

Coloration of Fibrin Fabric with Berberine Natural Dye with Ultrasonic Technique Using ZnO Nano Powder as Light Fastness Improving

M.M. Kamel and Hamada M. Mashaly

Department of Auxiliaries and Printing, Dyeing, National Research Center, Dokki, Giza, Egypt

Submitted: Oct 18, 2013; **Accepted:** Nov 24, 2013; **Published:** Nov 30, 2013

Abstract: Berberine, a natural cationic colorant, is the major component of Amur Cork tree extract was used as a natural basic dye since the synthetic basic dyes remarked high acute and chronic toxicity on human beings, carcinogenic effect on animals, in addition to a hazardous effect on aquatic marines. These factors have brightened the scope to carry out this research, by making a comparative dyeing study by ultrasonic and conventional heating techniques on anionized fibrin fabrics with the Berberine dye. It is found that the performance of ZnO nano particles as UV-absorbers can be efficiently transferred to fabric materials. The UV tests indicate a significant improvement in the UV absorbing activity in the ZnO-treated fabrics.

Key words: Berberine • Dyeing, Fibrin • Monochlorotriazine anionic reagent • Natural basic dye • Ultrasonic • ZnO nano powder.

INTRODUCTION

In recent years, there is a progressive increase in UV radiation effect on human skin caused by the depletion of the ozone in the earth's atmosphere [1]. As long-term exposure to UV light can result in a series of negative health effects such as acceleration of skin ageing, photodermatosis (acne), erythema (skin reddening) and even severe skin cancer. Developing textiles with UV protection functionality has been widely researched so far [2, 3] UV radiation on or near the earth's surface is an invisible component of sunlight, divided into UV-A (315-400 nm), UVB (280-315 nm) and UV-C (200-280 nm). Fortunately, the very high energy of the UV-C photons is mostly absorbed by ozone in the higher regions of the atmosphere, decreasing their relative intensity on the earth surface to almost zero. Therefore, to be useful in protecting the wearers from solar UV radiation, the main UV rays that should be blocked by textiles are UV-A and UV-B. Today, many approaches have been investigated to improve the UV protection function of cotton fabrics because cotton textiles are the most regular summer clothes but having the least UV-blocking ability. Among them, organic UV absorbers [4-7] nanoscaled inorganics such as ZnO [8, 9] and titanium hydrosols dyestuffs. Berberine, a natural cationic colorant, is the major component of Amur Cork tree extract. Due to ionic

interactions, while it shows high exhaustion towards protein fibers such as wool and silk, it exhibits little substantivity onto cellulosic fibers. In this context, in order to apply the colorant to cellulosic fibers, the new approach of employing the anionic agent containing a monochloro-s-triazinyl reactive group was conducted [10].

The use to modify the fibrin fiber using a prepared reactive anionic agent and to examine the feasibility of using this agent for improving exhaustion properties of Berberine is very essential. Berberine, the dye pigment present in the roots of barberry, is the only example of natural basic dyes [11]. As a dye, barberry has been mentioned since the 14th century in the records of Christian monasteries. Berberine is an alkaloid accompanied by its hydroxylated derivatives viz. berberubine, palmatine, columbamine, berbamine and oxyacanthine. The berberine base is unstable and assumes the aldehyde form berberinal whereas its salts are derived from the ammonium form. Fig. 1 represents the structure of Berberine, which shows it to be a basic or cationic dye [12-13]. Power ultrasonic can enhance a wide variety of chemical and physical processes, mainly due to the phenomenon known as cavitations in a liquid medium [14-20]. The usefulness of ultrasonic as a novel dyeing accelerant and its efficiency in increasing the dye uptake on different fabrics has been demonstrated [21, 22].

MATERIALS AND METHODS

Materials: Mill, scoured and bleached plain-weave fibrin fabric was used for this study. The fabric was purified in the laboratory by a mild treatment with a solution containing 5 g/l sodium carbonate and 2g/l non-ionic detergent (Hostapal CV, Clariant). The fabric was then thoroughly washed and air dried.

A commercial crushed Berberine roots was used, its properties are listed in Table 1 and its chemical structure is represented in the Fig.1.

Ferrous sulphate and stannous chloride were used as mordents; sodium carbonate and glacial acetic acid were used to adjust the pH values. All other chemicals used in this study were of laboratory reagent grade.

Instrument: Thermostated CREST bench top 575 HT ultrasonic cleaner of capacity 5.75 l, frequency 38.5 kHz and with a maximum 500 W output was used. The output power levels are from 100 to 500 W [11].

Methods: Conventional and ultrasonic extractions were carried out as described [11], the two method of extraction were used first using the conventional heating and the other using the ultrasonic energy, the dye concentration, the extraction temperature, the extraction time and the power level for the ultrasonic extraction were studied and the better results obtained when using 10% of the dye at 80°C for 40 min. at power level 300watt for the ultrasonic extraction.

Preparation of Monochloro-S-Triazine Anionic Agent [23]: Monochloro-S-triazine anionic agent I was prepared using a similar method described previously by Maciel *et al.* [24]. 2-Naphthyl amine 5, 7-disulphonic acid (9.09 g, 0.03mol) was dissolved in 50 ml water. After being neutralized with a sodium hydroxide solution, it was added slowly to a solution of 2-aniline-4,6-dichloro-1,3,5-triazine (0.03mol) in 30ml acetone with additions of 2 mol/l sodium hydroxide solution as necessary to maintain a pH between 6.5 and 7 throughout the process. The temperature of the reaction mixture was raised to 40°C/1h under stirring. The solids were removed by filtration, washed with ice-cold water, followed by acetone and dried in a vacuum below 40°C to provide the desired product.

Pretreatment of Fibrin Fabrics with the Anionic Agent I: Fibrin fabric was treated with the anionic agent (30% owf) (I) using the exhaustion method at 60°C and a liquor ratio of 50: 1. Sodium chloride (40 g/l) was added in parts over

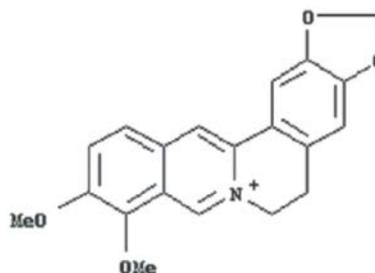


Fig. 1: Berberine Structure

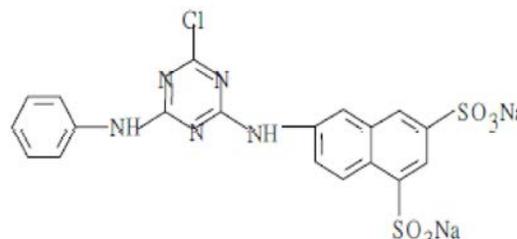


Fig. 2: Monochloro-S-triazine anionic agent I

Table 1: Characteristics of Berberine Dye Used

Botanical name	C.I. Name	Class	Part used	$\lambda_{max.}^{(nm)}$ in water
<i>Berberis aristata</i>	Natural yellow 18	Alkaloids	Root	420

15 minutes followed by a part-wise addition of sodium carbonate (20g/l) after 1h, then the temperature increase to 80°C. The reaction was maintained at 80°C for 2 hrs. After treatment, the fabric was washed with tap water, followed by washing for 30 minutes with a solution of 2 g/l non-ionic detergent (Hostapal® CV-Clariant) at 60°C. Finally, the fabrics were removed, rinsed thoroughly with tap water and dried at room temperature [23].

Synthesis of ZnO Nanoparticles: Zinc oxide nanoparticles were synthesized as the following procedure reported elsewhere [25] synthesis was carried out at a high degree of super saturation in order to achieve a nucleation rate much greater than the growth rate [24]. ZnCl₂ (5.5 g) was dissolved in 200 ml of water at 90°C in an oil bath. Then 16 ml of 5M NaOH aqueous solution was added drop-wise to the zinc chloride solution with a gentle stirring over a period of 10 min at 90°C. The particles were separated from the supernatant dispersion by sedimentation. The supernatant solution was discarded and the remaining suspension was washed five times with distilled water to lower the concentration of NaCl. Each time, the dilution ratio between the concentrated suspension and the washing solution was about 1:10. The complete removal of NaCl from the suspension was checked using the solution of AgNO₃. The purified

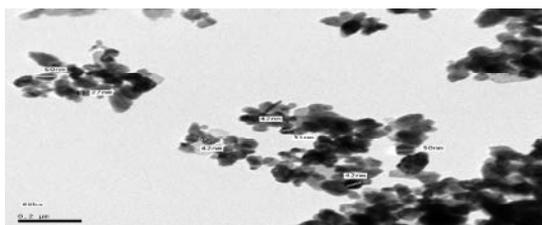


Fig. 3: Transmison Electron Microscope (TEM) photo of ZnO nano powder

particles were then peptized with 2-propanol in an ultrasonic bath for 10 min at room temperature. The peptization process is necessary to disrupt the micro-agglomerates and to release the nanoparticles of zinc oxide. The particles were then collected by centrifugation at 6,000 rpm for 15 min. The washing procedure was repeated three times. Thermal treatment of the particles at 250°C for 5 h leads to the formation of ZnO.

Fabric Treatment: The fabric samples (130g/m²) were conditioned at 21°C and 65% RH. Samples (10 cm x 10 cm) were soaked for 10 min in 2-propanol dispersion of ZnO nanoparticles (5% w/w) under gentle magnetic stirring. The fabrics were then squeezed on a padding mangle to 70% expression to remove the excess dispersion and dried in an oven at 130° C for 15 min under atmospheric pressure (dry heat). In order to evaluate the nanoparticles adhesion to the textile fibers, the treated fabrics were washed five times as per the standard method (UNI EN ISO26330:1996) and the washing cycles were performed at 30°C with reference detergent without optical brighteners [25]. The drying step was carried out on a horizontal flat surface. The fabric specimens were tested before and after the washing cycles using UV spectrophotometry.

Dyeing Procedure: Fibrin was dyed in a bath containing different amounts of sodium chloride (0-30 g/l), 10 % Berberine dye with liquor ratio 40:1, using conventional heating (CH), at different pH values (2-9) for different time intervals (20-120 min.) and at different temperatures (40-80°C). For comparison, the same conditions of dyeing were carried out using ultrasonic technique (US) with sonic power of 500 W. The pH values were recorded with Hanna pH meter and adjusted with dilute solutions of sodium carbonate as the dye extract pH was 5.6. The dyed samples were rinsed with cold water, washed in a bath of liquor ratio 40:1, using 3g/l non ionic detergent (Hostapal CV, Clariant) at 60°C, for 30 min, then rinsed and finally dried at ambient temperature.

Mordanting Methods: Anionic treated fibrin with compound I was mordanted by i) pre-mordanting and ii) post-mordanting methods. Ferrous sulphate and stannous chloride mordants with concentration of 10 g/l were used. In the pre mordanting method, the treated fibrin samples were first immersed in aqueous solution of mordants for 45 min. at 30°C. The mordanted samples were then dyed by the Berberine dyeing bath. In the post-mordanting method, dyeing was carried out on the treated fibrin samples in absence of mordant, followed by mordanting in a separate baths with the mordents for 45 min. at 30°C [11].

UV/ Vis Absorption Spectra: The uv/vis absorption spectra in water were recorded using a shimatzu uv/vis spectrophotometer. The reflectance of the dyed soaped samples was measured on a Perkin-Elmer Lambda 3B UV/Vis spectrophotometer. Relative colour strengths (K/S values) were determined using the Kubelka-Munk equation:

$$K/S = \frac{(1-R)^2}{2R} \frac{(1-R_0)^2}{2R_0}$$

Where

R = Decimal fraction of the reflectance of the dyed fabric,
K = Absorption coefficient and S = scattering coefficient.

Fastness Testing: The dyed samples were tested according to ISO standard methods. The specific tests were ISO 105-X12 (1987), colour fastness to rubbing; ISO 105-C02 (1989), colour fastness to washing and ISO 105-E04 (1989), colour fastness to perspiration

RESULTS AND DISCUSSION

Power ultrasonic has great potential for application in a wide variety of industrial processes. It offers potential cost saving in time, chemicals, energy and reduced effluent. In this context, applying ultrasonic in textile colouration was of interest. Thus, exploiting power ultrasonic in dyeing fibrin fabrics using Berberine dye as a natural basic dye was done in two steps.

Ultrasonic Extraction: The dye 10% extracted at 80°C for 40 min. at power level 300 w as in previous work reported by Kamel *et al.* [11].

Ultrasonic Dyeing: Comparative study between the conventional dyeing (CH) and the ultrasonic dyeing (US) techniques as well as the different factors that may affect these processes in dyeing were investigated.

Effect of Dye Bath pH: The pH values of the dye bath have a considerable effect on the dyeability of the treated cotton samples with Berberine dye under both (US) and (CH) techniques as shown in Fig. 4. It is clear that both (CH) and (US) have improved the dyeability of the samples at pH9, with much higher values at all points in the (US). The higher pH conditions led to high exhaustion since the cationic Berberine was more attractive to the negatively charged sulfonate anions under basic conditions. It is proposed that these results might be related to the dissociation of the sodium salts ($-\text{SO}_3^- \text{Na}^+$) of the anionic agent in the dyeing solution. In other words, the sodium salts of the sulfonates were generally dissociated to the sodium ions (Na^+) and the sulfonate anions ($-\text{SO}_3^-$) in water. However, in acidic conditions the extent of the sulfonic acid form ($-\text{SO}_3\text{H}$) might be greatly increased due to protonation to the sulfonate anions. The dissociations of the sulfonic acids are much weaker than those of the sodium salts of sulfonates. Thus, the resulting number of available anionic sites on fibers in alkaline conditions is relatively larger than those sites in acidic conditions and the exhaustion of the cationic Berberine was increased in alkaline dyeing solutions. The pH 9 offers sufficient negative charges on the sulphonic groups which are capable to attract the cationic Berberine dye by ionic forces. This ionic attraction would increase the dyeability of the fibre as clearly observed in Fig.4.

Effect of Salt Addition: Fig. 5 shows the effect of salt concentration on the colour strength obtained for the dyed samples under both (US) and (CH) techniques. It is clearly indicated that the colour strength slightly increases with the increase of salt concentration in the (US) and (CH) techniques with pronounced increase in the (US) than the (CH). In case of (US), a plateau is attained at 5 g/l salt and then started to decline slightly with excess concentrations, whereas on using (CH) the maximum colour strength was attained at 10 g/l salt, then remains nearly stable with excess concentrations. Sodium chloride salt retards the dye migration and thus obtaining better level dyeings. The chlorine atoms of the ionized salt blocked the hydrogen protons of the anionic reagent sulphonic groups, thus, regulating and increasing the

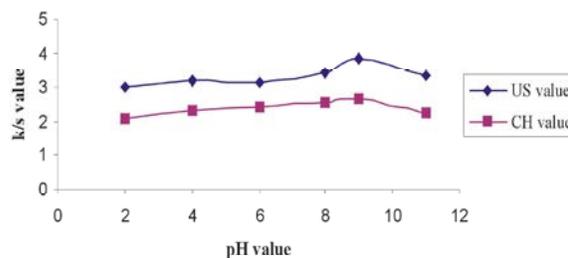


Fig. 4: Effect of Dye Bath pH

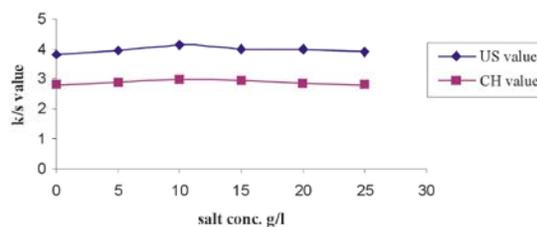


Fig. 5: Effect of Salt Addition

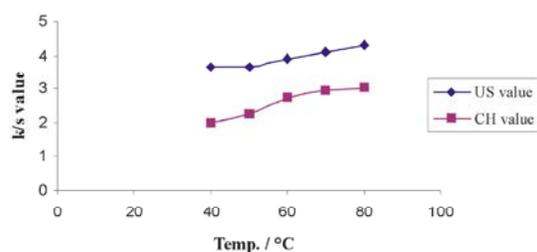


Fig. 6: Effect of Dyeing Temperature

attraction between the cationic Berberine dye and the sulphonates group of the anionic reagent ionic forces. In case of (US) technique, there is a decline in the colour strength with salt concentrations up to 5g/l; this may be explained by ion crowding in the dyeing bath.

Effect of Dyeing Temperature: The effect of temperature on the dyeability of the treated fibrin samples with Berberine dye was conducted under (US) and (CH) techniques at different temperatures (40- 80°C). As shown in Fig. 6, it is clear that the colour strength increases with increase in dyeing temperature in both cases of (US) and (CH) techniques with pronounced increase in the (US) case than the (CH) one. The increase in dye-uptake can be explained by fiber swelling that enhanced the dye diffusion. On the other hand, the ultrasonic power provides de-aggregation of dye molecules which leads to further enhancement of dye diffusion and thus, better dyeability compared with (CH) technique.

Effect of Dyeing Time: The Effect of dyeing time was conducted using 10g/100 ml water Berberine dye to reveal the effect of ultrasonic power on the de-aggregation of dye molecules in the dye bath as indicated by higher dye-uptake. As shown in Fig. 7, the obtained colour strength increased as the time increased in both (US) and (CH) techniques with much higher values at all points in the (US) case. In case of (US) technique, a plateau is attained after 60 up to 80 min. and then started to decline slightly with prolonged time. Whereas, in case of (CH) technique, the decline in colour strength began after 100 min. The decline in the colour strength may be due to the desorption of the dye molecules because of the prolonged dyeing time.

Effect of Ultrasonic Power: The effect of ultrasonic power on the dyeability of treated cotton samples with Berberine dye was conducted at different power levels (100-500W). As shown in Fig. 8, the colour strength of the dyed samples seemed to be directly proportional with the supplied power. This behavior investigates the assisting effect of ultrasonic power on the dyeability of treated fibrin samples with Berberine dye. This assistance is due to dispersion (breaking up of micelles and high molecular weight aggregates into uniform dispersions in the dye bath), degassing (expulsion of dissolved or entrapped gas or air molecules from fiber into liquid and removal by cavitations which facilitates the dye-fiber contact) and diffusion (accelerating the rate of dye diffusion inside the fiber by piercing the insulating layer covering the fiber if any and accelerating the interaction or chemical reaction, if any, between dye and fiber).

Effect of Reuse Number of the Dye Bath: Fig. 9 shows the effect of reuse number on the colour strength obtained. It is clear that US reuse is more effective than in the case of CH and as expected, repeating the reuse of the dye bath always leads to different coloured samples from one batch to another until complete exhaustion of the dye bath.

Fastness Properties: Fastness properties of the CH and US dyed fabrics are shown in Tables 2a and b. The results indicate fair to good fastness properties of the dyed samples using both ultrasonic and conventional techniques with better results in case of using the mordents (post mordantig) for the rubbing and light fastness, there is no difference in washing and perspiration for the dyed fabrics using both methods of

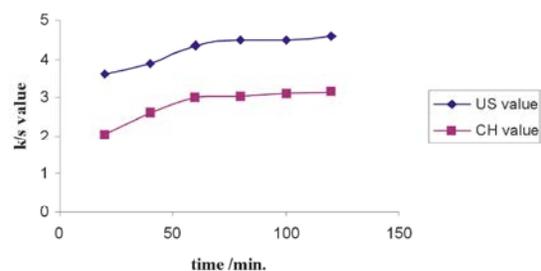


Fig.7: Effect of Dyeing Time

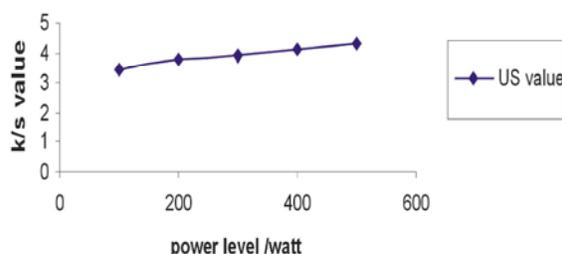


Fig. 8: Effect of Ultrasonic Power.

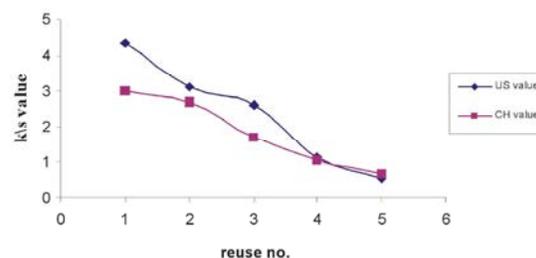


Fig. 9: Effect of reuse number of the dye bath

dyeing, the shade of the fabric that mordanted shows an increase of shade in case of using ferrous sulphate than that of stannous chloride in both CH and US dyeing methods.

The Total Color Difference (ΔE): CIE Lab Difference: Now, in a lot of dye houses, there is a data match system which helps colorist to obtain different shades and to judge about the acceptance of these shades against a particular standard. The most widely used equation is CIE Lab difference equation.

$$\Delta E = L^2 + [(a^2 + b^2)]^{1/2}$$

ΔE : The total difference between the sample and the standard

L : Represent white-black axis

a : Represent the red- green axis

b : The yellow -blue axis

Table 2a: Fastness properties of treated dyed cotton under conventional heating technique.

Samples	Rubbing		Washing			Washing						Light
	Dry	Wet	Washing			Alkaline			Acidic			
			Alt	St*	St**	Alt	St*	St**	Alt	St*	St**	
Control	4	3-4	3-4	3	3	2-3	3-4	3	3	4	3-4	4-5
Pre-mordanting												
Alum	4-5	4	3-4	3-4	3-4	3	4	3	3	4	3-4	5
Stannous chloride	4-5	3-4	3-4	3-4	3-4	2-3	4	3	2-3	3	3	5
Post- mordanting												
Alum	4-5	4	3-4	3	3-4	3	4	3-4	3-4	4-5	4	5
Stannous chloride	4	3-4	4	4	4	3-4	4	4	3-4	4	4	5

Control: anionized fabric Alt.: alteration St.*: staining on cotton St.** staining on wool

Table 2 b: Fastness properties of treated dyed cotton under ultrasonic technique.

Samples	Rubbing		Washing			Washing						Light
	Dry	Wet	Washing			Alkaline			Acidic			
			Alt	St*	St**	Alt	St*	St**	Alt	St*	St**	
Control	4-5	3-4	4	3-4	3-4	3-4	3-4	4	3	3	3	4-5
Pre-mordanting												
Alum	4-5	3-4	3-4	3-4	3-4	3-4	3	4	3-4	3	4	5
Stannous chloride	4	3-4	3	3	3	3-4	3	3-4	3-4	2-3	4	5
Post- mordanting												
Alum	4-5	3-4	3	3-4	4	4	3	4	4	3-4	4	5
Stannous chloride	4	3-4	3	3	3	3	3-4	4	4	3-4	4	5

Table 3a: Color alteration value (ΔE) after light exposing for the conventional and ultrasonically dyed fibrin fabric.

Time of irradiation in hrs	ΔE	Conventional dyeing					Ultrasonic dyeing				
		Fe pre	Sn pre	Fe post	Sn post	Blank	Fe pre	Sn pre	Fe post	Sn post	Blank
0h	ΔE	79.95	92.20	71.31	91.50	89.68	80.72	89.39	79.75	88.61	90.39
35h	ΔE	77.31	86.51	70.01	82.91	86.61	74.85	85.81	70.30	81.63	86.99
70h	ΔE	75.32	82.73	68.23	80.18	81.83	72.52	81.87	68.69	78.67	81.99
105h	ΔE	74.41	80.51	68.07	79.06	79.95	71.70	79.90	67.82	77.76	79.94
140h	ΔE	74.22	79.46	67.39	78.39	78.79	70.23	78.63	67.32	77.34	79.23
175h	ΔE	73.34	78.17	67.11	77.65	77.68	70	77.78	67.01	76.51	77.84

Fe pre: Ferrous sulphate pre mordanting Sn pre: Stannous chloride pre mordanting

Fe post: Ferrous sulphate post mordanting Sn post: Stannous chloride post mordanting

Table 3b: Color alteration value (ΔE) after light exposing for the conventional and ultrasonically dyed fibrin fabric pre treated with zinc oxide nano powder.

Time of irradiation in hrs	ΔE	Conventional dyeing					Ultrasonic dyeing				
		Fe pre	Sn pre	Fe post	Sn post	Blank	Fe pre	Sn pre	Fe post	Sn post	Blank
0h	ΔE	77.25	87.75	72.59	86.77	83.45	69.46	86.13	70.87	83.31	79.62
35h	ΔE	76.12	84.10	71.14	82.14	81.45	72.29	83.46	69.38	80.19	82.41
70h	ΔE	74.10	80.95	70.23	79.16	78.84	71.60	79.63	68.33	78.46	77.77
105h	ΔE	72.89	79.44	69.10	78.32	77.65	70.26	78.23	67.41	77.62	77.01
140h	ΔE	69.86	76.65	68.68	77.67	76.77	69.93	77.75	66.86	76.75	76.73
175h	ΔE	68.69	76.21	68.11	76.12	76.16	69.03	77.33	66.41	76.19	76.02

Table 3c: Color alteration value (ΔE) after light exposing for the conventional and ultrasonically dyed fibrin fabric post treated with zinc oxide nano powder.

Time of irradiation in hrs	ΔE	Conventional dyeing					Ultrasonic dyeing				
		Fe pre	Sn pre	Fe Post	Sn post	Blank	Fe pre	Sn pre	Fe post	Sn post	Blank
0h	ΔE	78.77	90.89	73.97	86.63	85.91	75.55	86.40	72.09	83.80	85.31
35h	ΔE	70.20	82.29	66.60	82.23	80.76	68.60	82.40	67.03	79.25	78.81
70h	ΔE	68.24	80.52	65.96	79.48	78.72	68.15	79.35	66.16	77.53	76.17
105h	ΔE	68.22	78.34	64.41	77.88	77.35	68.19	77.75	66.02	76.38	74.82
140h	ΔE	68.12	78.14	63.94	77.32	77	66.86	76.16	65.01	76.31	74.22
175h	ΔE	68.01	76.91	63.02	76.29	75.87	66.31	75.68	64.70	75.66	74.01

We have measured ΔE for all dyed samples (blank, pre and post mordanting) before irradiation and after irradiation from 0 to 175 hours according to CMC 2:1 equation which gives more accurate results, the results indicates that the color alteration ΔE between the CH and the US dyeing are small but the alteration rate differ between the treated and the untreated fabrics with ZnO nano powder also this holds true in case of the pre and/or post treated fabrics since the effect of using ZnO nano powder as anti UV absorbent before dyeing give better results than the post treated fabrics and also better than the un treated fabrics as shown in Tables 3a, b and c also the results of (US) dyed fabrics are better than the (CH) dyed fabrics.

CONCLUSION

The reactive dichloro-s-triazinyl anionic agent was synthesized and applied to the fibrin fibers. The dyeing properties of Berberine using the conventional and ultrasonic energy were determined. The exhaustion of Berberine to the fibrin fibers with the anionic agent system was higher than that of the untreated sample and the use of ZnO nano powder decrease the rate of alteration (ΔE) in color in case of pre -treated fabrics than that of post and non treated fabrics and the (US) dyed fabrics better than the (CH) dyed fabrics. In the case of the anionic agent (I) system, the extent of the shade change of Berberine dyeing was not very high with the use of the mordant for both the pre and post mordanting.

REFERENCES

1. Wanga, Q. and P.J. Hauser, 2010. Developing a novel UV protection process for cotton based on layer-by-layer self-assembly. Carbohydrate Polymers, 81: 491-496.
2. Reinert, G., F. Fuso, R. Hilfiker and E. Schmidt, 1997. UV-protecting of textile fabrics and their improvement. Textile Chemist and Colorist, 29: 36-43.
3. Schindler, W.D. and P.J. Hauser, 2004. An Excellent Introduction to the Chemical Finishing of Textiles with Useful Practical Information from the Authors. Chemical Finishing of Textiles. Cambridge: Woodhead Publishing.
4. Akrman, J. and J. Prikryl, 2008. Application of benzotriazole reactive UV-absorbers to cellulose and determining sun protection of treated fabric spectrophotometrically. Journal of Applied Polymer Science, 108: 334-341.
5. Czajkowski, W., J. Paluszkiwicz, R. Stolarski, M. Kazmierska and E. Grzesiak, 2006. Synthesis of reactive UV absorbers, derivatives of monochlorotriazine, for improvement in protecting properties of cellulose fabrics, Dyes and Pigments, 71: 224-230.
6. Riva, A., I.M. Algaba and M. Pepio, 2006. Effect of the finishing oil of acrylic fibers in the optical rotation of the Raman scattered light, Journal of Cellulose, 13: 697-704.
7. Tragoonwichian, S., E.A. O'Rear and N. Yanumet, 2008. Admicellar polymerization of 2-hydroxy-4-acryloyloxybenzophenone: The production of UV-protective cotton, Colloids and Surfaces A: Physicochemical and Engineering, 329: 87-94.
8. Becheri, A., M. Durr, P. Lo Nostro and P. Baglioni, 2008. Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV Absorbers, Journal of Nanoparticle Research, 10: 679-689.
9. Vigneshwaran, N., S. Kumar, A.A. Kathe, P.V. Varadarajan and V. Prasad, 2006. Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites. Nanotechnology, 17: 5087-5095.
10. Kima Tae-Kyung, S.H. Yoona and Y.A. Sonb, 2004. Effect of reactive anionic agent on dyeing of cellulosic fibers with a Berberine colorant. Dyes and Pigments, 60: 121-127.

11. Kamel, M.M., H.F. Mansoure, H.M. Mashaly and A.A. Haron, 2007. Clean Dyeing Technology with Basic Natural Dye on Cotton Fabrics using Ultrasonic Technique. *Man-made Textile in India* August. pp: 280-287.
12. Gulrajani, M.L., D. Gupta and S.R. Maulik, 1999. Studies on dyeing with natural dyes: Part-II-Dyeing of berberine on acrylic Fiber. *Indian Journal of Fiber and Textile Research*, 24(9): 223-225.
13. Hauser, P.J., 2000. Printing Cationized Cotton with Direct Dyes. *AATCC*, 32(6): 44-52.
14. Kamel, M.M., Reda M. El-Shishtawy, B.M. Youssef and H.M. Mashaly, 2005. Ultrasonic assisted dyeing: III dyeing of wool with lac natural dye. *Dyes and Pigments*, 63: 103-110.
15. Kamel, M.M., Reda M. El-Shishtawy, B.M. Youssef and H.M. Mashaly, 2007. Ultrasonic assisted dyeing: IV dyeing of cationised cotton with lac natural dye. *Dyes and Pigments*, 73: 279-284.
16. Saligram, A.N. and S.R. Shukla, 1993. Study on Effect of Proteolytic Enzyme Degumming on Dyeing of Silk. *American Dyestuff Reporter*, 82(8): 801-808.
17. Tiwari, V. and S. Padma Vankar, 2001. Unconventional natural dyeing using microwave and sonicator with alkanet root bark: part II. *J. Colourage*, 48(5): 493-499.
18. Tiwari, V., B.G. Pade and V.S. Padma, 2000. Unconventional natural dyeing using microwave and sonicator with alkanet root bark. *J. Colourage*, 47(3): 21-26.
19. Shanker, R. and V.S. Padma, 2005. Ultrasonic energised dyeing of wool with *Mirabilis jalapa* flowers. *J. Colourage*, 52(2): 57-61.
20. Petal, B.H., B.J. Agarwal and H.M. Petal, 2000. Application of natural dyes in textile industry and the treatment of dye solutions using electrolytic technology. *J. Colourage*, 47(9): 141-153.
21. Vankar, P.S., A. Mishra, B. Ghorpade and V. Tiwari, 2000. Sonicator dyeing of cotton with eucalyptus bark using copper and chromium mordants ecofriendly. *J. Colourage*, 47: 25-28.
22. Mashaly, H.M. and M.M. El-Zawahry, 2009. Effect of Reactive Anionic Agents on the Dyeing of Linen Fabrics with Cationic Dyes. *Textile Research Journal*, 13: 53-64.
23. Clipson, J.A. and George A.F. Roberts, 1989. Differential dyeing cotton. 1-Preparation and evaluation of differential dyeing cotton yarn. *JSDC*, 105 April.
24. Maciel, A.V., Da Nova M. Wagner and M.D. Vânia, 2010. A Novel Synthesis of Nano structured ZnO via Thermal Oxidation of Zn Nanowires Obtained by a Green Route, *Materials Sciences and Applications*, 1: 279-284.
25. Kathirvelu, S., D'Souza Louis and Dhura Bhaarathi, 2009. UV protection finishing of textiles using ZnO nanoparticles. *Indian Journal of Fibre & Textile Research*, 34: 267-273.