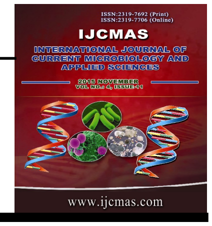
Int.J.Curr.Microbiol.App.Sci (2015) 4(11): 587-596



International Journal of Current Microbiology and Applied Sciences
ISSN: 2319-7706 **Volume 4 Number 11 (2015) pp. 587-596**
http://www.ijcmas.com

Original Research Article

The Dye Ability and Antimicrobial Activity of Wool Fibers Dyed with Reactive Dyes and Pre- Treated with Chitosan

Fatma A. Mohamed[1], N.F. Ali[1*] and RSR EL-Mohamedy[2]

[1]Textile Research Division, National Research Centre, 12311 Dokki, Cairo, Egypt
[2]Plant Pathology Department, National Research Center, 12311 Dokki, Giza, Egypt

**Corresponding author*

A B S T R A C T

Reactive dyes previously synthesized were applied on wool fibers along with different degree of molecular weight chitosan to impart antimicrobial characteristics. The effect of chitosan application on the dyeing properties of wool fibers were studied by measuring the color strength (K/S) values of the treated substrates at various concentrations of chitosan and the dye. The results proved that the chitosan treated wool fibers showed high dye uptake than the untreated fibers. The treated fibers exhibit higher antimicrobial activity than the untreated, the chitosan treatment enhances the antimicrobial characteristics of the dyes. Tests on fastness properties of the dyed wool fibers and wool fibers pre-treated with chitosan were carried out and the results showed that, rubbing, washing and perspiration of all the aforementioned dyes are excellent to good fastness of the salt-free dyeing were both satisfactory. Also the colorimetric CIE L*a*b* C*h° data of the dyed wool fibers were evaluated and revealed good results.

Keywords

Chitosan, Wool fiber, Antimicrobial, Dyeability, Fungi, *Aspergillius nigar*, Reactive dyes

Introduction

In the textile industry, chitosan has been widely applied to provide antimicrobial properties, increase dyeing ability, and prepare beneficial fibers (Zhang, 2008; Froehling, 2001). Chitosan is deacetylated derivative of chitin obtained from crustaceans-like crab and shrimp shell wastes. It has many remarkable useful chemical and physical properties such as biodegradability, non-toxicity, antimicrobial activity, antioxidant, etc. (Enescu, 2008; Jocic *et al.*, 2005; Yang *et al.*, 2010).

Chitosan, is a naturally available biopolymer which can be used to increase the cationic property on wool fibers links to amino groups present in its chemical structure. It was reported that chitosan pretreatment successfully reduces the difference of dyeing performance between damaged and undamaged wool fibers through the increasing of dyeing rate and dyeing ability (Froehling, 2001).

Recently chitosan used as a functional finish on textile substrates to impart antimicrobial properties and increase dye uptake of fabrics on wool fabrics (Sadeghi-Kiakhani and Safapour, 2015; Dev *et al.,* 2009). The effect of chitosan application on the dyeing properties of wool fibers was studied by measuring the *K*/*S* values of the treated substrates at various concentrations of chitosan and the dye. The antimicrobial properties of chitosan and natural dyes both when applied independently and collectively on the fibers were assessed. The results proved that the chitosan treated wool fibers showed increase the dye uptake of the fibers. The treated fibers were found to be antimicrobial and the chitosan treatment enhances the antimicrobial characteristics of the dyes (Sadeghi-Kiakhani and Safapour, 2015; Dev *et al.,* 2009).

In medical field, chitosan films have been tested as curative wound dressing and as scaffolds for tissue and bone engineering (Liu *et al.,* 2001). Additionally the reactive functional groups present in chitosan (amino group at the C2 position of each deacetylated unit and hydroxyl groups at the C6 and C3 positions) can be readily subjected to chemical derivatization allowing the manipulation of mechanical and solubility properties (Britto *et al.,* 2005) enlarging its biocompatibility.

Dendrimers as biologically active macromolecules having branched structure, many reactive end groups, highly ordered, and compacted shape. This unique structure creates the best places for the host molecules between the branches (Blencowe *et al.*, 2009; Calabrett *et al.*, 2007; Sashiwa *et al.*, 2000). Recently, dendrimers have been applied for the elimination of dyes from colored effluents, extraction of dyes, increasing the dyeing ability of textiles, and development the antimicrobial finishing of textiles (Sashiwa *et al.,* 2002; Sadeghi-Kiakhani *et al.,* 2013a,b).

The pretreatment of wool fibers with chitosan eliminates the differences in dyeing behavior between damaged and undamaged wool fibers and also increase the rate of dye uptake and the exhaustion of acid and reactive dyes. The role of the chitosan coating in the dyeing process clarified. Similar color fastness properties were obtained on both untreated and chitosan-treated wool fabrics. The chitosan coating on wool fabrics has been examined by scanning electron microscopy. Evidence for the presence of chitosan was sought using a colorimetric method. It is believed that an approximately uniform and adherent chitosan sheath is formed on individual wool fibers (Stephen Davidson and Xue, 1994).

In our study the wool fibers were treated with chitosan with different molecular weights to improve the dye ability of the fibers and impart antimicrobial activity, then wool fibers were dyed with synthesized reactive dyes. The *K*/*S* was evaluated for the treated substrates at various concentrations of chitosan also, the fastness properties of dyed wool fibers untreated and treated with chitosan were then measured. The antimicrobial activity of untreated and treated wool fibers was evaluated.

Materials and Methods

Materials

Wool fibers 10/2 g/m^2, supplied by El Mahalla company-Egypt.

Chemicals

Chitosan high molecular weight (210,000), Poly (D-glucoseamine), was referred to as chitosan III.

Chitosan medium molecular weight (100,000), Poly (D-glucoseamine), was referred to as chitosan II.

Chitosan low molecular weight (1800), Poly (D-glucoseamine), was referred to as chitosan I, was purchased from ROTH, Germany. Dye 1 and dye 2 was synthesized according to the published procedure (Mohamed and Ahmed, 2012).

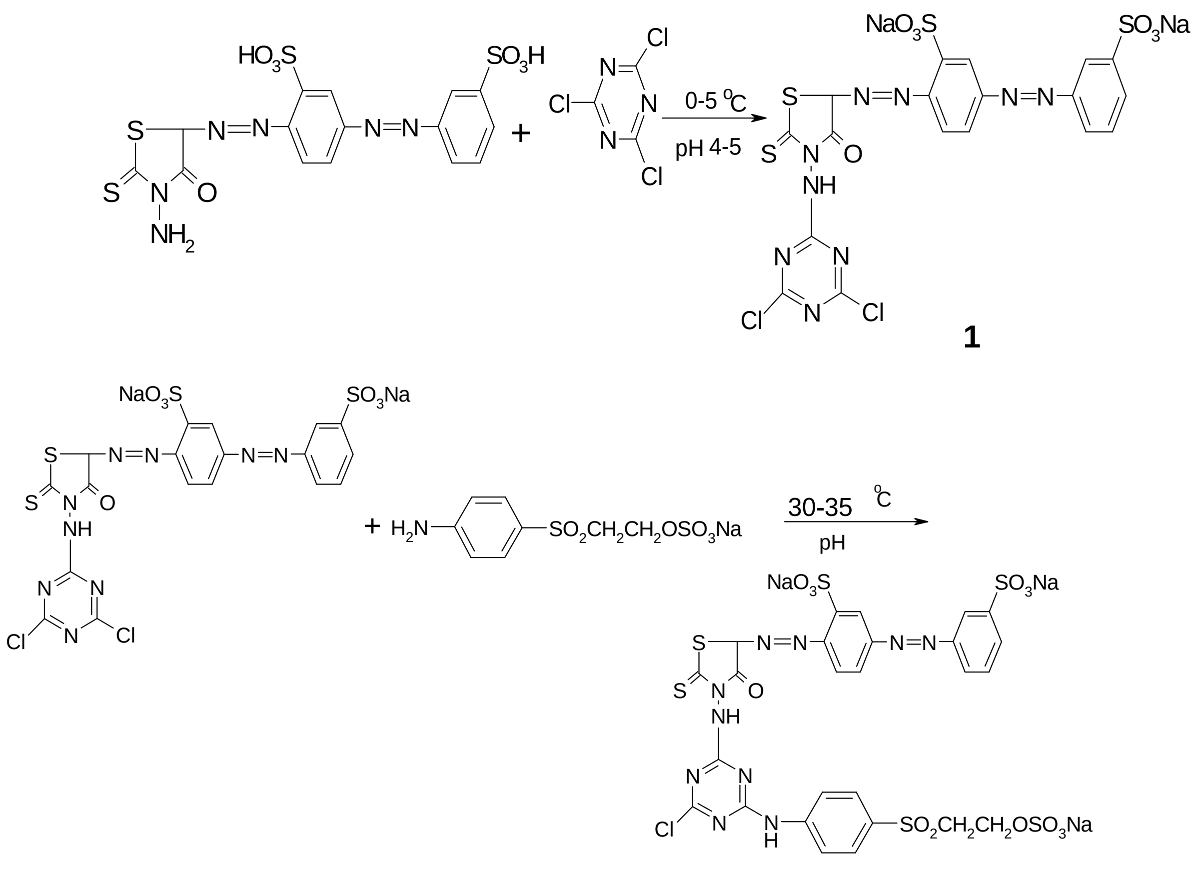
Pretreatment with chitosan

Chitosan (low, medium and high molecular weights) solutions were freshly prepared by dissolving 1.0 g/l) in distilled water containing acetic acid (4g/l). The wool fibers were immersed in these solutions at a 50:1 liquor ratio for 30 min, and then thoroughly washed, and air dried at room temperature.

Dyeing procedures

In the dyeing process, the amount of synthesized reactive dyes 1 and 2 (scheme 1) applied was with different concentration (1.0, 2.0 and 3.0 %) of owf in an Ahiba dyeing machine in the conventional dyeing, all conditions used were recommended by the dye manufacturer with the liquor ratio 50:1 at pH 4. Then the temperature was increased to the fixation temperature with the heating-rate of 2°Cmin^{-1}. The fixation temperature was that recommended for conventional dyeing 100°C. Then, the wool was dried in air.

Scheme.1



1

3

2

Antimicrobial treatment

The medium for the growth of the tested microbes (fungi and bacteria) was first prepared. 10 ml of isolate (*Staphylococcus aureus* and *Pseudomonas aeruginosa*) was grown for 48 hours on a nutrient broth medium (g/l: peptone 5.09; beef extract 1.5; yeast extract 1.5; NaCl 5.0; agar 20.0; and pH 7.5). The nutrient agar was prepared and autoclaved at 121^{o}C for 20 minutes. Sterilized Petri dishes were prepared with an equal thickness of the nutrient agar.

Test organisms: a 0.5-mm disk of the tested fungal (*Aspergillus niger* and *Penicillium* spp) was transferred individually to the center of a PDA (Potato Dextrose Agar: 200g potato, 20g Agar) plate, then incubated at 25 ± 2^{o}C for 5 days. The antimicrobial activity of chitosan-treated wool fiber with different concentrations (1.0, 2,0and 3.0 g/L) of high, medium and low molecular weights of chitosan was evaluated according to Rajni *et al.,* 2005.

Small disks chitosan-treated wool fiber was placed in the four corners of the previously prepared plates. After 72 hours of incubation at 25±2^{o}C, the zones of inhibition of each tested microbe were measured and calculated.

Measurements and analysis

Dye exhaustion

Uptake of the reactive dye by the wool fibers pretreated with chitosan and the wool fiber untreated was measured by sampling the dyebath before and after dyeing on a Shimadzu UV-2401PC UV/V is spectrophotometer at the λ_{max} value using a calibration curve previously obtained using known dye concentrations (g/l). The percentage of dyebath exhaustion (%*E*) was calculated using Eq. 1.

$$\%E = \left[1 - \left(C_2 / C_1\right)\right] \times 100 \quad 1$$

Where *C*1 and *C*2 are the dye concentrations in the dyebath before and after dyeing, respectively.

Color measurements

The color parameters of the un-treated dyed wool and pretreated wool with chitosan were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 10° standard observer (Hu *et al.,* 1987; Savarino *et al.,* 1989). The corresponding *K*/*S* values were calculated from the reflectance data at λ_{max} of the dyeing

Fastness testing

Dyed the wool pretreated with chitosan samples, after washing-off using 2 g/L nonionic detergent at 80°C for 15 min, were tested by standard ISO methods. Wash fastness (ISO 105-C02, 1989), crock fastness (ISO 105-X12, 1987), and fastness to perspiration (ISO 105-E04, 1989) were evaluated using the visual ISO Gray Scale for both color change (AATCC Evaluation Procedure (EP) 1-similar to ISO 105-A02) and color staining (AATCC EP 2—same as ISO 105-A03). Light fastness (carbon arc) was evaluated using ISO 105-B02.

Results and Discussion

Improvement of dye ability

A synthesized dyes 1,2 were applied to chitosan-treated wool fiber. The treatment of fibers was performed with different concentrations (1.0, 2.0 and 3.0 g/L) of high, medium and low molecular weights of chitosan according to the conventional dyeing method.

The data revealed that the dyeabilty increases for wool fibers treated with chitosan than untreated (Figures 1 & 2). Also, the higher exhaustion values obtained for monocloro triazine sulphato ethyl sulphone (MCT/SES) dye 2 than dye 1 means that at the fixation stage the probability of dye-fibers the covalent reaction would increase, resulting in higher fixation values of the heterobifunctional MCT/SES dyes compared to the monofunctional dye. This feature of MCT/SES dyes can also be attributed to their higher reactivity of being bifunctionally reacted with wool through their vinylsulphone precursor of sulphato ethyl sulphone (SES) group and the additional fixation of monocloro triazine (MCT) group in comparison with the monofunctional reaction of the monochlorotriazine. Also the wool fiber doesn't affect by dye concentration so, the results are nearly with other according to figures 1 & 2. Also, medium molecular weights of chitosan have higher exhaustion than low and high molecular weight (Figure 1 & 2).

Antimicrobial activity

Table 1 shows the dependence of the antimicrobial activity of wool fibers respective on the molecular weight and concentration of chitosan. Four strains of bacteria and fungi were used to assess the antimicrobial activity under the combined effect of chitosan and the reactive dyes. The antimicrobial activity is a manifestation of the concentration and molecular weight of chitosan. Antimicrobial activity, varies by varying the strains of bacteria and fungi, the bacterial reduction rate increases as the molecular weight and concentration of chitosan increases. The magnitude of such increase relies on the strain of bacteria and fungi.

Table.1 Antimicrobial activity of dyed wool fibers untreated and pretreated with different concentrations of chitosan of different molecular weight

Microbes	Growth reduction (%) of different microbes on fibers treated with chitosan at a concentration (g/l) of					
		0	1	1.5	2	2.5
Staphyloccus aureus	Chitosan I	10	20	50	55	60
	Chitosan II	12	30	50	52.0	62
	Chitosan III	20.0	55	60	70	75
Pseudomonas aeruginosa	Chitosan I	15	30	35	55	70
	Chitosan II	14	22	30	50	60
	Chitosan III	20	45	54	65	80
Asperigullas niger	Chitosan I	15	40	50	55	75
	Chitosan II	18	45	50	60	80
	Chitosan III	20	57	53	65	90
Penicillium Spp	Chitosan I	10	15	22	30	40
	Chitosan II	7	15	25	30	50
	Chitosan III	12	25	47	55	75

Chitosan I = Chitosan have low molecular weight; Chitosan II = Chitosan have medium molecular weight; Chitosan III= Chitosan have hight molecular weight.

Table.2 Colorimetric data of the dyed wool fibers was pretreated with chitosan low molecular weight using reactive dye 1 with different shade

Shade	∆ E	K/S	L*	a*	b*
1%	78.19	18.89	53.69	24.06	51.50
2%	77.72	25.09	50.71	27.67	51.99
3%	73.92	33.26	44.48	29.72	51.02

Table.3 Colorimetric data of the dyed wool fibers was pretreated with chitosan medium molecular weight using reactive dye 1 with different shade

Shade	∆ E	K/S	L*	a*	b*
1%	73.43	14.62	54.31	18.81	45.70
2%	77.47	33.07	48.86	27.83	53.29
3%	73.59	37.92	44.78	28.01	51.24

Table.4 Colorimetric data of the dyed wool fibers was pretreated with chitosan high molecular weight using reactive dye 1 with different shade

Shade	∆ E	K/S	L*	a*	b*
1%	73.88	20.68	50.00	24.14	48.88
2%	62.05	17.49	43.55	21.90	38.39
3%	71.12	33.74	43.36	27.57	49.18

Table.5 Colorimetric data of the dyed wool fibers was pretreated with chitosan low molecular weight using reactive dye 2 with different shade

Shade	∆ E	K/S	L*	a*	b*
1%	73.15	15.40	53.89	19.05	45.05
2%	73.50	25.94	47.94	26.18	49.18
3%	63.56	27.55	40.92	24.50	42.03

Table.6 Colorimetric data of the dyed wool fibers was pretreated with chitosan medium molecular weight using reactive dye 2 with different shade

Shade	∆ E	K/S	L*	a*	b*
1%	83.23	21.70	55.40	27.60	55.64
2%	67.61	21.73	45.86	22.81	44.14
3%	72.90	35.60	44.74	28.68	49.90

Table.7 Colorimetric data of the dyed wool fibers was pretreated with chitosan high molecular weight using reactive dye 2 with different shade

Shade	Δ E	K/S	L*	a*	b*
1%	81.42	16.01	58.24	21.96	52.49
2%	82.74	21.49	53.91	28.98	55.68
3%	72.81	31.51	45.59	27.52	49.66

Table.8 Fastness properties of dyed wool fiber and dyed wool was pretreated with chitosan low molecular weight which using reactive dyes 1, 2 (2% owf) at 100°C

Dye	Fastness to rubbing		Wash fastness			Fastness to Perspiration						Light
						Alkaline			Acidic			
	Dry	Wet	Alt	SC	SW	Alt	SC	SW	Alt	SC	SW	
1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6
untreated	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4

Table.9 Fastness properties of dyed wool fiber and dyed wool was pretreated with chitosan medium molecular weight which using reactive dyes **1, 2** (2% owf) at 100°C at

1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6

Table.10 Fastness properties of dyed wool fiber and dyed wool was pretreated with chitosan high molecular weight which using reactive dyes **1, 2** (2% owf) at 100°C at

1	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6

Figure.1 Exhaustion (E %) of untreated and treated wool fibers with different degree of chitosan at different concentrations of dye 1

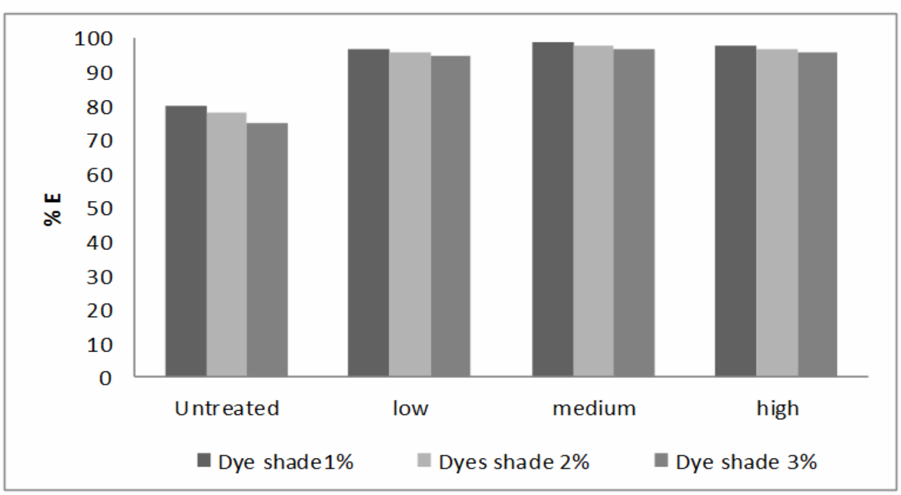
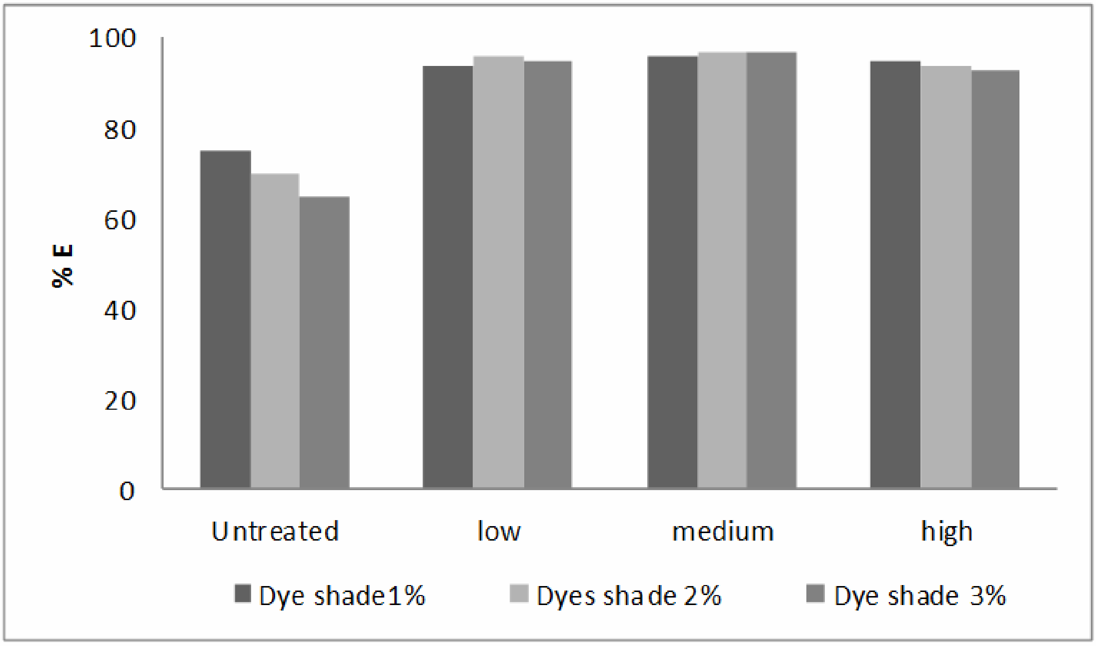


Figure.2 Exhaustion (E %) of untreated and treated wool fibers with different degree of chitosan at different concentrations of dye 2



Antimicrobial activity, expressed as growth reduction of the bacteria and fungi, could be explained as follows. The amino groups in chitosan interfere with the bacterial metabolism by stacking at the cell surface and binding with DNA to inhibit m-RNA synthesis (Julia and Pascual, 2000; Purwar and Joshi, 2004). chitosan of higher molecular weight shows more of a tendency to deposit on the surface of the fibers, resulting in amino groups more easily accessible to bacteria and fungi (Tanner, 2009; Gao, 2008). Wool fibers pretreated with chitosan display high growth reduction of microbes because the amino groups of chitosan afford dyeing sites for the dye. Dye adsorption increases also by increasing the molecular weight of chitosan which, in turn, increases the amino groups which are accessible for the dye molecules (Hebeish *et al.*, 2012; Ali *et al.*, 2011).

Colorimetric and fastness properties

Data show that wash fastness rating for staining of adjacent fibers in the case of dyed fibers is generally good and those for change in color are also acceptable. It should be mentioned that no change in color was observed; wash fastness was very good with rating of 4–5, very good fastness to rubbing in both dry and wet states was obtained with dry rubbing fastness as high as 4–5, while wet rubbing fastness was in the range of 3–4; Perspiration fastness properties (in both acidic and alkaline media) of dyed wool samples in terms of ratings for staining of adjacent fibers and change in color were very good (Table 8–10).

Also, the K/S of dyed wool of reactive dye 1 with high molecular weight chitosan at concentration 1% is higher than low and medium molecular weight also, the K/S of dyed wool of reactive dye 1 with medium molecular weight chitosan at concentration 2% and 3% is higher than others (Table 2–4). The K/S of dyed wool fibers with reactive dye 2 with medium molecular weight chitosan at concentration 1 and 3% is higher than low and medium molecular weight also, the K/S of dyed wool of reactive dye 2 with low molecular weight at concentration 2% is higher than other (Table 5–7). The color parameters were evaluated by means of the Cielab system and the modified CIE L* C * h^{o} (D65/10^{o}) system. The following colour parameters for the dyed samples were obtained by the digital Cielab system: L* – lightness, a* – redness if positive coordinate, or greenness if negative coordinate, b* – yellowness if positive coordinate, or blueness if negative coordinate, C* – chromaticity, h – hue of the colour, X – coordinate x, Y – coordinate y, Z – coordinate z (McDonald, 1997). As shown in (Table 2–7) chitosan treatment enhance the color difference data.

In conclusion, From the results of the present study, following conclusions can be shown that Chitosan-poly(propylene imine) was introduced as a potential non-toxic bio-polymer for multifunctional finishing of wool fibers; the dyeability of wool fibers was increasing and independent on the dye concentration, also the treated wool fibers with different degree of chitosan impart fiber high antimicrobial effect. Wool fibers pretreated with chitosan display high growth reduction of microbes. It was found that K/S increase with treated fibers than untreated. Overall, Chitosan-poly(propylene imine) could be considered as a novel efficient eco-friendly finishing compound for multifunctional treatment of wool fibers.

Acknowledgment

This project was supported financially by the Science and Technology Development Fund (STDF), Egypt, Grant No 10390

Reference

Ali, N.F., EL. Mohamedy, R.S.R., El-Khatib, E.M. 2011. Antimicrobial activity of wool fabric dyed with natural dyes. *Res. J. Textile Apparel,* 15(2): 71–76.

Blencowe, A., Tan, J.F., Goh, T.K., Qiao, G.G. 2009. Core crosslinked star polymers via controlled radical. polymerization. *Polymer,* 50(1): 5–32.

Britto, D., Campana Filho, S.P., Assis, O.B.G. 2005. *Polimeros Ciência Tecnologia,* 15(2): 129–132.

Calabrett, M.K., Kumar, A.M.C., Dermott, A.M., Cai, C. 2007. Antibacterial activities of poly(amidoamine) dendrimers terminated with amino and poly(ethylene glycol) groups. *Biomacromolecules,* 8(7): 1807–1811.

Dev, V.R.G., Venugopal, J., Sudha, S., Deepika, G., Ramakrishna, S. 2009. Dyeing and antimicrobial characteristics of chitosan treated wool fabrics with henna dye. *Carbohydr. Polymers.,* 75(4): 646–650.

Enescu, D. 2008. Use of chitosan in surface modification of textile materials. *Roumanian Biotechnol. Lett.,* 13(6): 4037–4048.

Froehling, P.E. 2001. Dendrimers and dyes-A review. *Dyes Pigments,* 48(3): 187–195.

Gao, Y. 2008. Recent advances in antimicrobial treatments of textiles. *Textile Res. J.,* 78(1): 60–72.

Hebeish, A., Ali, N.F., Abdel, J.I. 2012. Green strategy for development of antimicrobial printed textile fabrics. *Res. J. Textile Apparel,* 16(1): 77–85.

Hu, J., Skrabal, P., Zollinger, H.A. 1987. Comparison of the absorption spectra of a series of blue disperse dyes with the calorimetric evaluation of their dyeings. *Dyes Pigments,* 8(3): 189–209.

Jocic, D., Vılchez, S., Topalovic, T., Navarro, A., Jovancic, P., Rosa, J.M., Erra, P. 2005. Chitosan/acid dye interactions in wool dyeing system. *Carbohydr. Polymers,* 60(1): 51–59.

Julia, M.R., Pascual, E.P. 2000. Influence of the molecular mass of chitosan on shrink-resistance and dyeing properties of chitosan treated wool. *J. Soc. Dyers Colorists*, 116(2): 62–67.

Liu, X.F., Guan, Y.L., Yang, D.Z., Li, Z., Yao, K.D. 2001. *J. Appl. Polymer Sci.,* 79(7): 1324–1335.

Mohamed, F.A., Ahmed, K.A. 2012. Synthesis and application of reactive dyes with 3-Amino-2-thioxo-4-thiazolidinone nucleus. *J. Appl. Sci. Res.,* 8(10): 5009–5017.

Purwar, R., Joshi, M. 2004. Recent developments in antimicrobial finishing of textiles-A review. *AATCC Rev.*, 4(3): 22–26.

Rajni, S., Astha, J., Shikha, P., Deepti, G. 2005. Antimicrobial activity of some natural dyes. *Dyes Pigment*, 66(2): 99–102.

Sadeghi-Kiakhani, M., Arami, M., Gharanjig, K. 2013a. Dye removal from colored textile wastewater using chitosan-PPI dendrimer composite as a biopolymer: optimization, kinetic and isotherm studies. *J. Appl. Polymer Sci.,* 127(4): 2607–2619.

Sadeghi-Kiakhani, M., Arami, M., Gharanjig, K. 2013b. Application of a biopolymer chitosan-poly (propylene) imines dendrimer hybrid as an antimicrobial agent on the wool. *J. Iran. Polymer*, 22(12): 931–940.

Sadeghi-Kiakhani, M., Safapour, S. 2015. Eco-friendly dyeing of treated wool fabrics with reactive dyes using chitosanpoly (propylene imine) dendreimer hybrid. *Clean Technol. Environ. Policy*, 17(4): 1019–1027.

Sashiwa, H., Makimura, Y., Shigemasa, Y., Roy, R. 2000. Chemical modification of chitosan: preparation of chitosan-sialic acid branched polysaccharide composites. *Chem. Commun.,* 11: 909–910.

Sashiwa, H., Shigemasa, Y., Roy, R. 2002. Chemical modification of chitosan 11: chitosandendrimer composite as a tree like molecule. *Carbohydr. Polymers.,* 49(4): 195–205.

Savarino, P., Viscardi, G., Carpignano, R., Barni, E., Ferreo, G. 1989. Disperse and cationic dyes from aminophenyl-X-azolo- pyridines. *Dyes Pigments,* 11(3): 163–172.

Stephen Davidson, R., Yulin, Xue, 1994. Improving the dyeability of wool by treatment with chitosan. *J. Soc. Dyers Colourists,* 110: 24–29.

Tanner, B.D. 2009. Antimicrobial fabrics - issues and opportunities in the era of antibiotic resistance. *AATCC Rev.,* 9(11): 30–33.

Yang, H.C., Wang, W.H., Huang, K.S., Hon, M.H. 2010. Preparation and application of nanochitosan to finishing treatment with antimicrobial and anti-shrinking properties. Carbohydr. Polymers., 79(1): 176–179.

Zhang, R.P. 2008. Influence of wool anti-felting performance with chitosan/protease combination finishing. *Wool Textile J.,* 4: 1–4.