

Synthesis and Characterization of Novel Cu(II) and Co(II) Azo Dye Complexes and Their Application on Nylon 6 and Wool

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TWO models of azo disperse dye complexes were prepared by the reaction of 3-hydroxy-4-((2-hydroxyphenyl) diazenyl)-2-naphthoic acid (H₂L) with a divalent Cu(II) and Co(II) ions. The structures were confirmed by elemental analysis, spectral studies (¹H NMR, IR, UV–visible, ESR), and magnetic measurements. IR spectra of the isolated complexes suggest that the H₂L acts as a tetradentate ligand. The electronic spectra of the complexes and their magnetic moments suggest octahedral geometry. These dyes were applied to nylon 6 and wool fabrics. The results assessed for dyeing indicate an improving in washing and slightly enhanced in rubbing fastness rather than Fe (III) and Cr (III) complexes on wool fabrics, But approximately the same on nylon 6 fabrics.

Keywords: Copper, Cobalt, Complexes, Nylon 6, Wool and Washing.

In continuation of our previous work⁽¹⁾, using a divalent metal complexes *o,o'*-dihydroxyazo dyes and their divalent metal complexes used for obtaining dyeing properties of protein and polyamide fibres with excellent light and washing fastness and in electrophotography⁽²⁻⁵⁾ in industrial dyes⁽⁶⁾. Also, some azo-compounds possess excellent optical memory and photoelectric properties⁽⁷⁾. Recently, various studies have been done on the arylazoheterocycles and their metal complexes⁽⁸⁾. Several transition metal azodye complexes have been found to possess interesting biological properties⁽⁹⁾. In view of the biological significance and coordination behaviour of azo compounds, it was considered worthwhile to prepare and study azodye complexes of Cu(II) and Co(II) ions. It is in this context that the application and preparation of these complexes of considerable interest to dye chemists.

The present study describes the synthesis of 3-hydroxy-4-((2-hydroxyphenyl) diazenyl)-2-naphthoic acid (H₂L) which is obtained by diazotization of 2-hydroxy aniline and coupling with 3-hydroxy-2-naphthoic acid. The metallisation of H₂L with Cu(II) and Co(II) chlorides was carried out in absolute ethanol. The mode of chelating, the geometry and the nature of bonding of the complexes are discussed on the basis of elemental analyses, magnetic susceptibility and spectral studies (IR, UV–visible and ESR). The synthetic dyes were applied on nylon 6

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and wool fabrics. The dye exhaustion percentages (E) along with the fastness to light, washing and rubbing of the dyed fabrics were measured.

Experimental

General

All melting points were taken with an electrothermal melting point apparatus and were uncorrected. IR spectra were determined on a Mattson 1000 FTIR spectrophotometer in potassium bromid. The UV/Vis absorption spectra in ethanol were recorded using a Shimadzu UV-2401PC UV/vis spectrophotometer. Elemental analysis was performed by Tubitac at the National Research Center.

2-Hydroxy-aniline (used as diazotization material) was obtained from Aldrich and 3-hydroxy-2-naphthoic acid from Merck.

Preparation of 3-hydroxy-4-((2-hydroxyphenyl)diazonyl)-2-naphthoic acid (H_2L)

A mixture of 2-hydroxy-aniline (2 g, 18.34 mmol), water (20 ml) and concentrated hydrochloric acid (4 ml, 75.62 mmol) was stirred until a clear solution was obtained⁽¹⁾. This solution cooled down to the range 0-5°C and a solution of sodium nitrite (1.12 g, 16.23 mmol) in 10 ml water was then added dropwise, the temperature below 5°C. The resulting mixture was stirred for an additional 30 min in an ice bath and was buffered with solid sodium acetate.

3-Hydroxy-2-naphthoic acid (3.04 g, 18.34 mmol), dissolved in 8 ml 10% sodium hydroxide, was cooled down to the 0-5°C range in an ice bath. This solution was added gradually to the solution of the cooled 2-hydroxybenzene diazonium chloride and the resulting mixture was continually stirred in the same range (0-5°C) for 60 min. The crude precipitate was filtered and washed several times with cooled water and then purified by washing with hot glacial acetic acid to give a product with a melting point 231°C. The yield was (78%).

Preparation of complexes

The complexes were prepared by mixing equimolar amounts of H_2L with ethanolic solution of chloride salt of Cu(II) and Co(II). The reaction mixture was refluxed on a water bath for 2 hr. The precipitate was filtered off, washed with hot ethanol solution successfully and finally preserved in a vacuum desiccators over anhydrous $CaCl_2$ ⁽²¹⁾.

Dyeing of fabrics

The fabrics, nylon 6 (160 g/m²) and wool (320 g/m²) were introduced into a dye bath at 40°C (pH 4) and raised to 80°C (for nylon 6) or 90°C (for wool) over a 40 min period and then dyed at this temperature for 60 min with continuous stirring at a liquor ratio of 20:1 (with 1% dye o.w.f.). After cooling the dye bath and rinsing the samples with distilled water, they were with an aqueous solution containing 1 g/L detergent for 10 min at 90°C and a liquor ratio of 20:1. After that, the samples were rinsed at room temperature⁽¹⁾.

Physico-chemical measurements

The molar conductance of the complexes were determined by preparing 10^{-3} M solutions of the complexes in DMSO at room temperature and measured on a YSI Model 32 conductivity bridge. Magnetic moment values were evaluated at room temperature ($25 \pm 1^\circ\text{C}$) using a Johnson Matthey magnetic susceptibility balance. The electronic spectra of the complexes were recorded in DMSO solution on a Unicam UV₂-UV-visible spectrometer, in the range 200–900 nm. Infrared spectra of the complexes and parent ligand were recorded on Mattson 5000 FTIR spectrophotometer, in the range $500\text{--}4,000\text{ cm}^{-1}$ in KBr medium. ¹HNMR spectrum of the ligand was recorded in DMSO on an EM-390 (200 MHz) Spectrometer. ESR spectra were obtained on a Bruker EMX Spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW and modulation amplitude was set at 4 Gauss. The low-field signal was obtained after four scans with a tenfold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature. All metal salts used were pure (Fluka, Aldrich, or Merck). The analytical and physico-chemical data are given in Tables 1– 4.

TABLE 1 . Analytical and physical data of H₂L and its metal complexes.

Compound	Empirical Formula (F. Wt.)	Colour	M.P. (°C)	Yield (%)	%Found (Calcd.)			Λ _m [*]
					C	H	M	
H ₂ L	C ₁₇ H ₁₂ O ₄ N ₂ (308.312)	Redish-brown	280	89	66.87 (66.21)	4.11 (3.90)	-	-
[Cu ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	Cu ₂ C ₃₄ H ₃₀ O ₁₃ N ₄ (829.747)	Redish-brown	>300	85	50.105 (49.22)	3.53 (3.64)	15.23 (15.32)	5
[Co ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	Co ₂ C ₃₄ H ₃₀ O ₁₃ N ₄ (820.487)	brown	>300	80	50.63 (49.77)	3.72 (3.69)	14.45 (14.36)	3

TABLE 2 . Most important IR spectral bands of H₂L and its metal complexes.

Compound	ν(OH) naphthoic	ν(OH) phenolic	ν(C=O)	ν _{as} (COO)	ν _s (COO)	ν(N=N)	ν(M-O)	ν(M-N)
H ₂ L	3243	3421	1641	-	-	1582	-	-
[Cu ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	-	3402	-	1665	1445	1554	530	430
[Co ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	-	3406	-	1668	1442	1557	545	410

TABLE 3. Magnetic moments, electronic spectra and ligand field parameters of metal complexes of H₂L.

Compound	μ_{eff} (B.M)	Band position (cm ⁻¹)	D _q (cm ⁻¹)	B(cm ⁻¹)	B
[Cu ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	1.87	14285; 16667	-	-	-
[Co ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	4.98	14064; 17699	765	765	0.79

TABLE 4. Colour properties and exhaustion of H₂L and its complexes.

Dye	Fabric ^a	E(%)	λ_{max} (nm)	Light fastness	Washing fastness			Rubbing fastness	
					CC	SC	SW	Dry	Wet
H ₂ L	W	63	559	1 ^b	3-4	4	3-4	3	3-4
	N	68	540	1 ^b	3-4	4	4	3-4	3-4
[Cu ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	W	76	569	4-5 ^c	4-5	4	4-5	4-5	4
	N	74	573	4 ^c	4-5	4	4-5	4-5	3-4
[Co ₂ (L) ₂ (H ₂ O) ₄].H ₂ O	W	77	553	4-5 ^c	4	4-5	4-5	4-5	4-5
	N	72	542	4 ^c	4-5	4	4-5	4	4

a W = Wool, N = Nylon 6

b 10 h

c 80 h

CC change in colour

SC staining on cotton

SW staining on wool

Measurements and testing

For all dyeings, the dye exhaustion was measured by sampling the dye bath before and after dyeing. The dye concentration (g/l) of the dye bath was measured on Shimadzu UV-2401PC UV/vis spectrophotometer at λ_{max} of the dye. The percentage of dye exhaustion (percent *E*) was calculated using Eq. 1:

$$\% E = \left[1 - \left(\frac{C_2}{C_1} \right) \right] \times 100$$

where, C_1 and C_2 are the concentrations of the dye bath before and after dyeing⁽³⁾.

The dyed samples were washed-off using 2 g/l non-ionic detergent at 80°C for 30 min, and tested according to ISO standard methods (SDC, 1990). The specific tests were ISO 105-CO2 (1989), ISO-E04 (1989), and ISO 105-BO2 (1988) corresponding to colour fastness to washing, rubbing, and light, respectively.

Results and Discussion

The Cu(II) and Co(II) complexes decompose on heating >300 °C. The molar conductance values, in DMSO are 4, 6 $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ indicating that the complexes are non-electrolytes⁽¹⁰⁾. The colors, melting points, elemental analyses of the isolated complexes, are listed in Table 1.

IR and ¹H NMR spectra

The ¹H NMR spectrum of H₂L (Fig. 1) in d₆-DMSO shows two signals at 12.19 and 11.32 ppm assignable to the protons of (OH)_{naphthoic} and (OH)_{phenolic}, respectively⁽¹⁾. The appearance of the signal attributed to the proton of OH group at a high value downfield from TMS suggests the presence of intramolecular hydrogen bonding. The multiplet signals observed in the 6.92-8.67 ppm region are assigned to the aromatic protons.

The infrared spectrum of H₂L displays five main bands at 1582, 1641, 3041, 3243 and 3421 cm^{-1} assigned $\nu(\text{N}=\text{N})$, $\nu(\text{C}=\text{O})$, $(\text{CH}_{\text{aromatic}})$, $(\text{OH})_{\text{naphthoic}}$ and $(\text{OH})_{\text{phenolic}}$ vibrations, respectively⁽¹¹⁾.

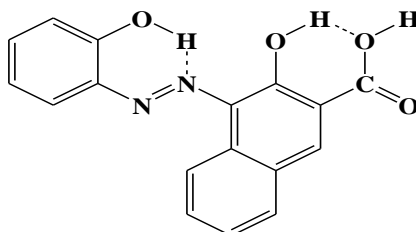


Fig. 1. 3-Hydroxy-4-((2-hydroxyphenyl)diazenyl)-2-naphthoic acid.

The two bands at 1273 and 1365 cm^{-1} are attributed to $\delta(\text{OH})_{\text{phenolic}}$ and $\delta(\text{OH})_{\text{naphthoic}}$. The appearance of $(\text{OH})_{\text{naphthoic}}$ and $(\text{OH})_{\text{phenolic}}$ as a broad band at lower wavenumbers and the two weak broad bands in the 1900-2080 and 2150-2230 cm^{-1} regions suggest intramolecular hydrogen bonding ($\text{O}-\text{H}\cdots\text{O}$)⁽¹²⁾ (Table 2).

Comparison of the infrared spectrum of the ligand with those of its metal complexes reveals that H₂L behaves as a tetradentate ligand.

In $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ and $[\text{Co}_2(\text{L})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ complexes (Fig. 2), H₂L acts as a binegative tetradentate ligand coordinating via azo nitrogen (N=N), $(\text{OH})_{\text{phenolic}}$, $(\text{OH})_{\text{naphthoic}}$ and carboxylate group (COO) with the displacement of the hydrogen atom from the two latter groups. This mode of chelating is

supported by the shift of both $\nu(\text{N}=\text{N})$ and $\nu(\text{OH})_{\text{phenolic}}$ vibrations to lower wavenumber; also, the absence of the band at 1260 cm^{-1} of $\delta(\text{OH})$ of the free acid in the two complexes, indicates that the hydrogen ion in the free acid molecule is substituted by the metal ion. The disappearance of $(\text{OH})_{\text{naphthoic}}$. Also, the infrared spectra of these complexes show new bands at $530, 545$ and $410, 430\text{ cm}^{-1}$ assignable to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$, respectively⁽¹³⁾.

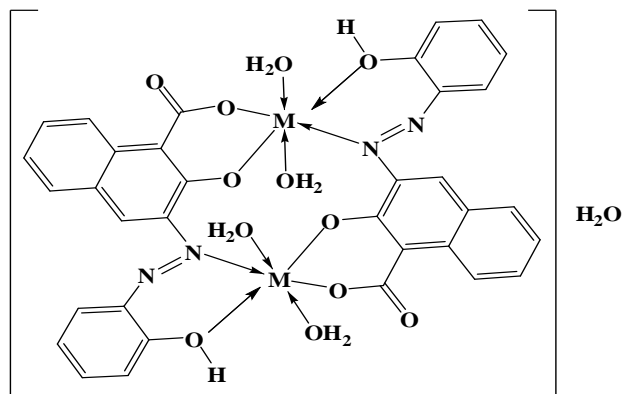


Fig. 2. The proposed structure of $[\text{Co}_2(\text{L})_2(\text{H}_2\text{O})_4].\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_4].\text{H}_2\text{O}$ complexes.

Electronic and magnetic moment measurements

The Cu(II) complex has magnetic (1.87 B.M.), which is close to the spin value for one unpaired electron and within the general range for Cu(II) complexes. The electronic spectrum of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_4].\text{H}_2\text{O}$ complex (Fig. 3) contains a broad band at 16667 cm^{-1} with a shoulder at 14285 cm^{-1} which assigns to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{E}_{1g} \rightarrow {}^2\text{A}_{1g}$ transitions, respectively⁽¹⁴⁾ (Table 3).

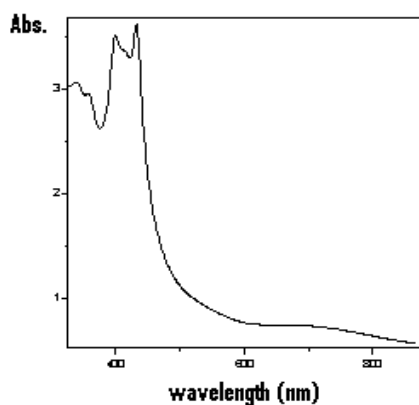


Fig. 3. The electronic spectrum of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_4].\text{H}_2\text{O}$.

The electronic spectrum of $[\text{Co}_2(\text{L})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ complex (Fig. 4) shows two bands at 14064 and 17699 cm^{-1} attributed to ${}^4\text{T}_{1g}(\text{F})\rightarrow{}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F})\rightarrow{}^4\text{T}_{1g}(\text{P})$ transitions, respectively, in an octahedral configuration⁽¹⁴⁾. The calculated values of D_q , B , β and ν_2/ν_1 are in good agreement with those reported for octahedral Co(II) complexes. Also, the magnetic moment (4.98 B.M.) is consistent with octahedral geometry around the Co(II) ion.

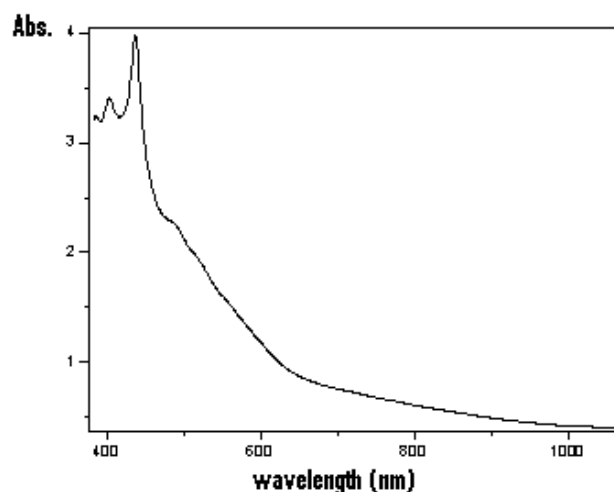


Fig. 4. The electronic spectrum of $[\text{Co}_2(\text{L})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$.

ESR studies

The solid-state ESR spectrum (Fig.5) of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ exhibits axially symmetric g-tensor parameters with g_{\parallel} (2.27) $> g_{\perp}$ (2.06) > 2.0023 indicating that the copper site has a $d_{x^2-y^2}$ ground-state characteristic of tetrahedral, square planar or octahedral stereochemistry⁽¹⁵⁾. The spin-Hamiltonian parameters of Cu(II) complex were calculated. In axial symmetry the g-values are related by the expression, $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$, where G is the exchange interaction parameter. According to Hathaway⁽¹⁶⁾, if the value of G is greater than 4, the exchange interaction between Cu (II) centres in the solid state is negligible, whereas when less than 4, a considerable exchange interaction is indicated in the solid complex. The calculated G value was 3.8 suggesting that there is copper-copper exchange interaction.

The tendency of A_{\parallel} ($160 \times 10^{-4}\text{ cm}^{-1}$) to decrease with increasing of g_{\parallel} is an index of an increase of the tetrahedral distortion in the coordination sphere of copper⁽¹⁷⁾. In order to quantify the degree of distortion of the Cu(II) complexes, we selected the f factor $g_{\parallel}/A_{\parallel}$ obtained from the ESR spectra. Where, the f factor is regarded as an empirical index of tetrahedral distortion⁽¹⁸⁾. Its value ranges between 105 and 135 for square planar complexes, depending on the nature of the coordinated atoms. In the presence of a tetrahedral distorted structure the

values can be much larger⁽¹⁹⁾. For this complex, the $g_{\parallel}/A_{\parallel}$ quotient is 141, demonstrating the presence of significant dihedral angle distortion in the d_{xy} -plane and indicating a tetrahedral distortion from square-planar geometry. Super hyperfine structure for this complex was not seen at higher fields, excluding any interaction of the nuclear spins of nitrogen ($I = 1$) with the unpaired electron density on Cu(II).

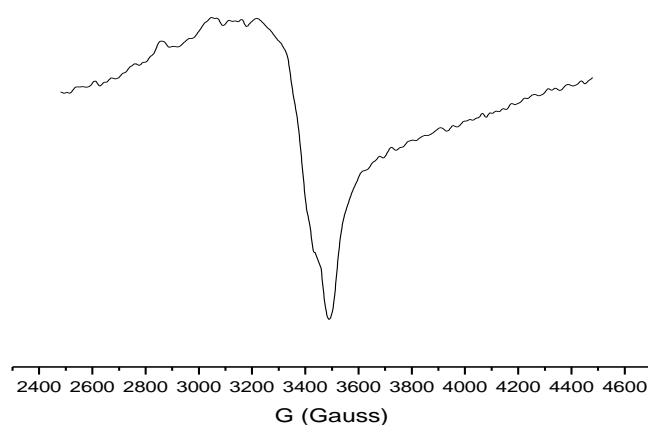


Fig. 5. Room temperature solid state X-band ESR spectrum of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ complex.

Molecular orbital coefficients, α^2 (covalent in-plane σ -bonding) and β^2 (covalent in-plane π -bonding) were calculated⁽²⁰⁾.

$$\alpha^2 = \left(\frac{A_{\parallel}}{0.036} \right) + (g_{\parallel} - 2.0023) + \frac{3(g_{\perp} - 2.0023)}{7} + 0.04$$

$$\beta^2 = \frac{(g_{\parallel} - 2.0023)E}{-8\lambda\alpha^2}$$

$\lambda = 828 \text{ cm}^{-1}$ for the free ion and E is the ${}^2\text{B}_{1-g} \rightarrow {}^2\text{A}_{1-g}$ transition.

As a measure of the covalency of the in-plane σ -bonding $\alpha^2 = 1$ indicates complete ionic character, whereas $\alpha^2 = 0.5$ indicates 100% covalent bonding, with the assumption of negligibly small values of the overlap integral. The β^2 parameter gives an indication of the covalency of the in-plane π -bonding. The smaller β^2 , indicates the larger covalency of the bonding.

The values of α^2 (0.77) and β^2 (0.87) for the complex indicate that the in-plane σ -bonding and in-plane π -bonding are appreciably covalent and are consistent with very strong in-plane π -bonding in this complex. These results are anticipated because there are appropriate ligand orbitals to combine with the d_{xy} orbital of the Cu(II) ion. The higher values of β^2 compared with α^2 indicate that the in-plane π -bonding is less covalent than the in-plane σ -bonding. These data are highly consistent with other reported values⁽²¹⁾.

Dyeing properties

The isolated compounds were used as a disperse dyes on nylon 6 and wool. The colour properties and exhaustion (E) are given in Table 4.

The effect of dyeing time on the exhaustion percentages of all dyes was investigated on nylon 6 and wool on exhaustion as shown in Fig. 6 & 7.

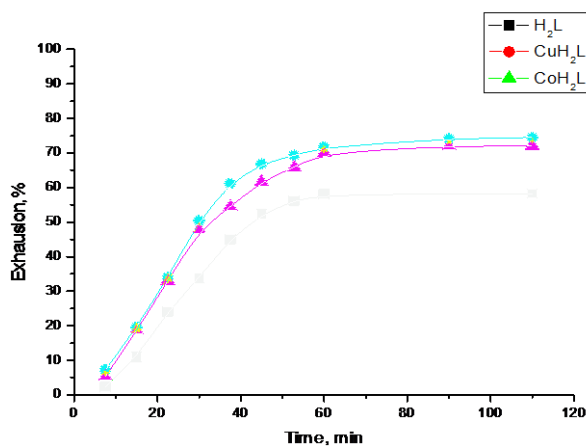


Fig. 6. Extent of dye exhaustion on nylon 6 at various dyeing time.

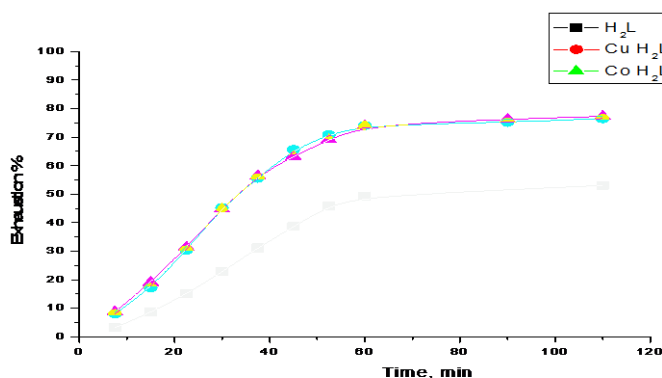


Fig. 7. Extent of dye exhaustion on wool at various dyeing time.

Increasing the dyeing time up to 60 min leads to increase the dye exhaustion for nylon 6 and 80 min for wool was accompanied with a significant enhancement in exhaustion (for copper and cobalt complexes) at pH 4. As can be seen from Table 4, the exhaustion of copper and cobalt complexes reached 74, 72% on nylon 6 while 76 and 77 % on wool, respectively.

Furthermore, the exhaustion of 3-hydroxy-4-((2-hydroxyphenyl)diazenyl)-2-naphthoic acid (H₂L) showed 63% on nylon 6 and 68% on wool with moderate wash fastness ratings. In spite of, copper and cobalt dye complexes showed a lower value of dye exhaustion rather than chromium and ferric complexes but washing and rubbing fastness properties has been enhanced when applied on nylon 6 and wool fabrics specially with cobalt complex. This is in agreement with a previously reported work⁽³⁾.

Conclusions

3-hydroxy-4-((2-hydroxyphenyl)diazenyl)-2-naphthoic acid (H₂L) has been used to produce diverse azo disperse dye complexes with Cu(II) and Co(II) ions. The isolated complexes have been synthesised and characterized by elemental analysis, spectral studies (¹H NMR, IR, UV-visible, ESR) and magnetic measurements. These dyes were applied to nylon 6 and wool fabrics. Dye exhaustion has been calculated according to the absorbance of the original and residual dyes in the dye bath. The fastness of washing and rubbing to the dyed fabrics has been improved.

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تشبيد وتوصيف اصباغ ازو جديده من متراكبات النحاس والكوبلت الثنائيه و تطبيقتها على النايلون ٦ والصوف

حاتم السيد جعفر و رانيا زكى *

قسم النسيج – المركز القومى للبحوث – القاهرة و * قسم الكيمياء – كلية العلوم – جامعة المنصورة- المنصورة – مصر .

تم تحقيق الهدف من البحث من خلال التطبيق العملى فى النقاط التاليه:

- تشبيد صبغة ال ٣ -هيدروكسى-٤-(٢-هيدروكسى فينيل) دايازينيل)-٢- حامض النافثويك (H3L) المشتقة عن طريق تزاوج ملح الديازونيوم لل-٢-امينو فينول مع ٣-هيدروكسى ٢- حامض النفثويك ثم بتكوين صيغتين متراكباتين من املاح النحاس و الكوبلت الثنائيه واثبات التركيب البنائى للثلاث صبغات باستخدام التحليل العنصرى لتعيين ذرات الكربون والهيدروجين وعناصر النحاس و الكوبلت وايضا باستخدام الدراسات الطيفية المختلفه مثل الاشعه تحت الحمراء لتعيين المجموعات الوظيفيه بها مثل مجموعات الهيدروكسيل و الكربوكسيل والرنين النووى المغناطيسى لطيف ذرة الهيدروجين لتحديد عددها واماكنها داخل هذه الصبغات وكذلك الطيف المغناطيسى الالكترونى لاثبات كيفية التخالل لهذه العناصر.

تم تطبيق هذه الصبغات على اقمشة النايلون ٦ والصوف اجراء اختبارات الثبات ضد الغسيل و الاحتكاك و الضوء و قياس مدى استنفاد هذه الصبغات على تلك الاقمشه. وقد اظهرت اقمشة النايلون ٦ والصوف المصبوغه بهذه الصبغات المتراكبه بالنحاس و الكوبلت نتائج جيده تجاه ثباتها ضد الغسيل و الاحتكاك ولكنها كانت اقل مقاومة تجاه الضوء بالمقارنه بالاقمشه المصبوغه بالحديد و الكوبلت. كذلك اظهرت اقمشة النايلون ٦ والصوف المصبوغه بهذه الصبغات المتراكبه بالنحاس و الكوبلت مقاومة تجاه البكتريا الجرام (+) والجرام (-) مثل الاشريشيا كولاي و الاستافلوكوكس وخاصة على اقمشة الصوف مما يجعلها تندرج تحت نطاق الاقمشه الطبيه التى يمكن ان تستعمل فى تصنيع الستائر و اغطية الاسره و المفارش فى المستشفيات و الفنادق وغيرها كم يمكن ان تستخدم فى ضمادات الجروح .