World Journal of Pharmaceutical and Life Sciences
WJPLS

MODIFICATION OF WOOL AND SILK FIBERS BY PRETREATMENT WITH QUATERNARY AMMONIUM SALT AND DYEING WITH NEW METAL COMPLEX DYE

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ABSTRACT

Our present study focuses mainly on the synthesis and dyeing of azo metal complex on silk and wool fibers. The present paper describes the synthesis of a new metal complex acid dye obtained from the reaction of acid red 151 with a metallic ion (Co^{2+}), and its structure was confirmed by ^{1}HNMR and IR spectroscopy. The pretreatment of silk and wool fibers by quaternary ammonium salt was carried out by conventional and microwave methods. The absorbance of the original and residual dye in the dye bath calculated from dye exhaustion. The color data of untreated and pretreated silk and wool fibers at different conditions was calculated. The fastness properties of washing, rubbing, perspiration and light to dyed fibers have been measured.

KEYWORDS: Synthesis dye, metal complex, wool fiber, silk fiber.

INTRODUCTION

Azo dyes and their derivatives have attracted growing interest over the years because of their versatile applications in various fields. There are different categories of azo dye such as reactive, direct, vat and metal complex dyes. Among the most famous types of these dyes are the metal complex dyes which are considered the predominant dye class for the dyeing of wool, nylon and silk due to but they have to meet very high requirements as regards their application (Bluss, 1995) and superior fastness properties to washing and light compared with that of non-metallized acid dyes (Yorkshire, 2004; Zarkogianni *et al*., 2014).

Metal complex dyes have played important role in the textile industry. Chromium Cr (III) and cobalt Co (III) complexes are used most frequently for the dyeing of wool and synthetic fabric (Hrdina, 2004). These metal complex derivatives which show considerable biological activity may represent an interesting approach for designing new antibacterial drugs.

The utility of the metal complex dyes is due to their versatile applications in the field of dyeing in the textile, printing systems, optical storage technology, cosmetics, drugs, foods coloring (Kondil, 1998; Daniel, 1962; Woisetscla¨ger, 1999) and in analytical chemistry. Metallizable azo dyes containing one heterocyclic donor atom suitably located for the formation of the annulated chelate complex have received much attention in research (Gaber et al., 2007; Patel et al., 2010; Kaim, 2002), the most common being those containing a hetero nitrogen atom in a position adjacent to the azo group (Patel et al.,2011; Karcı, 2013). Utilization and synthesis of azo dyes is availability of raw materials and simple synthetic procedures (Otutu, 2011; Kirkan et al., 2008). Metal complex dyes has high molar extinction coefficient, medium to high fastness, high solubility, high substantively and diversity in structures (Abdallah, 2012; Chhowala et al., 2015).

In the present work, a new azo-dye with metallic ion (Co^{2+}) complex using the Acid red 151 as ligand was synthesized and characterized. At the same time, spectrophotometric analysis was performed for the qualitative investigation of the aggregation behavior of the metal complex dye, at different concentrations in aqueous solutions.

2. EXPERIMENTAL

2.1 Materials
- Mill-scoured and bleached wool and silk fibers.
- Ethanol was obtained from Fluka Chemite AG. All other chemicals used in study were of laboratory reagent grade and applied without further purification.
- Quaternary ammonium salt supplied from Fluka Chemite AG.

2.2. Equipments

- FT/IR spectra were recorded using JASCO FT/IR-4700 spectrometers with high resolution 0.4 cm^{-1} using ATR accessory.
- The ^{1}HNMR spectra were recorded at room temperature on a Bruker Advance II 400 spectrometer at 400.13 MHz, the samples were dissolved in hexadeuterio dimethyl sulfoxide. The 1H chemical shifts was referenced to the central signal of the solvent (δ= 2.55).
- UV/Visible spectra were measured on a Shimadzu UV-2401 PC UV/Vis spectrophotometer using distilled water.
- The visual color strength (K/S) of dyed fibers was measured on Data color International SF 600 plus.

2.3. Synthesis of dye

The cobalt complex was prepared by mixing dye 151 and $Co(Cl)_2$ 6. H_2O in ethanol solution by molar ratio 2:1 was refluxed for 4h and kept overnight at room temperature and after cooling, the precipitate was separated by filtration, washed with distilled water and dried in an oven at 50ºC, dried under vacuum. Yield: 89.5 mg (88.8%).

The wool and silk fibers treated with the quaternary ammonium salt by the following methods:

- The conventional method was carried out for wool and silk fibers at (30, 45, 60 and 75 min).
- Microwave method was carried out at (2-7 minutes) for wool fibers and at (2-5 minutes) for silk fibers.

2.4. Dyeing procedure

Dyeing of untreated and pretreated wool and silk fibers was carried out by exhaustion method. The factors affecting the dyeing process such as pH, dye concentration and time of dyeing were studied.

2.4.1. Effect of pH

The dyeing was applied at pH(3-7) for wool and silk fibers using 2% o.w.f. dye concentration, using 1g/l ammonium sulphate and L:R 1:50. Dyeing was performed at 40°C, allowing the temperature of the dye bath to raise to the boil over 30 min. The dyeing was continued at the boil for a further 60 min. At the end of the dyeing process, the samples were thoroughly rinsed and air-dried.

2.4.2. Effect of dye concentration

The dyeing was applied at various conc. of dye (1-5), at pH 5 for wool and silk fibers using 1g/l ammonium sulphate and L: R 1:50. Dyeing was performed as the previous conditions.

2.4.3. Effect of time

The dyeing was carried out at different time interval (20,40 and 60 min.) at pH 5 for wool and silk fibers using 2% o.w.f. dye concentration ,1g/L ammonium sulphate and L:R 1:50. Each dyeing was performed at 40°C, allowing the temperature of the dye bath to rise to the boil at (20, 40 and 60 min.). At the end of dyeing process, the samples were thoroughly rinsed and air dried.

2.4.4. Dyeing at the optimum condition

The treated fibers by the conventional method and microwave method were dyed at the optimum condition; pH 5 for wool and silk using 2% o.w.f. 1g/l ammonium sulphate and L: R 1:50. Each dyeing was performed at 40°C, allowing the temperature of the dye bath to raise to the boil over 30 min. Dyeing was then continued at the desired temperature 100˚C further 60 min.

2.5 Dyeing measurements

Measurements and testing dye exhaustion uptake of dye by the wool and silk fibers was measured by sampling the dye bath before and after dyeing. The dye concentration (g/l) of the dye bath was measured on a Shimadzu UV-2401PC UV-visible spectrophotometer at the λ_{max} value using a calibration curve previously obtained using known dye concentrations (g/l).The percentage of dye bath exhaustion (%E) was calculated using Eqn 1:

$$\% E= [1-C_2/C_1] \times 100$$

Where C_1 and C_2 are the dye concentrations in the dye bath before and after dyeing, respectively.

The relative color strength (K/S) and CIELAB coordinates (L*a*b*c* h and ΔE^*) of the dyed fibers were also measured using a Hunter lab's Ultra Scan PRO Spectrophotometer (USA) under illuminant D65, 10°standard observer(Judd et al., 1975).

2.5.1. Fastness testing

Dyed silk and wool samples with 2% shade (o.w.f) after washing-off using 2 g/l nonionic detergent at 80ºC for 15 min were tested by standard ISO methods (Methods of Tests for Color Fastness of Textiles and Leather, 1990). Wash fastness [ISO 105-C02 (1989)], and fastness to perspiration [ISO 105-E04 (1989)] were evaluated using the visual ISO grey scale for both color change. Light fastness (Xenon arc) was evaluated using ISO 105-B02.

3. RESULT AND DISCUSSION

Acid red 151 dye with the structure I shown in Figure 1 under went complexation reaction with Co^{2+} ion ,using metal- ligand (1:2 molar ratio), in which only the atoms of the – OH functional group are involved in the coordination reaction.
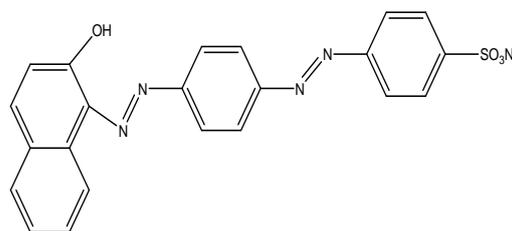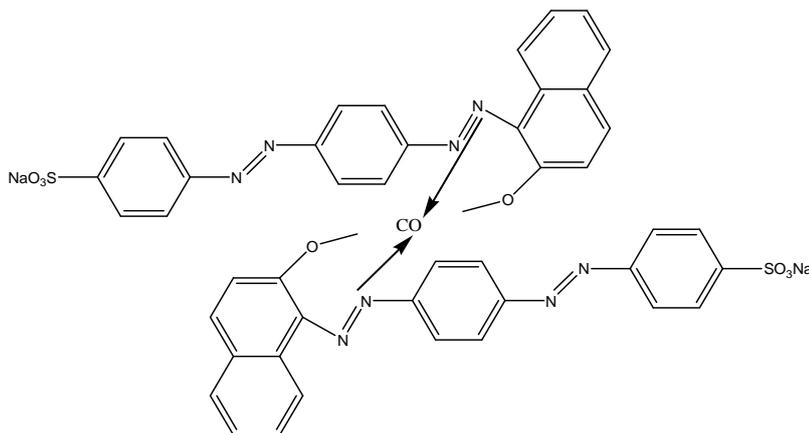

Figure 1: Acid red 151.

Figure 2: The proposed formula of the new Metal-complex dye.

The above structure was confirmed by structural data acquired using FT-IR, and ^{1}HNMR analyses. The FT-IR has proven to be, in this particular case, a suitable technique to give relevant information to elucidate the way of bonding of the ligand. The study of the infrared spectra reveals the migration of vibration frequencies for the functional groups which were directly involved in the metal ligand.

Dye structure was confirmed by IR (m/cm[-1]):1918.82 (aromatic C=C), 1594.84 (C=N),1307.5 (–SO$_3$H str) 829.241 (CN=NC, str) and 646.036 (Metal-O, str) cm^{-1}.

^{1}HNMR: d H(ppm) in [2H$_6$]DMSO: 11.142 (s ,1H , SO$_3$H), 7.621–7.888 (m,28H,Ar-H).

3.1. Effect of pH

The wool and silk fibers dyed at different pH (3- 7). Dye concentration was constant at (2 % owf). The pretreated wool fiber dyed at optimum pH 4 and gave high exhaustion at (95.42%) but the pretreated silk fiber dyed at optimum pH 5, gave high exhaustion (96.11%E) and the exhaustion decrease with increasing pH as shown in the figures(3,4) respectively.
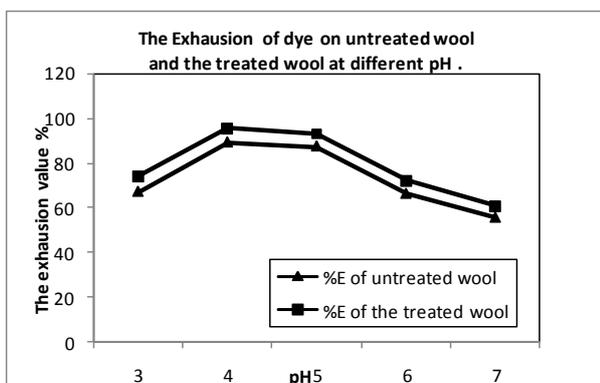

Fig. 3: The Exhaustion yield of dye on untreated and the pretreated wool fiber at different pH.
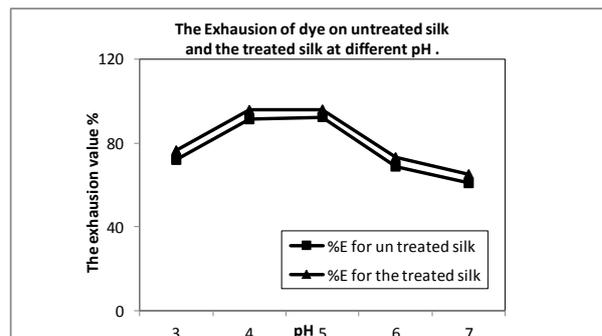

Fig. 4: The Exhausion yeild of dye on untreated and the pretreated silk fiber at different pH.

3.2. Effect of dye concentration

The exhaustion yield of the dye on wool and silk fibers were examined using different depth of shade (1-5 % owf) at 100 ˚C. Figures (5, 6) showed that lower dye concentration exhibited a higher extent of exhaustion than the higher concentration. This finding is attributed to the increase in dye aggregation and thus, resulting in the reduction of the penetration of the dye through the fiber.
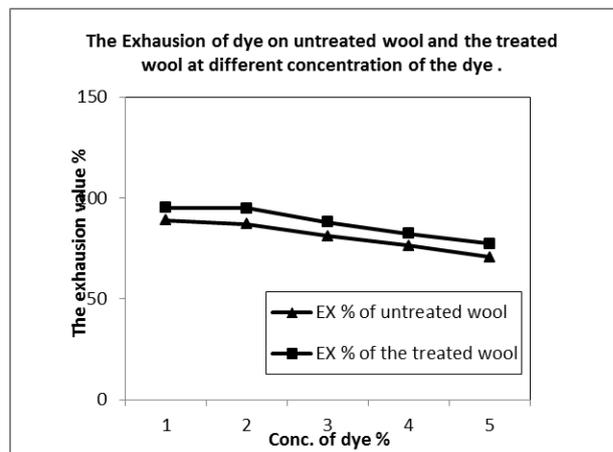

Fig. 5: The Exhaustion yield of dye on untreated and the pretreated wool fiber at different conc. of dye.
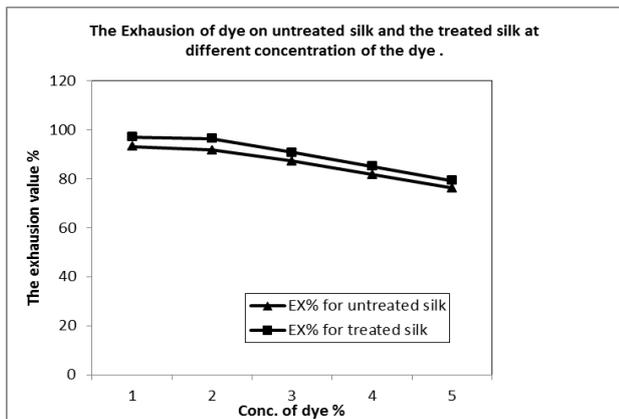
Fig. 6: The Exhaustion yield of dye on untreated and the pretreated silk fiber at different conc. of dye.

3.3. Effect of time

The exhaustion yield of the dye on wool and silk fibers were examined using different time (20-40-60 min.) at 100˚C. Figures(7,8) showing that the dyeing conducted at 60 min. as the optimum time, give very high exhaustion (94.11%E) for wool and very high exhaustion (96.85%E) for silk respectively.
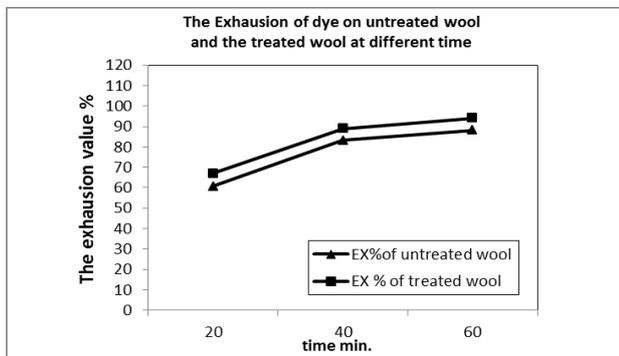

Fig. 7: The Exhaustion yield of dye on untreated and the pretreated wool fiber at different time.

Fig. 8: The Exhaustion yield of dye on untreated and the pretreated silk fiber at different time.

3.4. Dyeing of the treated fibers

As shown in figures (9-12) it is clear that the exhaustion yield for the pretreated wool and silk fibers by the conventional method (30-45-60-75 min) increases as the dyeing time increases up to 60 min for wool and silk, and then begins to decrease, because parts of the dye are desorbed again during the dyeing process. On the other

hand the exhaustion yield for the pretreated wool and silk fibers by the microwave method (2-4-6-7 min) for wool and (2-3-4-5 min) for silk give a higher value at 6 min for wool and 4 min for silk and then begins to stable.

Fig. 9: The Exhaustion yield of dye on wool at different time of conventional dyeing method.

Fig. 10: The Exhaustion yield of dye on silk at different time of conventional dyeing method.

Fig. 11: The Exhaustion yield of dye on wool at different time of microwave dyeing method.

Fig. 12: The Exhaustion yield of dye on silk at different time of microwave dyeing method.

3.5. Colorimetric and fastness properties

The colour data of untreated wool and silk at different condition showing in the tables (1-6) and colour data of pretreated wool and silk fiber by the two method set out in the tables (7-10).
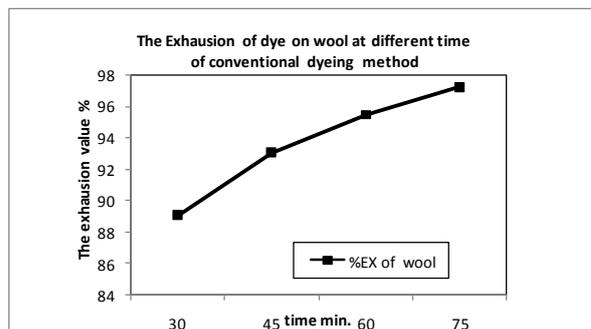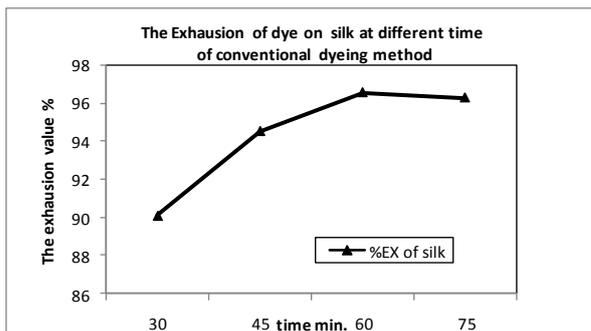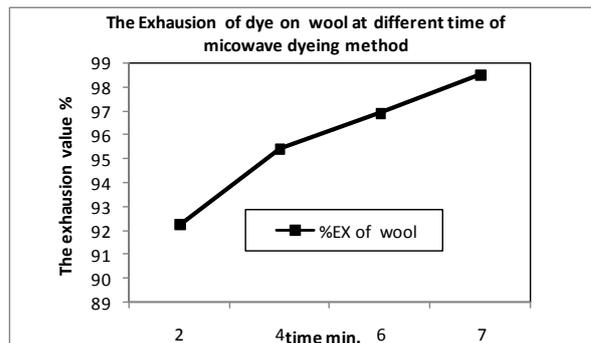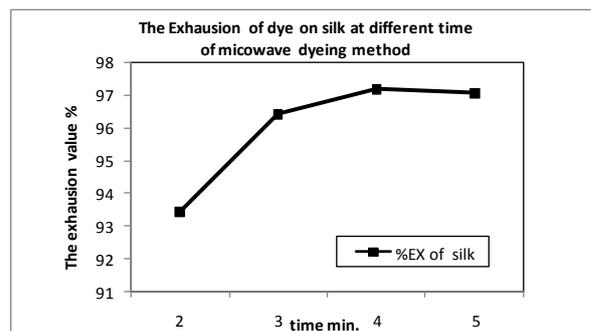
The fastness properties of the dye on wool and silk were evaluated. The results are set out in Tables (11,12) showed that the colour fastness to rubbing, washing and perspiration of the aforementioned dye is from excellent to good and approximately the same, depending on the proportion of the dye fixed.

Table 1: The colour data of untreated and pretreated wool at different conc. of dye.

Conc. of dye	Fibers	L*	a*	b*	c*	h	ΔE*	K/S
1	untreated	28.00	50.25	29.52	58.26	30.43	81.33	36.07
2	untreated	27.54	49.88	29.52	58.02	30.70	81.47	43.45
3	untreated	25.65	46.12	26.20	53.04	29.60	80.02	44.16
4	untreated	25.18	44.48	23.70	50.40	28.05	79.02	46.35
5	untreated	22.34	41.66	21.30	46.79	27.08	79.56	51.22
1	treated	30.01	52.05	30.82	59.66	32.53	83.64	38.23
2	treated	28.84	51.18	30.11	59.92	32.32	83.54	45.87
3	treated	26.75	48.52	28.50	55.14	30.40	82.11	47.23
4	treated	27.11	46.44	24.90	52.70	30.52	80.22	48.41
5	treated	24.44	43.06	23.39	48.99	29.58	80.66	53.12

Table 2: The colour data of untreated and pretreated wool at different pH of dye.

pH	Fibers	L*	a*	b*	c*	h	ΔE*	k/s
3	untreated	28.03	51.88	30.21	60.04	30.21	82.49	43.32
4	untreated	26.60	49.21	27.13	56.19	28.87	81.24	48.17
5	untreated	27.24	48.51	26.61	55.33	28.75	80.29	45.92
6	untreated	28.43	47.90	25.98	54.49	26.47	78.90	35.43
7	untreated	26.87	46.37	25.27	52.81	28.59	79.06	38.09
3	treated	30.23	53.18	31.41	62.24	32.52	84.39	45.22
4	treated	29.69	50.22	28.25	58.33	30.07	83.24	50.11
5	treated	28.84	49.54	28.46	57.33	30.77	82.44	47.52
6	treated	29.51	47.90	27.18	56.09	28.17	80.94	37.03
7	treated	28.91	46.37	27.97	53.88	29.89	80.46	39.11

Table 3: The colour data of untreated and pretreated wool at different time of dye.

Time	Fibers	L*	a*	b*	c*	h	ΔE*	k/s
20	untreated	26.86	48.93	27.76	56.26	29.57	81.04	38.44
40	untreated	26.64	46.82	25.48	53.30	28.56	79.54	47.57
60	untreated	25.15	46.35	25.28	52.79	28.61	80.41	49.50
20	treated	28.47	50.13	28.06	58.25	31.88	84.44	41.12
40	treated	28.52	48.52	27.41	55.40	30.86	81.14	50.17
60	treated	27.44	48.32	27.22	54.12	29.69	83.31	54.10

Table 4: The colour data of untreated and pretreated silk at different conc. of dye.

Conc. of dye	Fibers	L*	a*	b*	c*	h	ΔE*	k/s
1	untreated	28.20	50.27	29.57	58.66	30.47	81.53	36.87
2	untreated	27.55	49.98	29.82	58.52	30.74	81.57	43.55
3	untreated	25.95	46.18	26.70	53.74	29.65	80.42	44.56
4	untreated	25.28	44.98	23.78	50.80	28.45	79.72	46.37
5	untreated	22.74	41.86	21.37	46.99	27.18	79.66	51.62
1	treated	30.50	53.25	31.45	60.16	32.46	83.53	38.17
2	treated	29.85	51.58	32.98	61.12	33.14	84.75	45.88
3	treated	28.45	48.55	29.88	55.04	30.22	82.96	46.06
4	treated	27.08	47.58	25.55	53.85	30.66	81.58	50.00
5	treated	25.24	44.06	23.07	48.19	29.38	80.46	53.88

Table 5: The colour data of untreated and pretreated silk at different pH of dye.

pH	fibers	L*	a*	b*	c*	h	ΔE*	k/s
3	untreated	37.40	57.99	27.29	64.09	25.20	77.25	26.97
4	untreated	34.83	58.03	25.28	63.30	23.54	78.65	43.35
5	untreated	28.74	52.94	31.39	61.54	30.67	80.56	79.79
6	untreated	37.11	56.52	24.05	61.42	23.05	75.85	57.89
3	treated	39.80	60.11	30.87	67.49	28.70	80.85	29.91
4	treated	36.13	60.96	28.36	66.36	26.84	82.15	46.44
5	treated	31.54	54.15	34.44	65.96	34.47	85.46	92.12
6	treated	40.47	59.02	27.65	65.02	27.45	79.35	50.09

Table 6: The colour data of untreated and pretreated silk at different time of dye.

Time	Fibers	L*	a*	b*	c*	h	ΔE*	k/s
20	untreated	36.19	59.84	30.61	67.21	27.09	80.04	39.49
40	untreated	30.48	55.83	28.69	62.77	27.19	80.68	86.54
60	untreated	31.43	57.79	31.33	65.73	28.46	81.89	91.32
20	treated	40.23	61.14	32.46	69.81	30.49	83.44	41.02
40	treated	35.56	58.23	30.49	65.41	31.19	82.18	88.44
60	treated	34.13	60.79	35.03	68.33	28.46	83.09	98.22

Table 7: The colour data of the pretreated wool by microwave method at different time of dye.

Time	L*	a*	b*	c*	h	ΔE*	k/s
2	28.23	49.91	27.30	56.89	28.68	80.53	37.93
4	30.58	51.92	29.22	59.57	29.37	80.44	42.98
6	25.80	46.83	25.45	53.30	28.53	80.21	46.53
7	27.71	49.90	27.87	57.16	29.19	81.02	65.59

Table 8: The colour data of the pretreated wool by the conventional method at different time of dye.

Time	L*	a*	b*	c*	h*	ΔE*	k/s
30	29.22	50.91	27.30	56.99	28.88	81.53	35.33
45	31.08	52.94	29.60	59.87	29.57	82.44	41.08
60	25.90	46.89	26.45	54.30	29.53	82.91	46.03
75	27.89	50.90	28.87	57.86	29.59	83.02	59.59

Table 9: The colour data of the pretreated silk by microwave method at different time of dye.

Time (min.)	L*	a*	b*	c*	h	ΔE*	k/s
2	30.80	52.22	26.70	58.65	27.08	77.68	43.27
3	26.56	57.89	39.33	69.99	34.19	87.38	98.00
4	31.23	57.56	29.59	64.72	27.21	81.51	96.30
5	30.42	57.17	34.17	66.60	30.86	82.81	98.96

Table 10: The colour data of the pretreated silk by the conventional method at different time of dye.

Time	L*	a*	b*	c*	h*	ΔE*	k/s
30	29.22	50.91	27.30	56.99	28.88	81.53	35.33
45	31.08	52.94	29.60	59.87	29.57	82.44	41.08
60	25.90	46.89	26.45	54.30	29.53	82.91	46.03
75	27.89	50.90	28.87	57.86	29.59	83.02	94.59

Table 11: The fastness properties of the investigated dye on the untreated fibers are given.

Fiber	K/S	Fastness to rubbing		Wash fastness			Fastness to perspiration						Light
		Wet	Dry	Alt.	Sc	Sw	Alkaline			Acidic			
							Alt	Sc	Sw	Alt	Sc	Sw	
W	49.59	3-4	3	4	3-4	3	3-4	3	4	3-4	4	4	4-5
S	91.32	4	3-4	4	4	3-4	3-4	3	4	3-4	4	4	5

C, Cotton; W, Wool; S, Silk

Alt= alteration; Sc= Staining on cotton; Sw =Staining on wool.

Table 12: The fastness properties of the investigated dye on the pretreated fibers are given.

Method of the treatment	fiber	K/S	Fastness to rubbing		Wash fastness			Fastness to perspiration						Light
			Wet	Dry	Alt.	Sc	Sw	Alkaline			Acidic			
								Alt	Sc	Sw	Alt	Sc	Sw	
Conventional Method	W	59.59	4	4-5	4	4-5	4	4	4	5	4	5	4-5	5
	S	94.59	4-5	4-5	4-5	4	4-5	4	4	4-5	4	4-5	5	5-6
Microwave Method	W	65.99	4-5	4-5	4-5	4-5	4-5	5	4	5	4	5	4-5	5-6
	s	98.00	5	5	4-5	5	4-5	5	4-5	5	4	5	4-5	6

C, Cotton; W, Wool; S, Silk

Alt= alteration; Sc= Staining on cotton; Sw =Staining on wool.

4. CONCLUSION

A metal complex dye based on acid dye was prepared; this dye proven by NMR study and IR spectroscopy. The dyeing application of the prepared dye on wool and silk fibers showed excellent dyeing properties. Wool and silk pretreated with quaternary ammonium salt compared with untreated fibers produces even dyeing and higher color strength. This resulted in higher exhaustion with full penetration in wool and silk fibers. The pretreatments effectively enhanced the dyeing properties of wool and silk fibers. The results obtained indicated that the treated samples exhibit high quality of exhaustion and fixation with respect to the untreated.

5. ACKNOWLEDGMENTS

6. REFERENCES

1. Bluss K., Dyes and Pigments, 1995; 41; 149-157.
2. Yorkshire Chemicals. Bulletin, Yorkshire Chemicals, 2004.
3. Zarkogianni Maria, Eleftheriadis Ioannis, Nikolaidis Nikolaos and Tsasaroni Eforia "Synthesis, characterization and application of anionic metal complex azo dyes as potential substitutes for Cr-complex dyes" Textile Research Journal, 2014; 84(19): 2036–2044.
4. Hrdina R., LuStinec D., Stolin P., Burgert L., Lun6k Jr. S.and Holdapek M." Iron complexes of reactive azo dyes" Advances in Colour Science and Technology, 2004; 7(1).
5. Kondil SS. Transition Met Chem, 1998; 23: 461.
6. Daniel JW. Toxicol Appl Pharmacol, 1962; 4: 572.
7. Woisetscla¨ger OE, Su¨nkel K, Weigand W, Beck W. J Organomet Chem, 1999; 584: 122.
8. Gaber M, Mansour IA, El-Sayed YSY. "Spectrophotometric, conductometric and thermal studies of Ni(II), Co(II) and Cu(II) complexes with 2-(2-hydroxynaphthylazo)-4-hydroxy-6-methyl-1,3-pyrimidine". Spectrochem Acta Part A., 2007; 68: 305-11.
9. Patel DR, Patel AL, Patel BM, Patel KC. "Synthesis of some new bromine containing reactive dyes: their application and microbial studies". Int J Chem Sci, 2010; 8: 235-48.
10. Kaim W. "The co-ordination chemistry of 1, 2, 4, 5-tetrazines". Coord Chem Rev, 2002; 230: 127-39.
11. Patel DR, Patel KC. "Synthesis and characterization of reactive dyes based on 2-phenyl-3-[4'-(4''-aminophenyl sulphonamido)] phenyl-4(3H)-quinazolinone-6-sulphonic acid". Arab J Chem, 2011; 4: 279-85.
12. Karcı F. "Synthesis and absorption abilities of pyrazolo [5, 1-c] [1, 2, 4] triazine based disperse dyes". Chem Hetero Compd, 2013; 3: 492-500.
13. Otutu JO. "Synthesis of some new dispers dyes derived from N-phenyl naphthylamine". Orient J Chem, 2011; 27: 10-11-6.
14. Kirkan B, Gup R. "Synthesis of new azo dyes and Copper (II) complexes derived from barbituric acid and 4-aminobenzoyl hydrazone". Turk J Chem, 2008; 32: 9-17.
15. Abdallah SM. "Metal complexes of azo compounds derived from 4-acetamidophenol and substituted aniline". Arab J Chem, 2012; 5: 251-6.
16. Chhowala TN, Desai KR. "Synthesis and studies of eco-friendly acid dye metal complexes and its application on woolen fabrics". J Appl. Chem, 2015; 8: 5-10.
17. Judd, D. B., Wysezcki, G., Colour in Business, Science and Industry, 1975. 3rd Ed; New York: John Wiley & Sons.