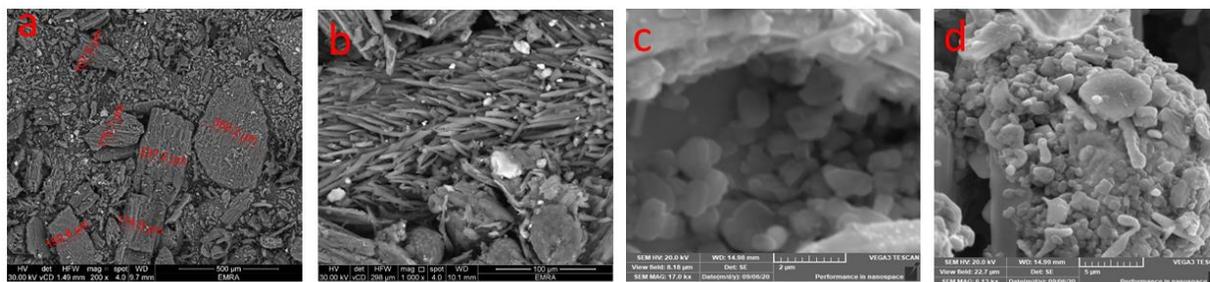


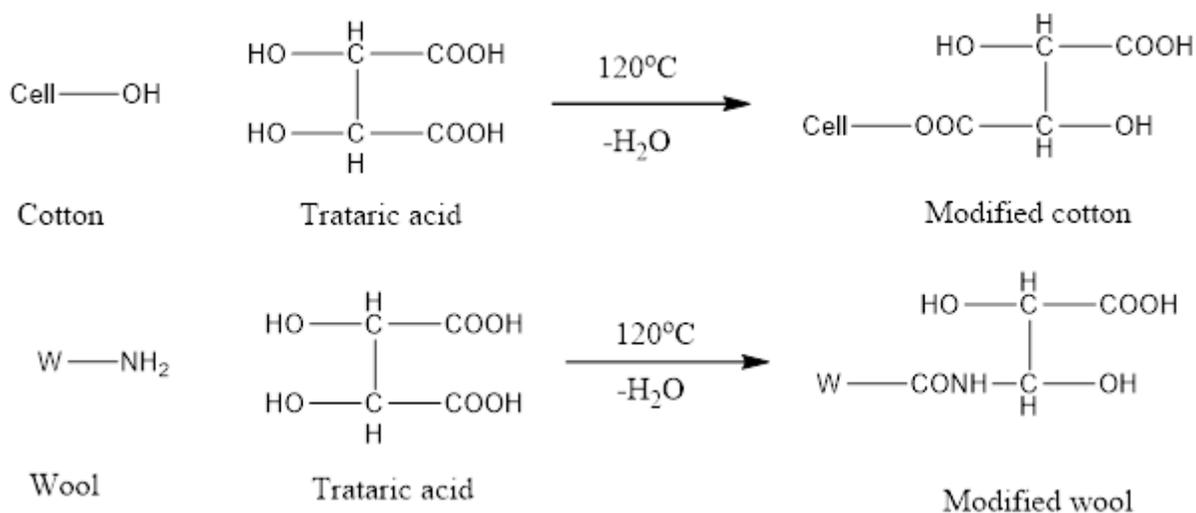
Fig. 2. scanning electron microscopy images of alkanet dye (a and b) and alkanet dye nanoparticles (c and d)

3.2. Printing of cotton, wool and polyester fabrics with alkanet dye nanoparticles

The main goal of the present study is printing of cotton, wool and polyester fabrics with a green printing paste consists of green thickeners such as carboxymethylcellulose, sodium alginate and Meypro gum and natural alkanet dye nanoparticles. Natural fabrics such as cotton and wool were pretreated first with tartaric acid as a mordant to increase their dye accessibility (scheme 2).

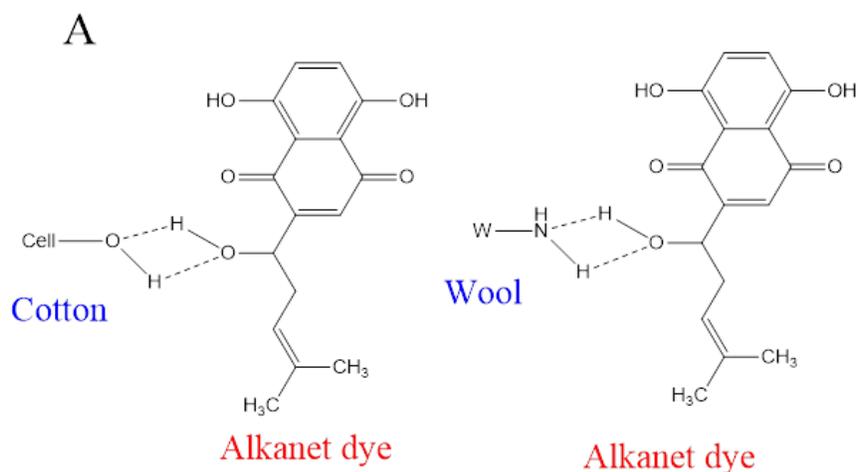
Mordanting of cotton and wool fabrics and their effects on printed fabrics

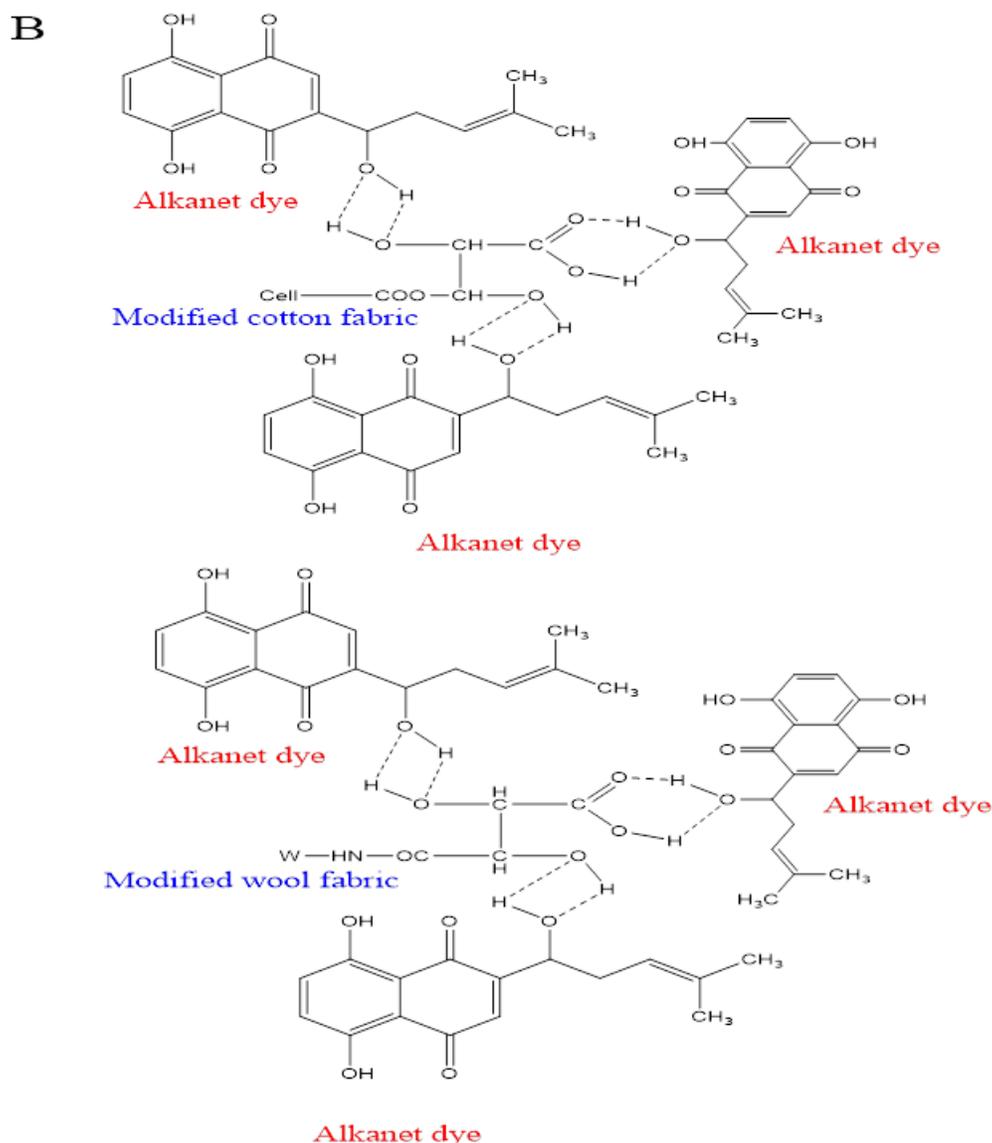
Cotton and wool fabrics can be modified through their reaction with tartaric acid to form the corresponding ester and amide [30, 31] derivative as shown in **scheme 2**. The reaction will be takes place in physical absorption at 50-60 $^{\circ}\text{C}$, then chemical reaction takes place in steam fixation process at 120 $^{\circ}\text{C}$. this process create more reactive site (hydroxyl and carboxylic groups in addition of native groups in cotton and wool fabrics).



Scheme 2. Modification of cotton and wool fabrics via reaction with tartaric acid

Scheme 3 shows the how mordant have great effect of both cotton and wool fabrics compared with unmodified fabrics. The main difference that unmodified fabrics have one accessible site form strong H. bond with one mole alkanet dye where the mordanted fabrics have three accessible sites can form stronger H. bonds with three mols alkanet dye. In addition, we can find that reaction fixation of cotton pass through ester bond while fixation of wool fabrics comes from amide bond formation, this will reflect the difference in colour strength and fastness properties of the printed fabrics.





Scheme 3. Reaction of alkanet dye with unmodified cotton and wool fabrics (A) and tartaric acid modified cotton and wool fabrics (B)

To investigate the effect of fabric premordanting on colour development of the used alkanet dye nanoparticles, different concentrations (0, 40, 60, 80, 100 and 120 g/l) of tartaric acid, is used in cotton and wool fabrics' treatment, separately, prior to printing process and the results are illustrated in **Fig. 3**.

It is shown from the **Fig. 3** that, an increasing of mordant concentration results in increasing of K/S values until 60 g/L concentration of tartaric acid for cotton and wool, whereas the value of K/S increase by 91.06 and 122.73% for cotton and wool prints, respectively, pretreated with tartaric acid compared with the untreated prints.

These results are referred to grinding and sonication effect of alkanet natural dye particles. Grinding increases the specific surface area of the alkanet dye nanoparticles due to particle size reduction [32]. A feasible technique for particle-size reduction is ultrasound. Ultrasonication's of solids leads to microjet and shock-wave-impacts on the surface, together with interparticle collisions, which can result in particle-size reduction [33]. Besides, comparing the results. Therefore, fabrics (cotton and wool) pretreated with 60 g/L tartaric acid as mordant used to improve printing of these fabrics with alkanet dye nanoparticles.

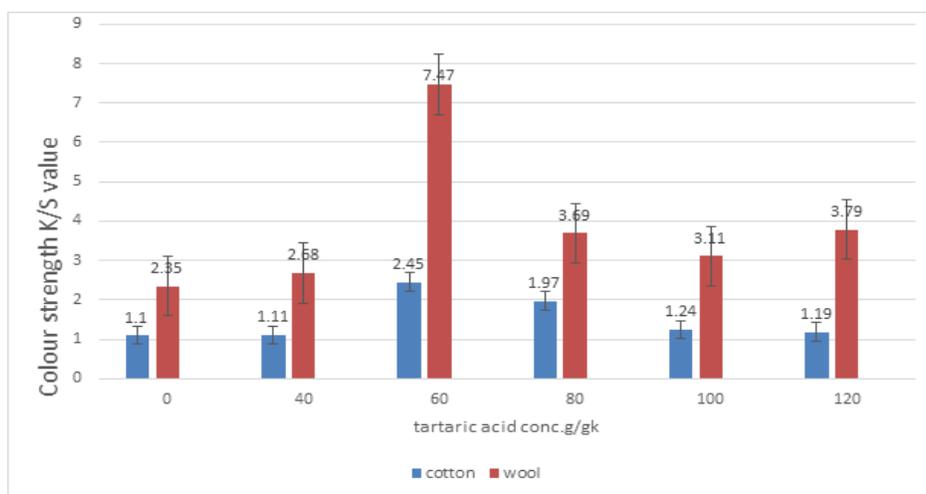


Fig. 3. Effect of concentration of mordant on K/S values of wool and cotton fabrics printed with alkanet nanoparticles

3.3. Factors affecting printing of cotton, wool and polyester fabrics with alkanet dye nanoparticle for the first recipe

Several factors have been studied to illustrate the great role of using alkanet dye nanoparticles as a new material prepared by green method compared with conventional dye.

3.3.1. Effect of thickener type

Three natural thickeners, carboxymethyl cellulose (CMC), sodium alginate and Meypro gum, have been used in the printing pastes to investigate the effect of thickener type. Colour change of printed fabrics express in K/S values were showed in Fig. 4 for cotton, wool and polyester fabrics. Different types of thickeners were used in the printing past to study the effect of thickener type on printing. These thickeners were sodium alginate, carboxymethylcellulose (CMC) and Meypro gum. The results of different thickeners were showed in Fig. 4. 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 was obtained by using CMC as thickener.

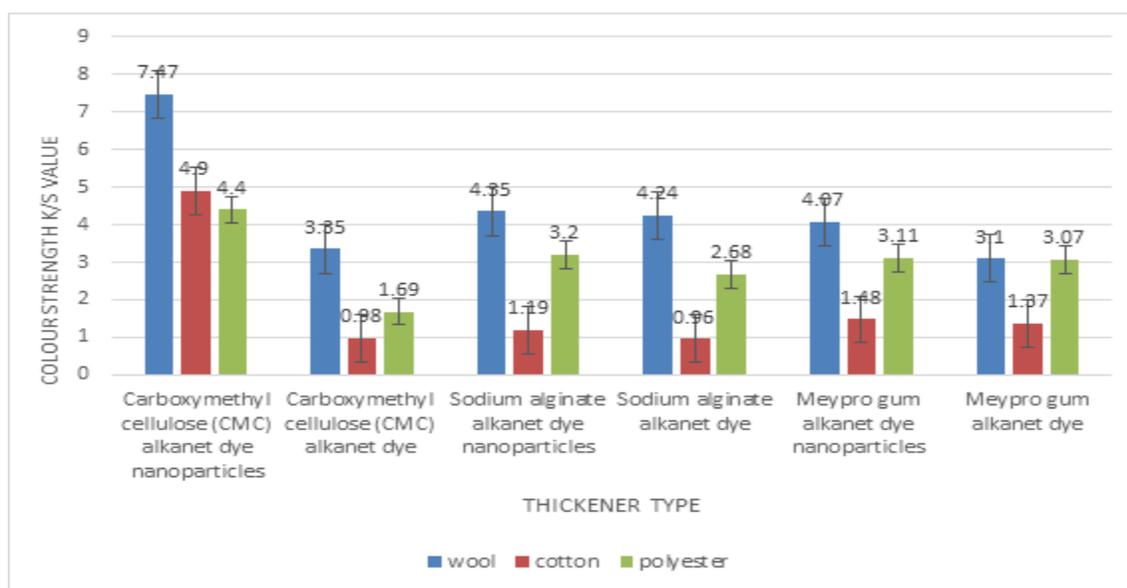


Fig.4 Effect of thickener type on K/S values of cotton, wool and polyester fabrics printed with alkanet dye and alkanet dye nanoparticles.

3.3.2. Effect of urea concentration

Urea considered an essential auxiliary in most printing pastes because of its ability to swell the fabrics that accelerate penetrating dye inside the fabrics [34]. In addition, it acts as a solvent for the dye i.e., used as 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 cotton, wool and polyester printed fabrics with alkanet dye nanoparticles was studied by using different urea concentrations to the printing pastes (0, 10,30,50,70 and 150 g/kg) and the results were plotted in Fig. 5. It is clear from Fig. 5 that as the concentration of urea increased, the K/S values increased for untreated and treated cotton and wool fabrics whereas it increased to maximum characters as synthetic fabrics. In most of the cases, the highest K/S value was obtained by using 150g/kg for wool and cotton and 10 g/kg for polyester. In addition, the treated fabrics higher than their corresponding untreated fabrics for cotton and wool. These results come from that the urea has solvation and disaggregation effects on the dye molecules in the printing paste and enhances solubility of dyes in the paste.

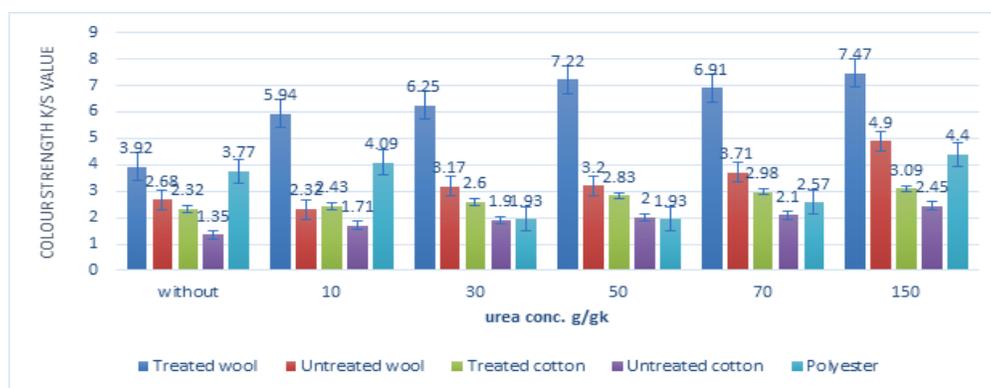


Fig. 5 Effect of urea concentration on K/S values of treated and untreated cotton, treated and untreated wool and polyester all fabrics printed with alkanet dye nanoparticles.

3.3.3. Effect of pH of the printing paste

The pH of printing paste has an important role for dye fixation rate. The rate of dye fixation has been increased as the pH of printing paste of wool decreased because of increased of dye concentration and ammonium ion sites numbers at lower pH values [35]. The influence of printing paste pH on the K/S values of printed wool, cotton (pretreated with tartaric acid) and polyester substrates with alkanet nanoparticles is studied, through using different values (5, 5.5, 6,6.5 and 7) as shown in Fig. 6. The optimum values of K/S were found at pH value of 5.5 and 8 for wool and cotton prints respectively, and at pH = 6 for polyester fabrics.

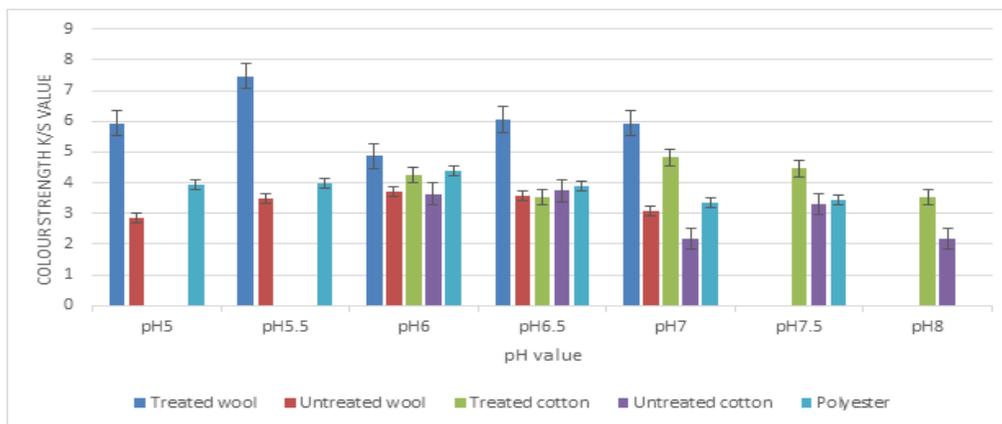


Fig. 6 Effect of pH value on K/S values of treated and untreated cotton, treated and untreated wool and polyester all fabrics printed with alkanet dye nanoparticles.

3.4. Factors affecting printing of cotton, wool and polyester fabrics with alkanet dye nanoparticle for the second recipe

Effect of Diammonium phosphates concentration

Printing paste pH is considered as an effective factor in colour variation and subsequently, the influence of printing paste pH on colour intensity of the prints is studied by applying values (5,5, 6, 6.5 and 7) and the results are exhibited in Fig. 7. It is clear from Fig. 7 that, maximum K/S values can be obtained at pH 6 for Cotton, wool and polyester substrate printed with alkanet nanoparticles respectively.

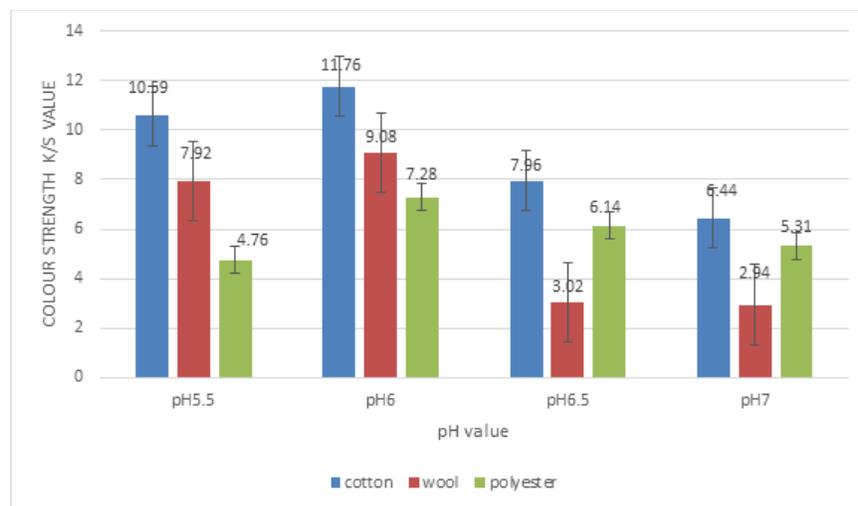


Fig. 7 Effect of pH value on K/S values of cotton, wool and polyester fabrics printed with alkanet dye nanoparticles.

3.4.3. Effect of urea concentration

Different concentrations of urea (0, 10,20,40,60 and 80 g/kg) were used to study its effect on colour strength of cotton, wool and polyester printed fabrics with alkanet dye nanoparticles. Fig. 8 shows that printed cotton, wool and polyester fabrics without urea has the highest K/S values. This may be because of swelling properties of urea that helps fixation of dye. So, the fixation here depends 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 fabric. Diammonium phosphate at 160 °C for 4 min., adjust the pH of the medium at 6. At this value binder can be chemically crosslinked on the fabrics and dye as shown in **Scheme 4**.



Scheme 4. Suggested equations for the reaction of binder with cotton fabrics in the presence of diammonium phosphate

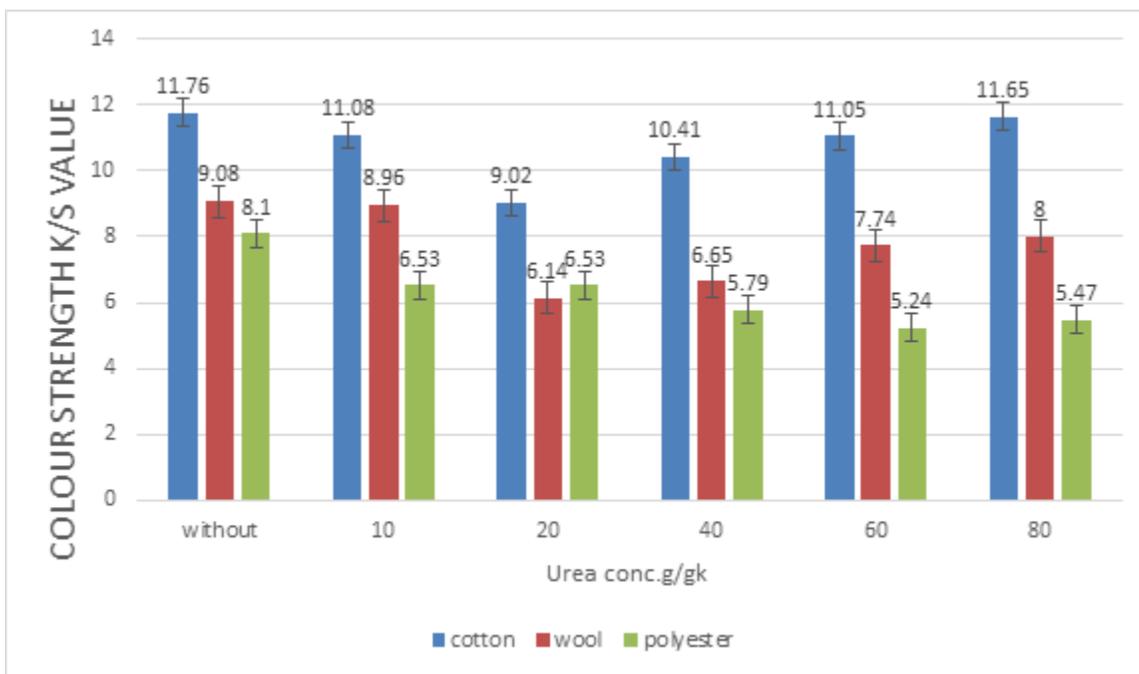


Fig.8 Effect of urea concentration on K/S values of cotton, wool and polyester all fabrics printed with alkanet dye nanoparticles.

3.4.4 Effect of binder concentration

To investigate the effect of binder concentration on the K/S values of printing goods, using different mounts of alkanet dye nanoparticles, viz. 80,100, 120, 140, 160. It is clear from Fig. 9, that the concentration of binder has a remarkable effect on the K/S of the printed samples. In most of the cases, the highest K/S value was obtained by using 140 g/kg

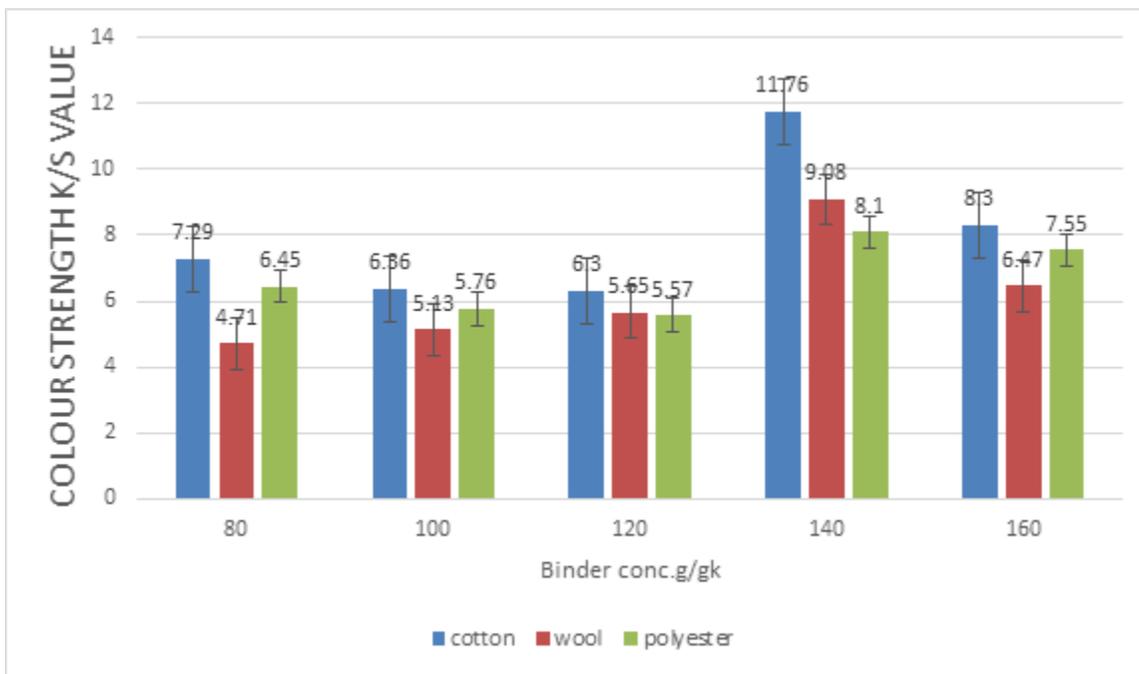


Fig.9 Effect of binder concentration on K/S values of cotton, wool and polyester fabrics printed with alkanet dye nanoparticles.

3.5. Fastness properties of the printed fabrics with first Paste recipe

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

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 dye) and second (as pigment) recipes

		K/S	Washing fastness		Rubbing fastness		Perspiration fastness				Light fastness	Mechanical properties*	
			St.	Alt.	Dry.	Wet.	Acidic		Alkaline			**Tensile Strength (KgF)	***Elongation at Break (mm)
							St.	Alt.	St.	Alt.			
wool	a*	3.35	4-5	4-5	4	3	5	5	5	5	4-5	36.00 ± 0.450	47.00 ± 0.850
	b*	7.47	5	5	4-5	3-4	5	5	5	5	4-5	36.00 ± 0.450	47.00 ± 0.850
	c*	4.48	4-5	4-5	4	2-3	5	5	5	5	5	32.50 ± 0.500	45.50 ± 2.508
	d*	9.08	5	5	4-5	2-3	5	5	5	5	5	32.50 ± 0.500	45.50 ± 2.508
Cotton	a*	0.89	4-5	4-5	4	2	5	5	5	5	5	44.50 ± 1.500	23.05 ± 1.500
	b*	4.9	5	5	4-5	2-3	5	5	5	5	5	44.50 ± 1.500	23.05 ± 1.500
	c*	6.2	4	4	4-5	2-3	5	5	5	5	4	43.50 ± 0.500	21.50 ± 2.500
	d*	11.76	5	5	5	2-3	5	5	5	5	4-5	43.50 ± 0.500	21.50 ± 2.500
Polyester	a*	1.69	4-5	5	3-4	2	5	5	5	5	4-5	34.00 ± 1.000	35.50 ± 1.500
	b*	4.4	5	5	4	2-3	5	5	5	5	4-5	34.00 ± 1.000	35.50 ± 1.500
	c*	4.74	4-5	5	4-5	2-3	5	5	5	5	4-5	33.75 ± 0.750	34.00 ± 0.750
	d*	7.65	5	5	4-5	2-3	5	5	5	5	4-5	33.75 ± 0.750	34.00 ± 0.750

a* printed with alkanet dye (first paste); b* printed with alkanet dye nanoparticles (first paste); c* printed with alkanet dye (second paste); d* printed with alkanet dye nanoparticles (second paste)

* Data are expressed as Mean ± S.D. for n=3

** Tensile strength for wool, cotton and polyester blank fabrics were 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 were 49.00 ± 1.000, 23.50 ± 1.500 and 36.50 ± 0.500 mm respectively

4. CONCLUSION

An ecological printing process of cotton, wool and polyester fabrics with alkanet natural dye nanoparticles using green print Paste. Ball milling is an effective process for producing alkanet dye nanoparticles in one step at ambient temperature and pressure. The prepared alkanet dye nanoparticles have been confirmed via UV-vis, XRD, TEM and SEM. Alkanet dye nanoparticles were used to print cotton, wool and polyester fabrics with dye printing and pigment printing techniques. The printed samples reveal very good to excellent fastness properties. Hence, the present process of printing cotton, wool and polyester fabrics with green print paste formulation by using alkanet as dye and pigment may find wide application in textile coloration.

5. REFERENCE

1. Mohamed, F.A., H.M. Ibrahim, and M.M. Reda, *Eco friendly dyeing of wool and cotton fabrics with reactive dyes (bifunctional) and its antibacterial activity*. Der Pharma Chemica, 2016. **8**(16): p. 159-167.
2. Eid, B.M., et al., *Durable Antibacterial Functionality of Cotton/Polyester Blended Fabrics Using Antibiotic/MONPs Composite*. Fibers and Polymers, 2019. **20**(11): p. 2297-2309.
3. Srivastava, R. and N.J.I.J.o.H.S. Singh, *Importance of natural dye over synthetic dye: a critical*. 2019. **5**(2): p. 148-150.
4. Saxena, S. and A. Raja, *Natural dyes: sources, chemistry, application and sustainability issues*, in *Roadmap to sustainable textiles and clothing*. 2014, Springer. p. 37-80.
5. Du, H., et al., *Simple crystallization approach for enhancing function of plant-based madder dye and performance of dyed fabric*. 2019. **5**(8): p. e02232.
6. Ojha, D., S. Deodiya, and R.J.I.J.o.T.K. Purwar, *Printing of Lyocell fabric with Rubia Cordifolia and Acacia catechu using Guar gum and Chitosan as Thickening Agent*. 2019. **18**(3): p. 615-620.
7. Forouharshad, M., M. Montazer, and B. Yadollah Roudbari, *Zirconium Oxochloride as a Novel Mordant for Natural Dyeing of Wool Yarns*. Journal of Textiles, 2013. **2013**: p. 565382.
8. Rehman, R. and M.I.J.M.P.o.S.A.N.S.f.D.D. Jilani, *Asma Shaheen1, Muhammad Asif Hanif1, Rafia Rehman1, Muhammad Idrees Jilani2, Alexander Shikov3*. 2019: p. 70.
9. Huma, Z.-e., *Pharmacognostic evaluation of Ehretia serrata Roxb. And Ehertia obtusifolia Hocht. A. DC. Family Boraginaceae*. 2019, university of Peshawar, Peshawar.
10. Ravindran, P., *The encyclopedia of herbs and spices*. 2017: CABI.
11. İşmal, Ö.E. and L. Yıldırım, *Metal mordants and biomordants*, in *The impact and prospects of green chemistry for textile technology*. 2019, Elsevier. p. 57-82.
12. Farouk, R., et al., *Simultaneous dyeing and antibacterial finishing of nylon 6 fabric using reactive cationic dyes*. World Applied Sciences Journal, 2013. **26**(10): p. 1280-1287.
13. Ibrahim, H., et al., *Combined antimicrobial finishing dyeing properties of cotton, polyester fabrics and their blends with acid and disperse dyes*. Egyptian Journal of Chemistry, 2019. **62**(5): p. 965-976.
14. Mohamed, F.A., et al., *Improving dye ability and antimicrobial properties of cotton fabric*. Journal of Applied Pharmaceutical Science, 2016. **6**(2): p. 119-123.
15. Mohamed, F.A., et al., *Improvement of dyeability and antibacterial properties of gelatin treated cotton fabrics with synthesized reactive dye*. Bioscience Research, 2018. **15**(4): p. 4403-4408.
16. Mohamed, F.A., et al., *Synthesis, application and antibacterial activity of new reactive dyes based on thiazole moiety*. Pigment and Resin Technology, 2018. **47**(3): p. 246-254.

17. Aysha, T., et al., *Synthesis, spectral study and application of solid state fluorescent reactive disperse dyes and their antibacterial activity*. Arabian Journal of Chemistry, 2019. **12**(2): p. 225-235.
18. Ibrahim, H.M., M.M. Saad, and N.M. Aly, *Preparation of single layer nonwoven fabric treated with chitosan nanoparticles and its utilization in gas filtration*. International Journal of ChemTech Research, 2016. **9**(6): p. 1-16.
19. El-Bisi, M.K., et al., *Super hydrophobic cotton fabrics via green techniques*. Der Pharma Chemica, 2016. **8**(19): p. 57-69.
20. Farag, S., et al., *Impregnation of silver nanoparticles into bacterial cellulose: Green synthesis and cytotoxicity*. International Journal of ChemTech Research, 2015. **8**(12): p. 651-661.
21. Sbai, S.J., et al., *The recent advances in nanotechnologies for textile functionalization*. 2020: p. 531-568.
22. Ibrahim, H., et al., *Preparation of cotton gauze coated with carboxymethyl chitosan and its utilization for water filtration*. Journal of Textile and Apparel, Technology and Management, 2019. **11**(1).
23. Ibrahim, H.M., et al., *A green approach to improve the antibacterial properties of cellulose based fabrics using Moringa oleifera extract in presence of silver nanoparticles*. Cellulose, 2020.
24. Ibrahim, H.M., M.M. Reda, and A. Klingner, *Preparation and characterization of green carboxymethylchitosan (CMCS) – Polyvinyl alcohol (PVA) electrospun nanofibers containing gold nanoparticles (AuNPs) and its potential use as biomaterials*. International Journal of Biological Macromolecules, 2020. **151**: p. 821-829.
25. El-Alfy, E.A., et al., *Preparation of biocompatible chitosan nanoparticles loaded by tetracycline, gentamycin and ciprofloxacin as novel drug delivery system for improvement the antibacterial properties of cellulose based fabrics*. International Journal of Biological Macromolecules, 2020. **161**: p. 1247-1260.
26. Ibrahim, H.M., et al., *Preparation of chitosan antioxidant nanoparticles as drug delivery system for enhancing of anti-cancer drug*, in *Key Engineering Materials*. 2018. p. 92-97.
27. Zhang, L., T. Tsuzuki, and X.J.C. Wang, *Preparation of cellulose nanofiber from softwood pulp by ball milling*. 2015. **22**(3): p. 1729-1741.
28. Hu, J.-z., P. Skrabal, and H. Zollinger, *A comparison of the absorption spectra of a series of blue disperse dyes with the colorimetric evaluation of their dyeings*. Dyes and Pigments, 1987. **8**(3): p. 189-209.
29. Savarino, P., et al., *Disperse and cationic dyes from aminophenyl-X-azolo-pyridines*. Dyes and pigments, 1989. **11**(3): p. 163-172.
30. Ibrahim, N., et al., *Options for enhancing performance properties of easy-care finished cellulose/wool blended fabrics*. 2008. **47**(3): p. 281-292.
31. Gaikwad, A.J.I.J.o.I.C., *Modification and application of cellulose fibers for the transport of carbonate ions*. 2014. **5**(1): p. 12.
32. Franco, F., et al., *The effect of ultrasound on the particle size and structural disorder of a well-ordered kaolinite*. 2004. **274**(1): p. 107-117.
33. Osman, H.J.W.A.S.J., *Eco-friendly printing of textile substrates with rhubarb natural dye nanoparticles*. 2014. **29**(5): p. 592-599.
34. Maamoun, D., et al., *Cotton/wool printing with natural dyes Nano-particles*. 2014. **9**(1): p. 90-99.
35. Broadbent, A.D., *Basic principles of textile coloration*. 2001: Society of Dyers and Colourists.