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Synthesis of new metal complex dye and its application on nylon fibers pretreated with chitosan

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Abstract The concept of preparing new metal complex dyes is vital and indispensable for improving the dyeing properties of the fiber, especially it has been previously treated with a natural product as chitosan. Our present investigation found to synthesize and application of new metal complex dye based on acid dye and the structures of the investigated compound which was confirmed by spectroscopic techniques. The dye is applied to nylon fibers pretreated with chitosan by the conventional method. The absorbance of the original and residual dye in the dye bath was calculated from dye exhaustion. Color measurements and fastness properties of washing, rubbing, perspiration, and the light were performed on the dyeing produced on nylon fibers.

Keywords: Metal complex, Cobalt, Nylon fibers, Chitosan

Introduction

Metal complexes especially chromium and cobalt complexes have known to be a special importance and widely used in dye groups for the textile dyeing industries (Adachi*et al.,* 2004). Azo-dyes are found to be a great success due to their enormous variety of applications (Hameed, 2007). These dyes are characterized by obtained easily and inexpensively using a wide variety of diazo and coupling components. They have high dyeing and wide applications in the dyeing of textile fibers, plastics, leather, paper printing, cosmetics, drugs, foods coloring as well as in many biological reactions (Özacar and Şengil, 2005; Dharmalingam *et al*., 2011 and Woisetschläger *et al*., 1999) for bio-medical studies and analytical chemistry(Amin and Mohammed, 2001). Innovations in azo dyes, especially acid dyes are obtained by adopting a slight change in dye intermediate structure which have been made as a result of intensive studies stimulated by the mounting need for a variety of derivatives of dyes (Otutu, 2011; Kirkanand Gup, 2008 and Shawaliand Mosselhi, 2003). On the other hand, the light stability in the acid dyes is enhanced by introducing the metal into the dye molecule by offering protection of the azochromophore against ultraviolet (UV) degradation (Maria *et al*., 2014). Nylon fibers can

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be dyed using many classes of dyes such as acid, disperse reactive, disperse dyes, and the most important of these types of metal complex dyes due to very good light fastness in pale shades, and good washing fastness, even in deep shades (Yildizand Boztepe, 2002 and Broadbent, 2001).

Chitosan is a natural product, it can be utilized for textile industry development. It is biocompatible and environment friendly. Chitosan can be reacted other functional properties for textiles such as antimicrobial and UV protection (Otutu, 2011). Chitosan is a natural polysaccharide-based cationic biopolymer which is derived from the chitin component of the shells of crustaceans. The advantageous properties of chitosan are nontoxicity, biocompatibility, biodegradability, antimicrobial activity and chemical reactivity. It can be used mainly for shrink resistance, and dyeability treatments (Zhang and Wang, 2010).

In the present work, a new metal ion (Co^{2+}) complex using the Acid red 151 as a ligand was synthesized and characterized. The spectrophotometric analysis was carried out for the qualitative investigation of the aggregation behavior in the metal complex dye at different concentrations in aqueous solutions. This dye is applied to nylon fiber pretreated with chitosan by the conventional method.

Materials and methods

Materials

Mill-scoured and bleached nylon fiber, 130 g/m^2 were obtained from El-Mahala Co., Egypt. Before dyeing, the fiber was treated with a solution containing 3 g/l non-ionic detergent (Hostapal CV, Hoechst) and 5g/l sodium carbonate at the boil for one hour and liquor ratio of 50:1(LR) thoroughly, then washed thoroughly in water and dried at room temperature. Ethanol was obtained from Fluka Chemite AG. All other chemicals used in the study were of laboratory reagent grade and applied without further purification.

FT/IR spectra were recorded using JASCO FT/IR- 4700 spectrometers with high resolution 0.4 cm-1 using the 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 hexadeuteriodimethylsulfoxide. The 1H chemical shifts were 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 colour strength (K/S) of dyed fibers was measured on Data color International SF 600 plus.

Synthesis of dye

The cobalt complex as in Figure 1 was prepared by mixing dye 151 and $\mathbf{CoCl_2 \cdot 6H_2O}$ in ethanol solution by molar ratio of 2:1 which was refluxed for 4h and kept overnight at room temperature (Ali*et al*., 2019). The formed solid complex was filtered, washed with ethanol (10 ml, 3 times) and finally dried under vacuum and the yield was 89.5 mg (88.8%).

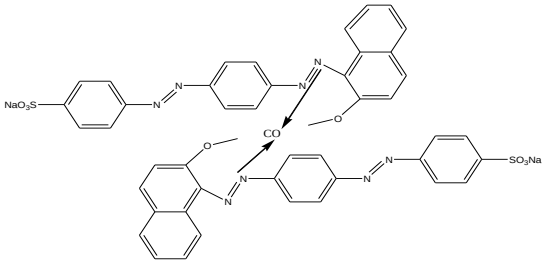

Figure 1. The proposed formula of the new Metal-complex dye

Treatment of nylon fibers with chitosan by the conventional method

Chitosan was freshly prepared by dissolving in 1.0 g/l in distilled water containing acetic acid (4g/l). The nylon 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 procedure

Effect of pH

The dye was applied at various pH (3-4-5-6-7) using 2% of weight of fiber (dye concentration), and 1g/l ammonium sulphate and liquor ratio at 1:50. Each dyeing was performed at 40 ℃, allowing the temperature of the dye bath to raise the boiling over 30 min. The dyeing was continued for boiling for further 60 min. At the end of the dyeing process, the samples were thoroughly rinsed and air-dried.

Effect of different concentrations of dye

The dye was applied at various concentration of dye (1, 2, 3, 4 and 5%) at pH 5 using 1g/l ammonium sulphate, and L: R at the ration of 1:50. Each dyeing was performed at 40 ℃, allowing the temperature of the dye bath to raise the boiling over 30 min. Dyeing was then continued at the desired temperature at 100˚C for 60 min, and all the dyed samples were rinsed with water and air dried at the end of the dyeing process.

Effect of different time

The dye was applied at a different time (20,40,60 min.) at pH 5 using 2%of weight of fiber (dye concentration), 1g/l ammonium sulphate, and L: R at the ration of 1:50. Each dyeing was performed at 40 ℃, allowing the temperature of the dye bath to raise the boiling over 30 min. At the end of the dyeing process, the samples were thoroughly rinsed and air-dried.

Dyeing measurements

Measurements and testing dye exhaustion uptake of dye by the nylon fiber were 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 λmax value using a calibration curve which previously was obtained using known dye concentrations (g/l). The percentage of dye bath exhaustion (%E) was calculated using the following Eqn :

$$\%E = [1-C2/C1] \times 100$$

Where C1 and C2 are the dye concentrations in the dye bath before and after dyeing, respectively.

The relative color strength (K/S) and CIELAB coordinates a* and b* are the chromaticity ,L* indicates lightness, C* represents chroma, h is the hue angle, and ΔE color difference of the dyed fibers which were measured using a Hunter lab's Ultra Scan PRO spectrophotometer (USA) under illuminant D65, 10 ºstandard observer (Juddand Wysezcki,1975).

Fastness testing

Dyed nylon samples with 2% shade of fiber weight after washing-off using 2 g/l nonionic detergents at 80 ^{o}C for 15 min, were tested by standard ISO methods (Methods of Tests for colour 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 greyscale for both color change. Lightfastness (Xenon arc) was evaluated using ISO 105-B02.

Results

Complexation reaction with CO^{2+} ion was carried out by reaction of metal-ligand and acid red 151 (1:2 molar ratio), in which the coordination reaction involved the – OH functional group only. Synthesized dye had been characterized by IR spectroscopy and ^{1}HNMR.Dye structure was confirmed by IR (m/cm^{-1}):1307.5 (–2SO_3H str) 829.241 (4N=N, str) and 646.36 (Metal-O, str) cm^{-1}.^{1}HNMR: d H (ppm) in [2H_6] DMSO: 11.142 (s, 2H, 2SO_3H), 7.60-7.82(m, 8H, 2naphthyl), 7.45(m, 16H, 4C_6H_4).

Effect of pH

The results showed that the exhausion of the treated and untreated fibers gave the highest value at pH 5. The exhaustion of the treated fibers was higher than the untreated at the same pH (Figure 2).

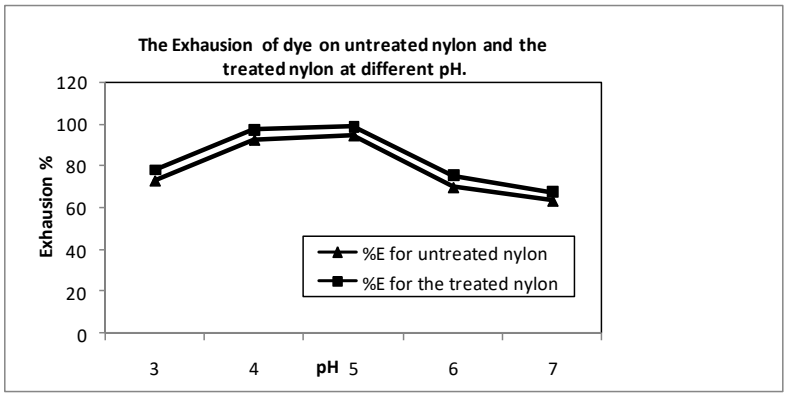

Figure 2. The Exhaustion yield of dye on untreated and the treatednylon fiber at different pH

Effect of dye concentration

Result showed dyeing at different depth of shade (1-5% owf) at 100 ˚C and pH 5 with the optimum pH (Figure 3). The exhaustion of dye in untreated nylon showed lower percentage of exhaustion than the treated nylon at all tested concentrations. It was due to the exhaustion increase aftertreatment. Chitosan added on the nylon surface which generated additive functional groups increased in hydrophilicity.

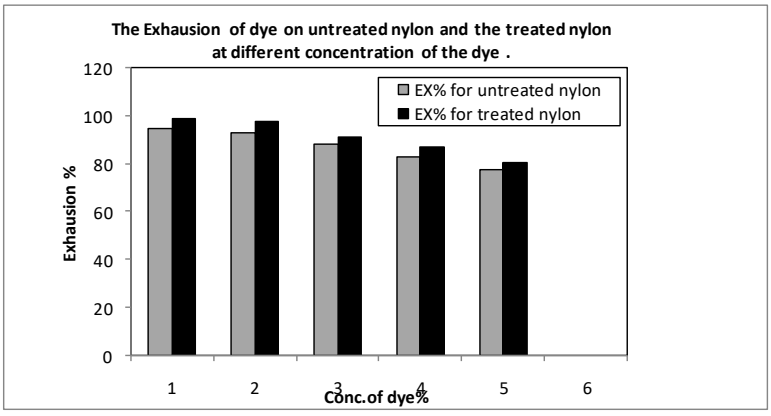

Figure 3. The Exhaustion yield of dye on untreated and the treated nylon fiber at different concentration of dye

Effect of different time

The exhaustion yield of dye in treated nylon was higher than the untreated nylon in all tested time.The dyeing was conducted at a different time of 20,40 and 60 min. at 100˚C as seen in Figure 4. Chitosan leaded to increase in the proportion of available dye sites, thus the exhausion of dye on treated fibers gave higher results with time than the untreated one.

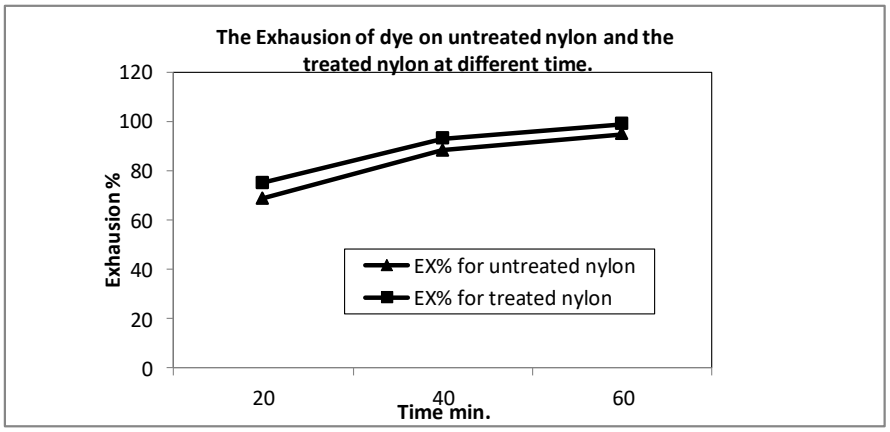

Figure 4. The Exhaustion yield of dye on untreated and the treated nylon fiber at different time

Colorimetric and fastness properties

The colour data of untreated and treated fibers and the colour yield were recorded as seen in Table1. It found that the treated fibers gave higher results than the untreated fibers and the colourimetric CIE L*a*b*C*h and ΔE data of the dyed fibers and K/S values in comparison to untreated ones. It was due to chitosan added on the nylon surface generated additive functional groups which caused an increase in hydrophilicity.

Table 1. The colour data of untreated and treated nylon at different concentration of dye

Conc. Of dye(%)	fibers	L*	a*	b*	c*	h	ΔE	K/S
1	untreated	39.44	53.24	32.67	62.46	31.54	89.17	50.84
2	untreated	38.46	54.11	33.37	62.96	32.94	89.57	54.25
3	untreated	37.38	58.17	33.77	63.06	32.24	91.24	55.22
4	untreated	36.12	58.45	34.78	63.16	33.14	92.02	56.41
5	untreated	35.01	59.95	35.97	64.06	33.54	92.17	57.87
1	treated	31.28	51.66	25.49	57.60	26.26	89.29	59.24
2	treated	31.11	52.01	26.45	58.74	26.69	89.89	62.01
3	treated	31.01	53.13	28.92	60.11	27.89	91.80	64.23
4	treated	27.41	53.55	29.12	64.24	28.03	92.46	70.11
5	treated	26.07	54.25	29.10	67.23	28.53	93.65	83.77

The colour data of untreated and treated fiber and the colour yield were recorded in Table 2. It found that the colourimetric CIE L*a*b*C*h and ΔE data of the treated dyed fibers is higher than the untreated dyed fibers with pH 5, then decreased. The treatment with chitosan leaded to increase the functional groups on the nylon fibers as a result the treated fibers gave higher values of the colourimetric data and K/S at the same pH level.

Table 2. The colour data of untreated and treated nylon at different pH

pH	Fibers	L*	a*	b*	c*	H	ΔE	K/S
3	untreated	37.75	59.91	39.93	72.00	33.68	89.27	77.11
4	untreated	36.04	49.88	40.52	75.02	33.73	89.47	96.45
5	untreated	32.98	63.70	46.46	79.68	34.91	92.24	97.07
6	untreated	35.58	44.48	45.75	78.04	35.05	92.02	96.35
7	untreated	37.01	59.08	45.67	78.57	35.52	82.17	78.76
3	Treated	38.41	52.23	32.31	66.75	27.42	89.67	79.97
4	Treated	33.94	59.85	33.15	68.42	28.98	90.05	98.61
5	Treated	30.07	66.87	44.78	73.02	27.87	94.16	99.05
6	Treated	36.06	54.27	31.01	62.54	29.80	93.13	97.00
7	Treated	37.47	52.47	26.79	58.92	27.05	85.73	82.32

The colour data of untreated and treated fiber and the colour yield were recorded in Table3. It found that the colourimetric CIE L*a*b*C*h and ΔE data of the treated dyed fibers was higher than the untreated dyed fibers with time.The treatment with chitosan increased the functional groups on the nylon fibers as a result the treated fibers gave higher values of the colourimetric data and K/S at 60 min.

Table 3. The colour data of untreated and treated nylon at different time

Time/min.	fibers	L*	a*	b*	c*	h	ΔE	K/S
20	untreated	38.23	62.68	37.37	72.97	29.57	79.54	46.64
40	untreated	32.15	59.93	42.09	73.24	28.56	80.01	76.04
60	untreated	31.22	51.37	30.24	59.61	28.61	80.41	95.15
20	treated	35.99	55.76	28.19	62.48	26.82	81.11	51.74
40	treated	23.36	37.64	18.67	42.02	26.39	83.78	78.37
60	treated	33016	56.43	30.82	64.29	28.64	85.54	96.05

The fastness properties of untreated and treated fiber were recorded in Table 4. Result showed that the colour fastness to rubbing, washing, perspiration, and light of treated dyed fibers expressed higher results when compared to the untreated fibers due to the treatment with chitosan.

Table 4. The fastness properties of the investigated dye on the untreated and treated fibers

Dyed sample	**K/S**	**Fastness to rubbing**		**Wash fastness**			**Fastness to perspiration**						
							Alkaline			**Acidic**			
		Dry	**Wet**	**Alt**	**SC**	**SW**	**Alt**	**SC**	**SW**	**Alt**	**SC**	**SW**	**light**
untreated	76.29	3-4	4	3-4	4	4	3-4	4	4	4	3-4	4	5
-treated	52.06	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	6

C =Cotton, W=Wool, Alt= alteration; Sc= Staining on cotton and Sw =Staining on wo

Discussion

The treated fiber showed very high exhaustion (98.81%E), but untreated fiber revealed high exhaustion (94.63%E) at pH5. Dyeing resulted a higher extent of exhaustion with the lower dye concentration than higher concentration. It believed that the proportion of available dye sites at lower dye concentrations was higher than at higher concentrations as also reported by Mohamed *et al.* (2020).

The dyeing showed very high exhaustion (98.87%E) for treated fiber, and 94.84 %E for the untreated fiber. Chitosan added on the nylon surface which generated additive functional groups increased in hydrophilicity. The results showed that the colourimetric CIE L*a*b*C*h and ΔE data of the dyed fibers were good and K/S values in comparison to untreated ones. The treated fibers gave higher exhaustion than the untreated fibers. The colour fastness to rubbing, washing, perspiration, and light of dyed fibers expressed good to excellent as also reported by Ali and Abd-Elsalam (2020).

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