

Original Research Article

Application of Novel Eco-friendly Natural Dye Extracted from Leaves of Neem on Silk Fabric

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ABSTRACT

In the present work, optimization of extraction natural dye from neem (*Azadirachta indica*) leaves with respect to dye bath concentration on silk fabric was studied before and after exposing to artificial day light for 160 h. The effect of different dye bath concentrations in the range 40-240 g/L on the reflectance spectra of the unexposed and exposed silk fabric was followed by using spectrophotometric technique. The absorption coefficient, optical band gap energy and extinction coefficient as well as color strength were calculated from the reflectance data and **the wash fastness was tested**. The color parameters: the relative brightness (L^*), color constants (a^* and b^*), whiteness index (W), color difference (ΔE), chroma (C^*), hue (H) and tint (T) and the CIE tristimulus values (x_r , y_r and z_r) were also determined. The obtained results showed that the absorption and extinction coefficients, color strength and color parameters were highly affected by changing dye concentration. In addition, it was also noticed that the variations in the values of the optical band gap energy with increasing dye concentration may be due to the induced structural change in the system. **In addition, the dyed silk samples have shown good washing fastness properties. The washing fastness grade for color change ranged from 4 to 5, whereas from 4 to 4/5 for color staining with all samples. The present study indicates that the natural dye extracted from neem leaves has good potential in textiles dyeing and meet the environmental future demands technology of high quality fantastic dyed pattern through an economical point of view.**

Keywords: *Azadirachta indica*; Neem plant; Natural dye; Silk fabrics; Textiles dyeing; Optical properties.

1. INTRODUCTION

Silkworm silk is a fine lustrous fiber produced naturally. Silk fiber consists of two biomacromolecules; fibroin (about 75%) and sericin (about 25%) by weight; which has been used as a premium textile material [1]. Silk fiber, also, consists of a filamentous protein, a non-filamentous protein and other impurities such as pigments, wax, carbohydrates and inorganic salts. Silk is a natural protein composed of 18 amino acids with various reactive functional groups [2]. Silk has gentle luster, smooth and soft texture, good drapability, good hygroscopicity and excellent comfortability [3]. Sericin strengthens the silk fiber, but it is necessary to degum before dyeing because it makes lack luster [4-6]. **Silk is a biocompatible [2,4], biodegradable material [7] with low inflammatory reaction in the body [6] and with superior mechanical properties [8].** Silkworm silk can be used as a good biomaterial in tissue engineering and in clinic surgery as stitches besides its application in fabrics. **Silk fiber has several weaknesses such as poor antibacterial activity, poor UV protection performance, deterioration, yellowing and wrinkling which during usage exerts negative appearance [9].** Silk fiber has a general chemical formula $[NH_2.CHR.COOH]$. It is bonded to dyes due to ionic interaction between the free chemical groups of dyes

and the carboxyl groups of silk. The most important groups for dyeing of silk are COOH and NH₂ [7]. In dyeing process, the dye solution is adsorbed and diffused into the fiber.

Textile dyeing processing industry is one of the major environmental polluters by using synthetic dyes in comparison with natural dyes [10,11]. Thus renewed international interests have arisen in natural dyes due to the increased awareness of the environmental and are safer in use with minimum health hazards [11,12]. The natural dyes present in plants and animals are pigmentary molecules which impart color to the materials [13]. They may have a wide range of shades, and can be obtained from various parts of plants including roots, bark, leaves, flowers, and fruit [14]. Furthermore, natural dyes are known to exhibit better biodegradability, less toxicity, eco-friendly alternative to synthetic dyes and some dyes also possess medical properties [15,16]. Moreover, naturally dyed textiles have therapeutic properties provides relief for arthritis, diabetes, headaches and over-excited nerves and is also good for blood circulation [17]. Natural dyes are applied as a green and sustainable dyeing process due to their biocompatibility, low toxicity, abundant availability, antibacterial activity, deodorizing performance, UV protection, and eco-friendliness [18,19].

Azadirachta indica commonly known as “Neem”, “Nimtree” and “Indian Lilac” belongs to Meliaceae botanical family and being abundantly available in nature [20]. *Azadirachta indica* is one of two species in the genus *Azadirachta*, and is native to India and the Indian subcontinent. The images in Figure 1 illustrate the neem tree, tender neem leaves used as medicine, neem flowers and neem fruits.

Neem is a fast-growing tree that can reach a height of 15–20 m and rarely 35–40 m. The branches are wide and spreading. The fairly dense crown is roundish and may reach a diameter of 15–20 meters in old, free-standing specimens. Neem tree can grow in many different types of soil, but it thrives best on well drained deep and sandy soils. The opposite, pinnate leaves are 20–40 cm long with 20 to 31 medium to dark green leaflets about 3–8 cm long. White and fragrant flowers were arranged in drooping axillary panicles of 25 cm long. The inflorescences belong to the third degree which bears 150-250 flowers of 5–6 mm long and 8–11 mm wide, each. In the same individual tree; protandrous, bisexual flowers and male flowers were existed. The fruit is a smooth and has different shapes from elongate oval to nearly roundish, and when ripe is 1.4–2.8 cm by 1.0–1.5 cm.

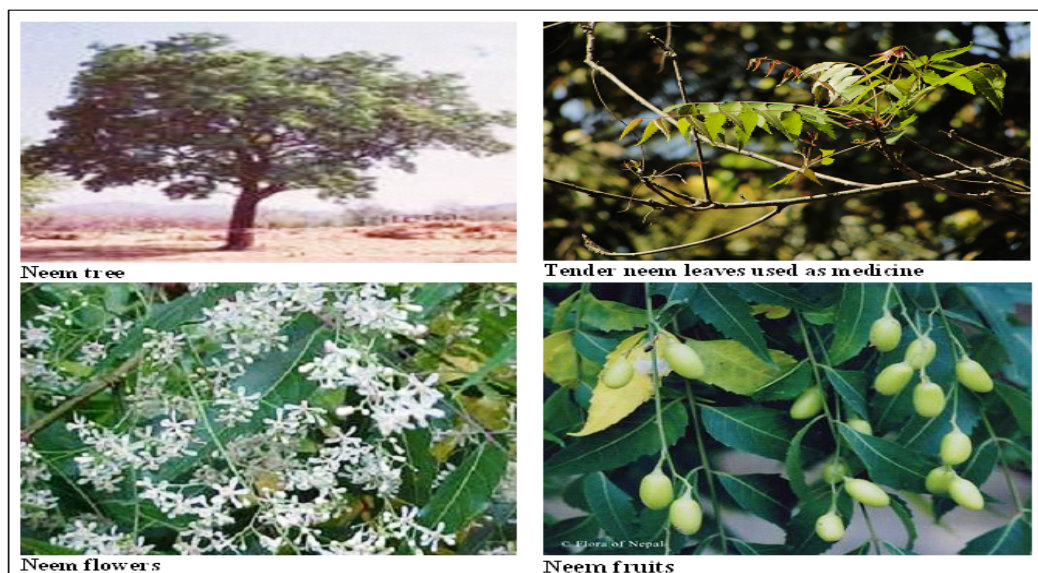


Fig. 1. Neem tree, tender neem leaves used as medicine, neem flowers and neem fruits

The principal constituents of neem leave include; protein (7.1%), carbohydrates (22.9%), minerals, calcium, phosphorus, vitamin C, carotene, etc. [20,21]. An extract from the leaves can be prepared as an alcoholic tincture or as tea and this alcohol extract has a dark green colour [22,23]. The chemical composition of the extract contains glutamic acid, tyrosine, aspartic acid, alanine, praline, glutamine and

cystine like amino acids, and several fatty acids (dodecanoic, tetradecanoic, elcosanic, etc.). But physically the neem leaves have a pleasant odor and plant pigments like chlorophyll mainly responsible for green color. The *Azadirachta indica* extract is reportedly officious against a variety of skin diseases, septic sources and infected burns. The most important quality of these compounds is that they are less toxic to warm blooded animals like human. Thus, considering its less toxicity and effectiveness against microorganism, it is expected to be one of the safest and most effective colorant cum antimicrobial agent for textiles [24,25].

In the present work, optimization of extraction natural dye from neem (*Azadirachta indica*) leaves with respect to dye bath concentration on silk fabric was studied before and after exposing to artificial day light for 160 h. The effect of 6 different dye bath concentrations (40, 80, 120, 160, 200 and 240 g/L) on the reflectance spectra of the unexposed and exposed silk fabric was followed by using spectrophotometric technique. The color parameters (L^* , a^* , b^* , W , ΔE^* , C^* , H and T) and the CIE tristimulus values (x_r , y_r and z_r), were determined. The absorption coefficient, optical band gap energy and extinction coefficient as well as color strength were also calculated.

2. EXPERIMENTAL DETAILS

2.1 Materials

2.1.1 Fabric samples and extraction of colorant

In the present investigation, white silk fabrics of 55 g/m² in weight and 0.06 cm in thickness produced in Akhmim, Egypt, was used without any purification. Dried leaves of neem plant were used for obtaining the neem dye without the application of any mordant in the dyeing process. 50 g of neem leaves were immersed after crushing in 500 mL of distilled water and allowed to boil for 1 h. It was mentioned that, the dyeing process was done without the application of any mordant.

A Shimadzu (VIS) Double Beam Spectrophotometer with standard illuminant C (1174.83) model V-530 and band width 2.0 nm in the range 200-700 nm with accuracy $\pm 0.05\%$ was used to evaluate the optical density of the extract solution after filtration. The determination of the optical density was taken as a measure of concentration. The absorption spectrum of the aqueous extract of the neem leaves was shown in Figure 2. From the figure, three peaks were presented: the first peak at UV range has $\lambda_{\max} = 320$ nm of optical density 3.765; the second peak at $\lambda_{\max} = 370$ nm of optical density 3.402; and the third one at visible region has $\lambda_{\max} = 400$ nm of optical density 3.569. The dried leaves of neem plant were found to discharge color in hot water very easily. Increasing the quantity of leaves from 20 to 120 g per 1000 mL water boiled for 1 h was accompanied with the increase in color strength and depth in color (easily seen by naked eye). The extracted dye (for all concentrations) was exposed to artificial day light for 160 h and then examined spectrophotometry. The absorption spectrum of these aqueous extract of neem leaves show three peaks at the same positions as that presented in Figure 2.

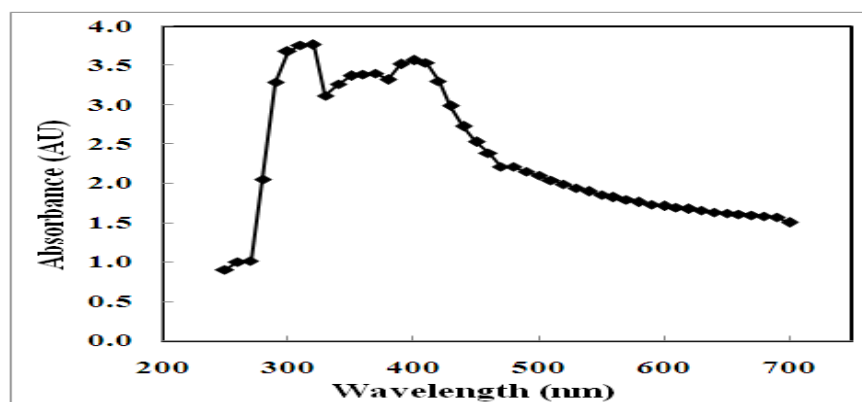


Fig. 2. The absorption spectrum of the aqueous extract of the neem leaves

2.2.2 Dyeing method

Silk fabrics were dyed by using a liquor ratio of 1:50 at pH = 5, at temperature 60 °C for 45 minutes for each concentration [26]. The samples were thoroughly washed with cold water and then dried at ambient temperature. Different shades were obtained by using various concentrations (40, 80, 120, 160, 200 and 240 g/L) ranging from hell yellow to dull yellow.

2.2.3. Reflection measurements

The measurements in the visible region from 400-700 nm for the unexposed and exposed undyed and dyed silk fabrics with different concentrations of neem dye was carried out using a Shimadzu (VIS) Double Beam Spectrophotometer with standard illuminant C (1174.83) model V-530 and band width 2.0 nm covers the range 200-2500 nm with accuracy $\pm 0.05\%$.

The effect of different neem dye bath concentrations on the absorption coefficient, optical band gap energy, extinction coefficient and color strength of the dyed silk fabrics have been determined. From the reflectance spectra, the absorption coefficient (α), extinction coefficient (K) and the color strength (α/S) were calculated in the visible range covered from 400-700 nm by using the following equations [27-32].

$$\alpha = (1/d) \ln [(1-R)^2/T] \quad (1)$$

$$K = \alpha/4\pi \quad (2)$$

$$\alpha/S = (1-R)^2/2R \quad (3)$$

Where R is the reflectance, T is the transmittance ($\approx 10^{-3}$) and d is the thickness of the sample (about 0.06 cm). α represents the absorption coefficient (is dependent on the dye stuff) and S is the scattering coefficient (is dependent on the substrate). On other hand, the color properties were analyzed using the CIE Colorimetric System, CIE 1931 2-degree Standard Observer. The tristimulus values (x_r , y_r , and z_r), the relative brightness (L^*), color constants (a^* and b^*), whiteness index (W), color difference (ΔE), chroma (C^*), hue (H) and tint (T) were performed [33-37].

All the silk fabrics under test were exposed to artificial day light using Tera Light Fastness Tester [38] for 160 h at a temperature of 25 ± 2 °C and at a relative humidity of $65 \pm 5\%$. A standard blue scale was hanged alongside the samples (ISO 105-B02).

2.2.4. Determination of fastness properties

The silk samples were washed as stated by the conditions mentioned in AATCC Test Method 61-2009 to determine the change in color and staining of adjacent fabrics after washing. A specimen of the textile in contact with one or two specified adjacent fabrics was mechanically agitated under specified conditions of time 30 minutes and at 50 °C in a soap solution without fluorescent whitening agent (WOB), then rinse and dried. The rating scale of washing fastness for color change was from 1 (very poor), 2 (poor), 3 fair, 4 (good) to 5 (excellent). This was assessed with reference to the original fabrics using the gerg scale.

3. RESULTS AND DISCUSSION

3.1. Absorption Coefficient, Extinction Coefficient and Color Strength

The reflectance percentages (R%) as function of wavelength in the visible range 400-700 nm for undyed as well as unexposed (a) and exposed (b) neem dyed silk fabrics with different dye bath concentrations (40, 80, 120, 160, 200 and 240 g/L) were shown in Figure 3. It is clear from Figure 3a for the unexposed dyed silk fabrics that, R% values increase markedly with increasing wavelength for all samples and decrease gradually with increasing the dye bath concentration up to 240 g/L in comparison with the

undyed sample. These observed variations indicate that, there is a high color change as a function of wavelength by increasing neem concentration. Similar behaviors and trends with more variations were observed for all samples after exposing to artificial day light for 160 h (Figure 3b).

The absorption coefficients (α) of the undyed as well as the unexposed (a) and exposed (b) silk fabrics dyed with different concentrations were calculated in the visible wavelength range 400-700 nm (i.e., photon energy range 3.10-1.77 eV) by using Equation 1 from the reflectance spectra (Figure 3) and were represented as functions of wavelength and photon energy in Figures 4 and 5, respectively. It is clear from the figures that remarkable decrease in the absorption coefficient values with increasing the wavelength for all samples. Also, α values increase with increasing the concentration of neem through the whole wavelength and photon energy ranges for both the unexposed and exposed samples to artificial day light for 160 h.

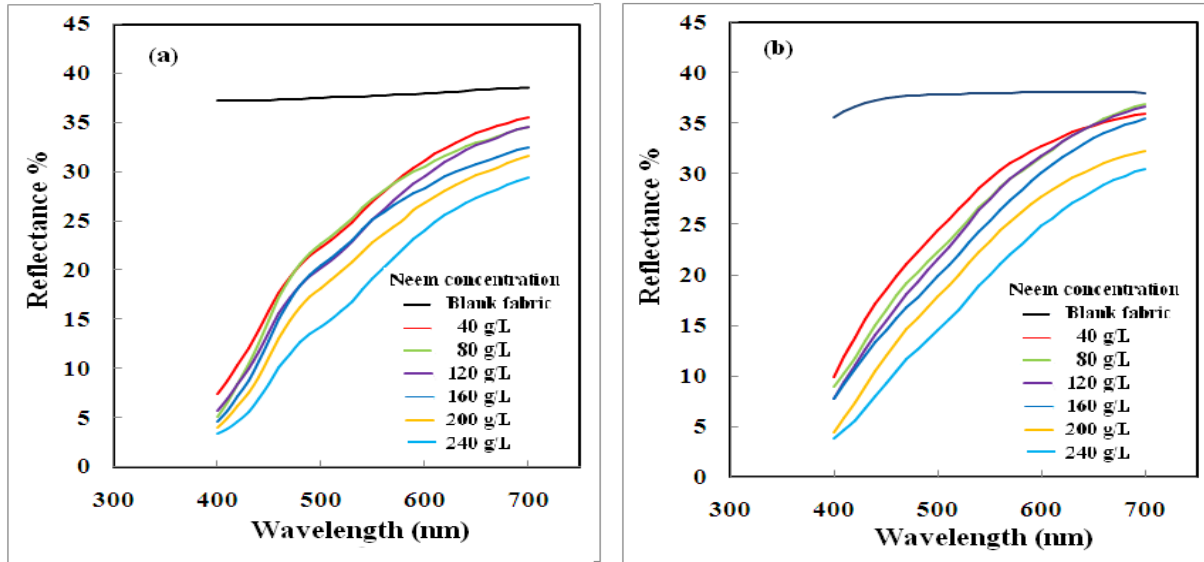


Fig. 3. The reflectance % spectra of undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h as functions of wavelength in the visible region

As reported previously [39-41], the change in the absorption coefficient may be due to the change in the chemical bonds between the fabric and the dye which form other molecular species and leads to the formation of new color centers. The detected increase in absorption coefficient values either by increasing the neem concentration and/or exposure to the artificial day light may be attributed to the change in the molecular configuration of the fabric which may indicate to the formation of new color centers. In addition, the data indicates that dyeing with neem and/or exposure with day light leads to rupture of the bonds and formation of free radicals. These observed variations may be due to modification in molecular structure introduced as a result of the degradation process. In addition, the dye components role was to strength the linkage between the reactive species of the silk fabric chemical groups and their polar groups.

The energy represents the width of the tail localized states in the normally forbidden band gap was given by applying Urbach relation as [27-30]:

$$\alpha = \alpha_0 \exp [h\nu/E_b] \quad (4)$$

where α_0 (= constant) is the absorption coefficient at $h\nu = 0$, ν is the frequency of radiation, and E_b is the band tail energy value. Figure 6 shows the dependence of $\ln \alpha$ on $h\nu$ for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h. It is clear from the figure that, each curve could not be represent by straight lines relation which means that the absorption does not follow the quadratic relation for inter-band transitions to verify Urbach rule

[30]. On other hand, as observed from Figure 6b that the variation between $\ln \alpha$ and $h\nu$ are more regular with increasing the neem concentration for the exposed samples but still showed complicated behaviors which may due to the change in the total number available states caused by exposing to the artificial light according to the compromise between the degradation and/or cross-linking processes [42,43]. In addition, the observed changes may be due to the variation in the internal fields due to the interaction between neem and silk fabrics chemical groups.

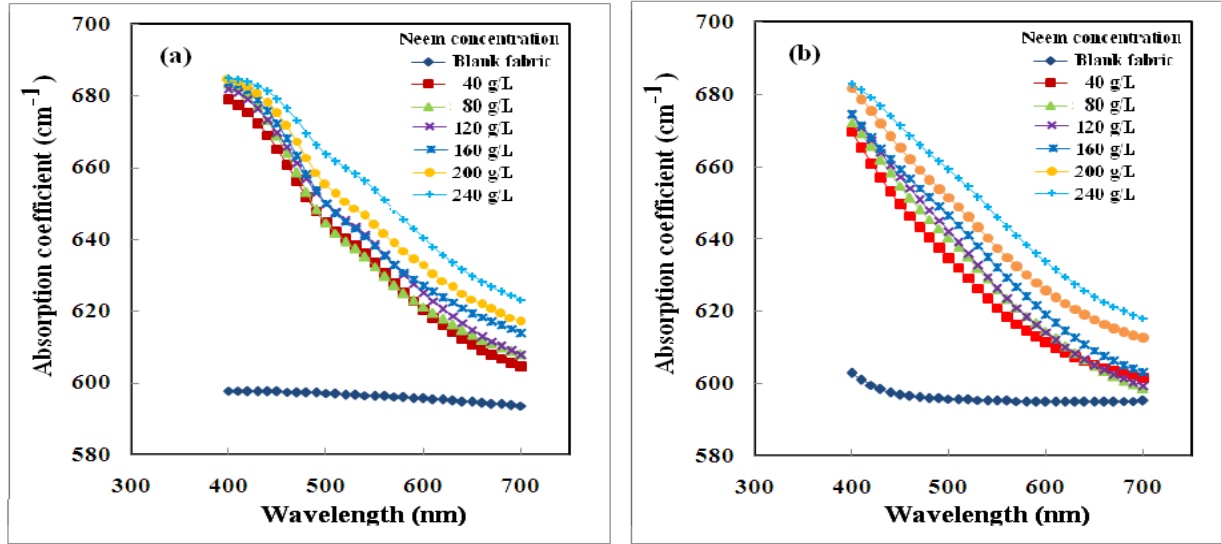


Fig. 4. Plots of the absorption coefficient values of undyed as well as neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h against wavelength

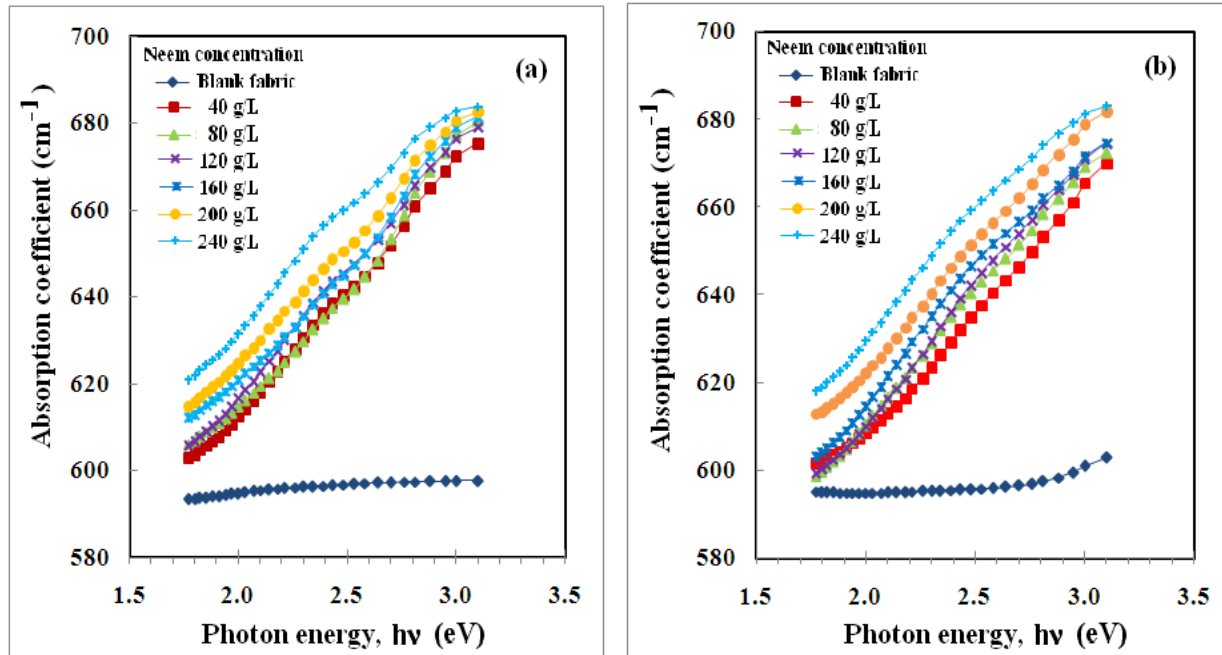


Fig. 5. Plots of the absorption coefficient values of undyed as well as neem silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h against photon energy ($h\nu$)

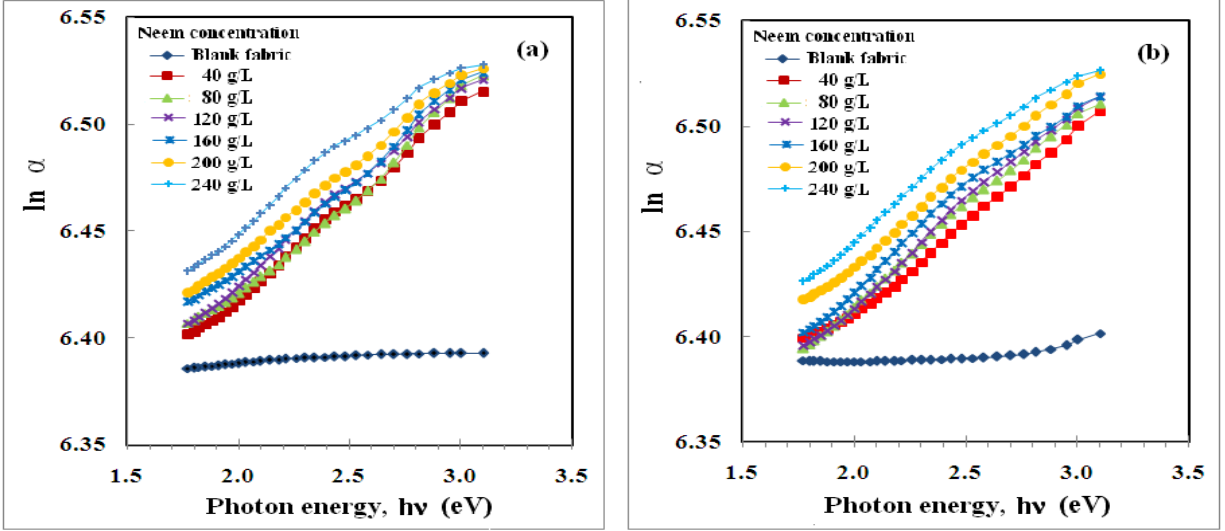


Fig. 6. Variation of $\ln \alpha$ with $h\nu$ for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

According to Tauc's model and from the following relation, the power part obeys the Tauc was given as [30,31]:

$$\alpha h\nu = B (h\nu - E_g)^n \quad (5)$$

Where B is the band tail parameter in the range from 10^5 to 10^6 (cm.eV) $^{-1}$ which represents the slope of Tauc's edge and n is the electronic transition equals $\frac{1}{2}$ or 2 for allowed direct or indirect transitions, respectively. Figure 7 shows the variations of $(\alpha h\nu)^2$ with $h\nu$ for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h. From the figure, the values of allowed direct energy gap (E_d) were calculated by extending the linear parts of the curves to zero absorption and were tabulated in Table 1. It is observed from the table that, firstly, the E_d values increase with increasing the dye bath concentration up to 80 g/L and then decrease gradually for the unexposed samples. The E_d values of the fabrics exposed to the artificial light show the same behavior with increasing the dye bath concentration. These increases indicate that the values of E_d show the dependence on the composite and creation of localized states in the band gap. Moreover, the obtained increase in the optical energy gap (E_d) may be attributed to the change in molecular configuration which leads to rupture of the bonds and formation of free radicals and then structural changes were occurred [27,41-44].

Table 1. Values of the direct energy gap (E_d) for undyed and neem dyed silk fabrics with different neem concentrations before and after exposure to artificial day light for 160 h

Concentration of neem (g/L)	Direct energy gap (E_d) (eV)	
	Before exposure	After exposure
Undyed fabric	1.481	1.604
40	1.746	1.784
80	1.773	1.740
120	1.726	1.742
160	1.723	1.719
200	1.689	1.726
240	1.621	1.652

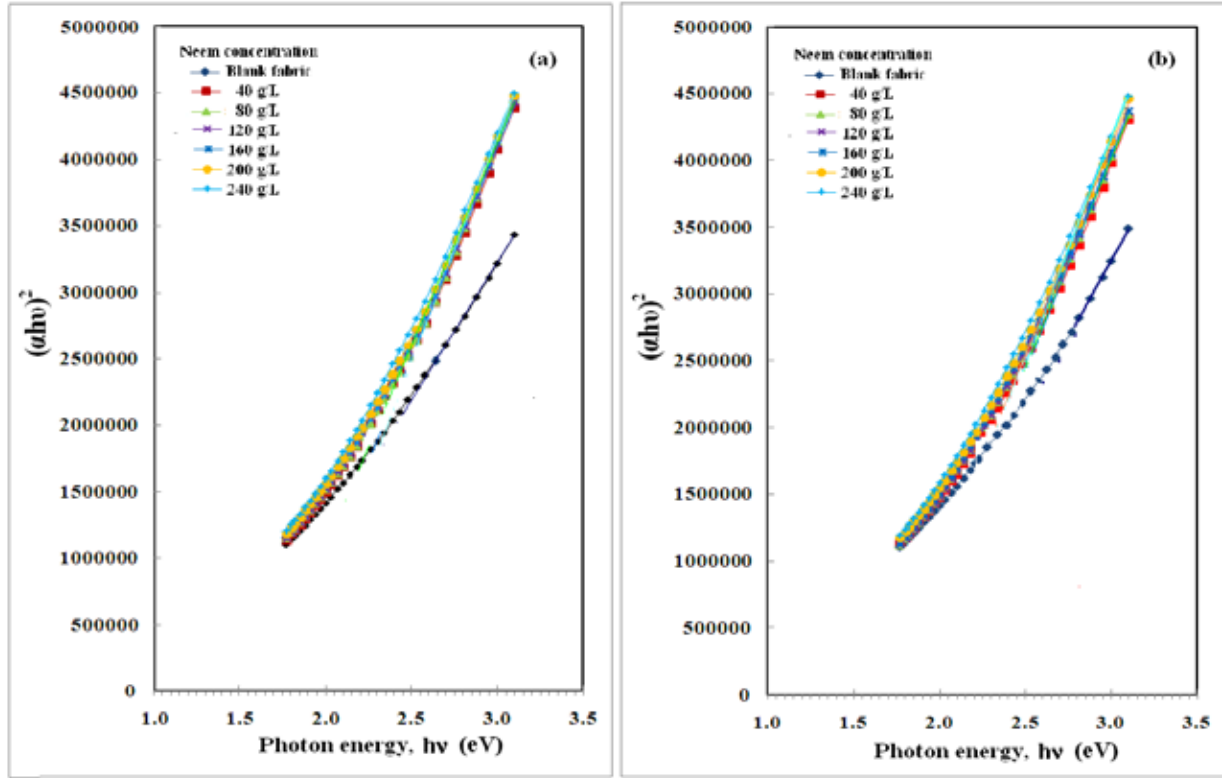


Fig. 7. Variations of $(\alpha h\nu)^2$ with photon energy ($h\nu$) for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

Figure 8 shows the dependence of $(\alpha h\nu)^{1/2}$ on the photon energy ($h\nu$) for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light. Again, as mentioned before, the obtained changes may be due to the change in molecular configuration which leads to structural variations.

The extinction coefficient (K) characterized the photonic material and represented the properties of the material to light and can be calculated by using Equation 2 [29]. The variations in the extinction coefficients (K) as functions of wavelength for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h were illustrated in Figure 9. It was noticed from the figure that, the variation behaviors of K for all samples were similar through the whole wavelength range. In addition, the values of the extinction coefficient were found to be small (in the order 10^{-4}). This indicates that silk fabrics may be considered as an insulating material at room temperature [45]. Moreover, the increase in the extinction coefficient values with increasing the concentration of neem dye without or with exposure to artificial light shows that the fraction of light lost could be due to scattering.

By determining the color strength (α/S) value of a dyed material, a close relationship to the amount of dye absorbed by the fabric was obtained. Using Equation 3, the effect of increase in the neem dye bath concentration on the color strength of the nopr-dyed for the unexposed (a) and exposed (b) silk fabrics was illustrated in Figure 10. It is clear from the figure that the values of the color strength decrease sharply with increasing wavelength for all samples. On other hand, α/S values increase with increasing the quantity of neem leaves in the extraction bath up to 240 g/L for both unexposed and exposed samples through the whole wavelength region. This means that, higher the concentration of neem higher is the coloring component extracted and higher is the color strength of the fabric dyed with these extracts which means that a deepest shade was occurred.

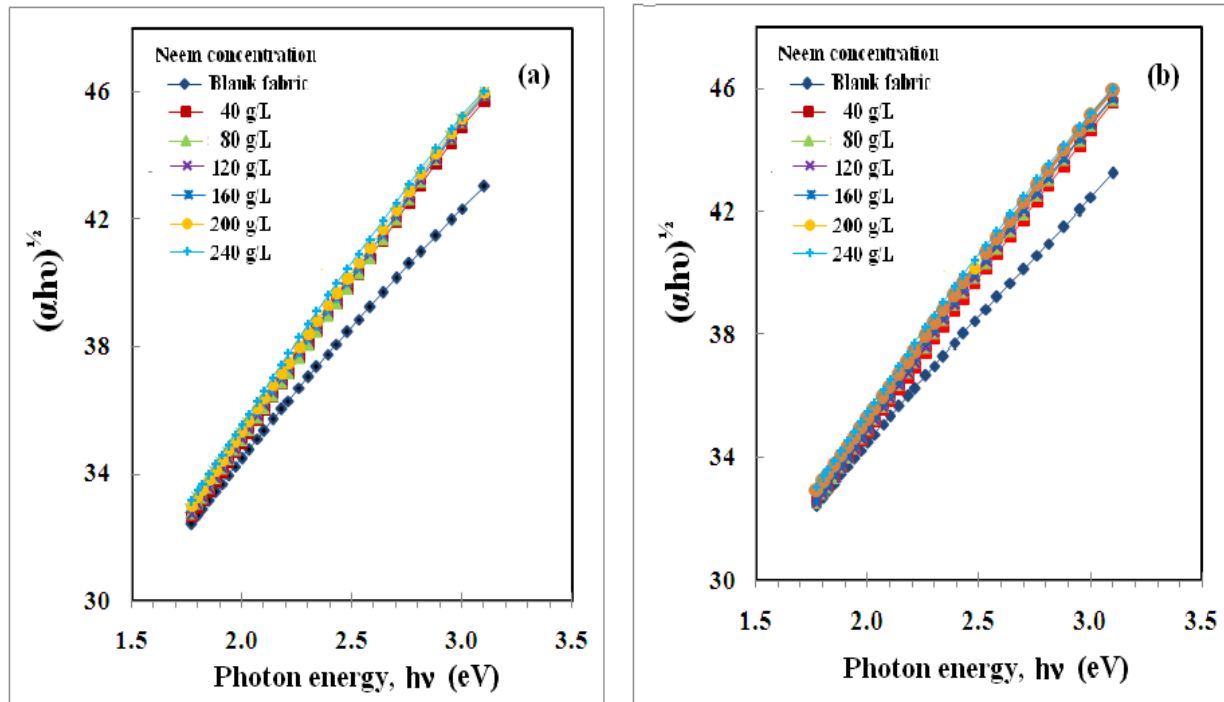


Fig. 8. Variations of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

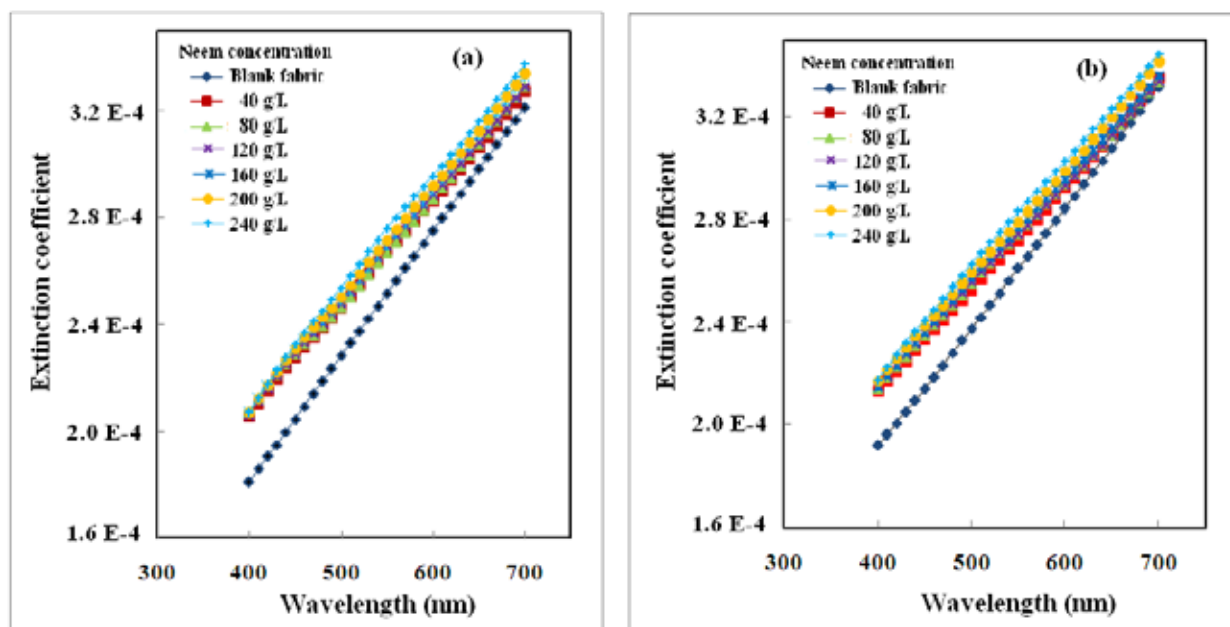


Figure 9: Dependence of the extinction coefficient on wavelength for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

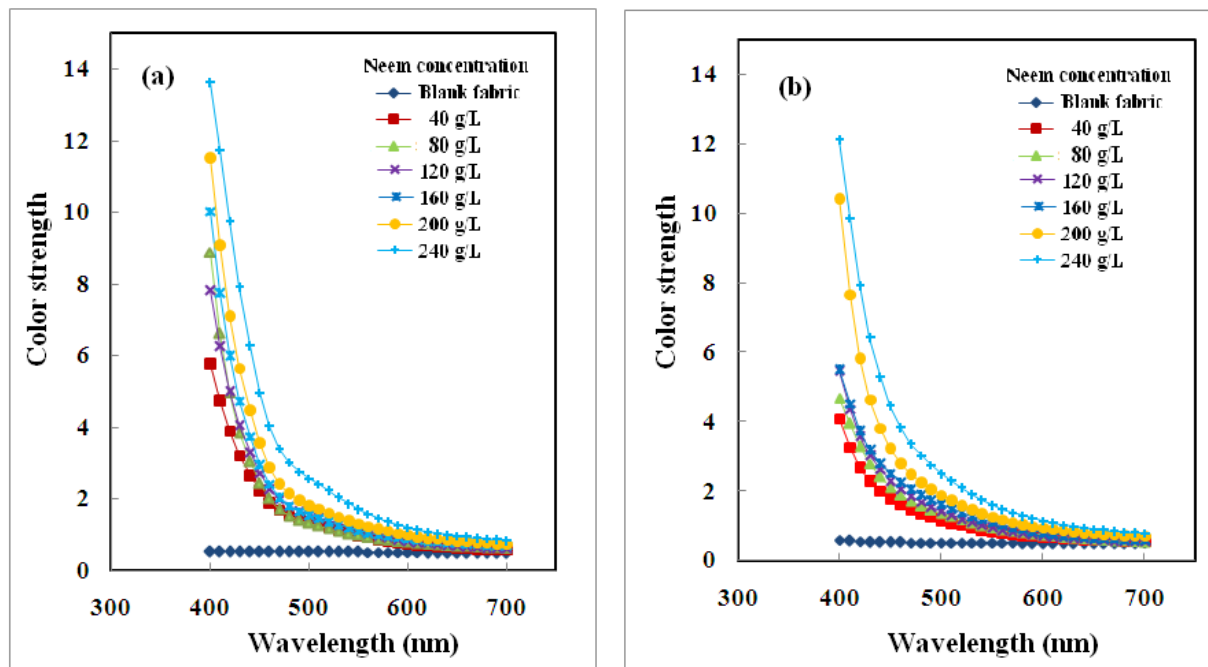


Fig. 10. Dependence of the color strength on wavelength for undyed and neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h.

In addition, the effect of the dye bath concentration can be attributed to the correlation between dye and silk fibers. Since neem dye is a water soluble dye and containing anionic groups, these groups would interact ionically with the protonated terminal amino groups of silk fabrics through ion exchange reaction. Then, due to this ionic attraction, the dye-ability of the fiber would increase with increasing the neem dye concentration. This increase in the dye-ability may be due to: 1) the enhanced desorption of the dye, 2) the greater availability of the dye molecules in the vicinity of the fiber, and 3) the increase in diffusion due to the increase in the amorphousity of the fiber. The present data are in good agreement with the previously reported results [46-48].

3.2. Tristimulus Values and Color Parameters

The variations of the tristimulus values (x_r , y_r , and z_r), the relative brightness (L^*), color constants (a^* and b^*), whiteness index (W), color difference (ΔE), chroma (C^*), hue (H) and tint (T) for undyed and neem dyed silk fabrics with different dye bath concentrations (40, 80, 120, 160, 200 and 240 g/L) before and after exposure to artificial day light for 160 h were calculated from the values of the reflectance percentage spectra represented in Figure 3. The tristimulus reflectance values (x_r , y_r and z_r) for the undyed silk fabric as well as the unexposed (a) and exposed (b) neem dyed silk fabrics with different dye bath concentrations were plotted against wavelength (400-700 nm) and were illustrated in Figures 11, 12, 13 and 14, respectively. It was observed from the figures that, the behaviors of x_r , y_r and z_r for the samples are similar and there are no change in the peak positions either without or with exposure to the artificial day light.

Table 2 illustrates the maximum tristimulus reflectance values at their peak positions for undyed and neem dyed silk fabrics under investigation. It was noticed from the table that, the tristimulus values decrease with increasing the neem dye bath concentration. Also, the tristimulus values of the exposed silk fabrics to artificial day light were higher than those of the unexposed values for all samples. In addition, the x_r , y_r and z_r values for all samples either unexposed or exposed to artificial day light were lower than that of the undyed silk fabric.

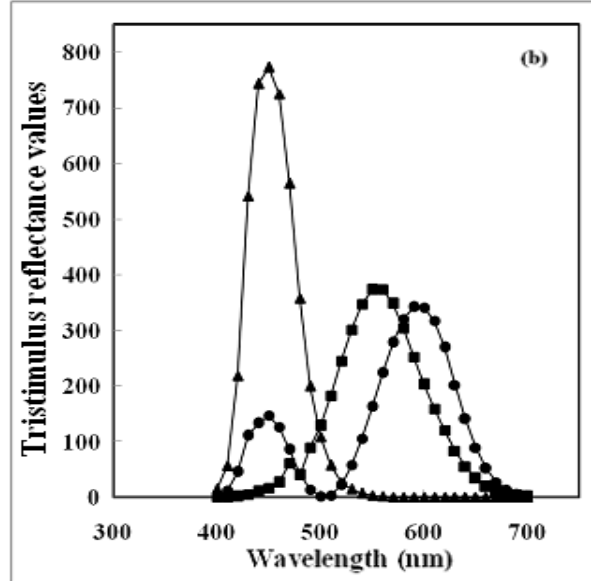
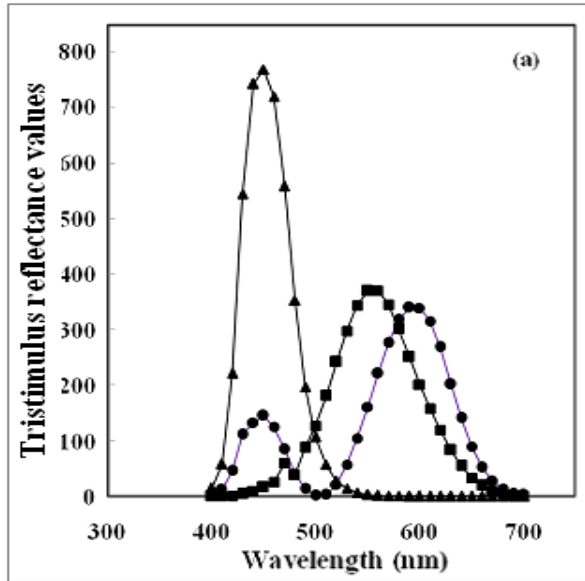


Fig. 11. Variations of the tristimulus reflectance values [x_r (▲), y_r (■) and z_r (●)] with wavelength for undyed silk fabrics before (a) and after (b) exposure to artificial day light for 160 h

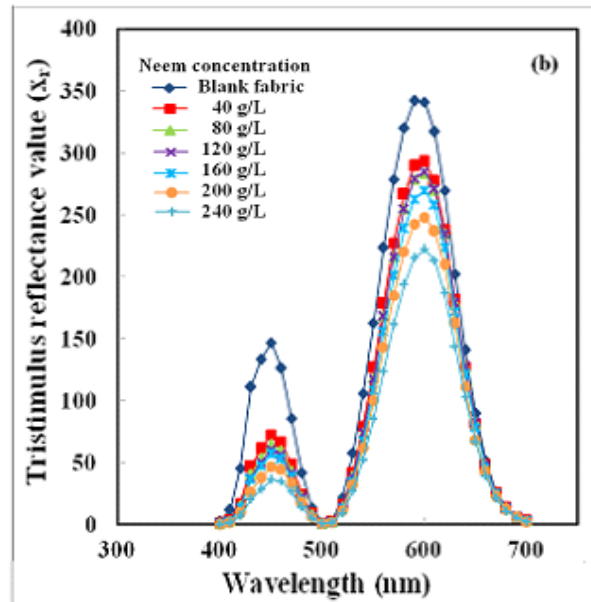
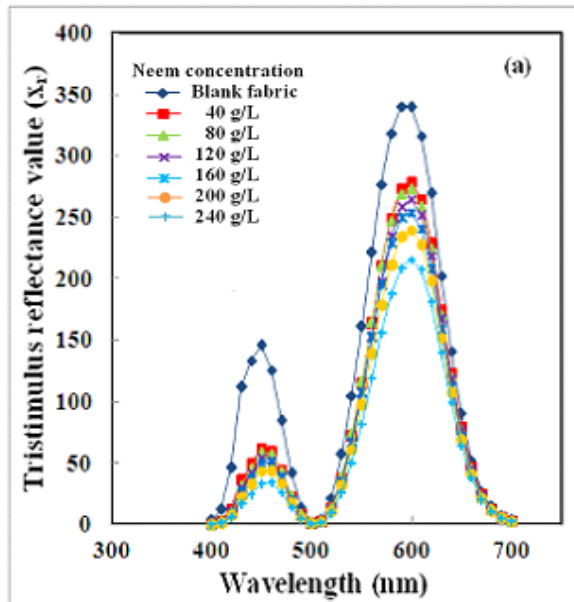


Fig. 12. Variation of the tristimulus reflectance value (x_r) with wavelength for neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

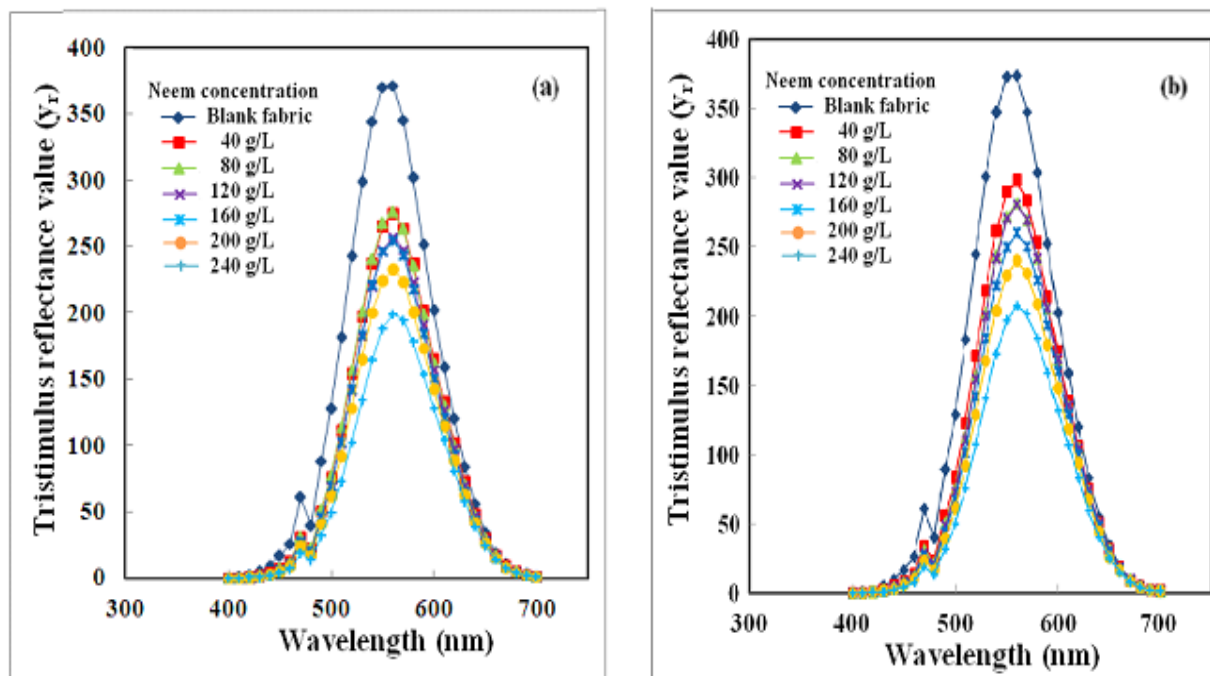


Fig. 13. Variation of the tristimulus reflectance value (y_r) with wavelength for neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

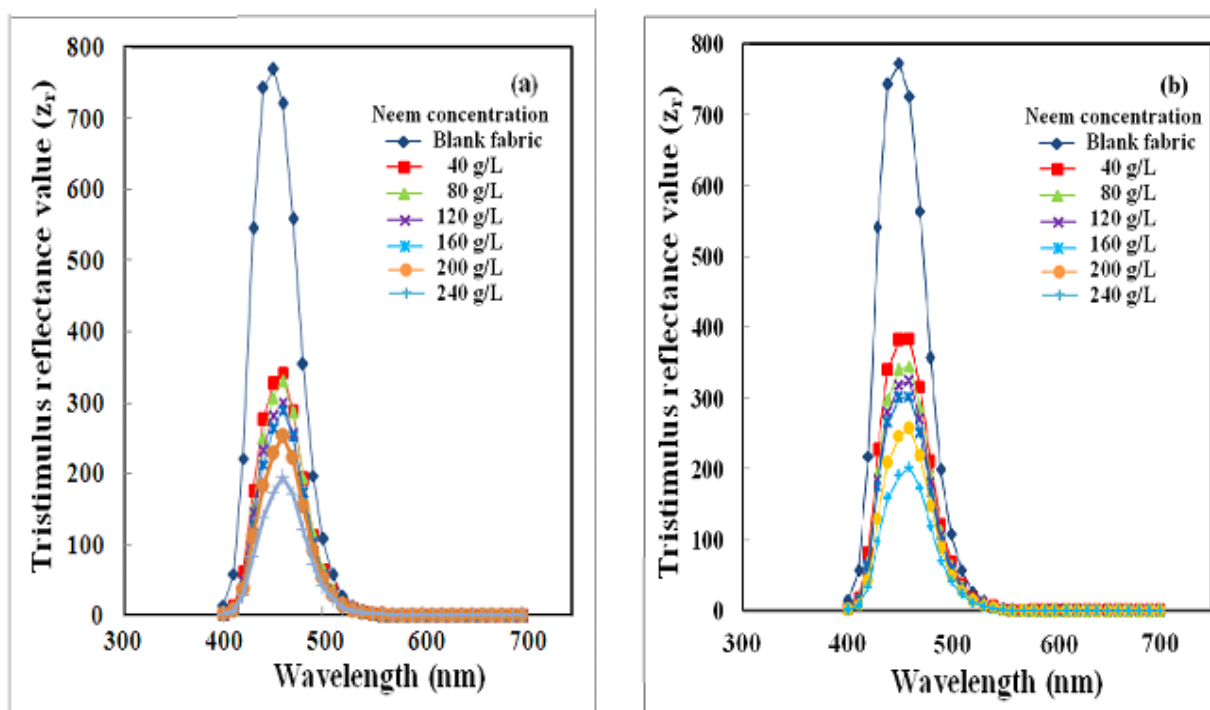


Fig. 14. Variation of the tristimulus reflectance value (z_r) with wavelength for neem dyed silk fabrics with different dye bath concentrations before (a) and after (b) exposure to artificial day light for 160 h

Table 2. The maximum tristimulus transmittance values (x_t , y_t and z_t) at their peak positions for undyed and neem dyed silk fabrics with different dye bath concentrations before and after exposure to artificial day light for 160 h

Concentration of neem (g/L)	x_r		y_r		z_r
	$\lambda = 450 \text{ nm}$	$\lambda = 600 \text{ nm}$	$\lambda = 560 \text{ nm}$	$\lambda = 460 \text{ nm}$	
Unexposed silk fabric samples					
Undyed fabric	146.0691	339.8218	371.4584		743.6189
40	62.0946	279.0685	274.9741		342.0297
80	58.1611	273.4286	270.1697		330.7398
120	53.5936	264.8124	257.2465		300.4856
160	50.1397	254.0206	254.8922		289.2546
200	43.3988	239.9007	232.9487		252.2351
240	33.0628	215.7222	199.1904		194.2606
Exposed silk fabric samples to artificial day light for 160 h					
Undyed fabric	146.6637	340.8764	373.810		773.141
40	72.5489	292.7307	298.1331		382.4428
80	64.5259	283.5043	281.8621		340.7334
120	60.6367	284.5782	280.7478		319.0635
160	56.9633	269.5439	259.9992		300.2829
200	46.8626	248.1558	239.6284		247.0369
240	36.2294	222.0694	207.3794		190.9841

The color properties such as: the relative brightness (L^*), color constants (a^* and b^*), whiteness index (W), color difference (ΔE), chroma (C^*), hue (H) and tint (T) were analyzed using the CIE Colorimetric System, CIE 1931 2-degree Standard Observer and were tabulated in Table 3. From the table it was noticed that: The relative brightness, L^* , shows decrease in their values with increasing neem concentration and exposure to artificial day light which means that the fabric becomes fader in color. The values of the color constant, a^* , increase by increasing neem concentration and exposure to artificial day light which indicates that, there is an increase in red component instead of green component. The values of the color constant, b^* , increase by increasing neem concentration and exposure to artificial day light which indicates that there is an increase in yellow component instead of blue one. The detection of the whiteness index (W) and tint, T , values indicated opposite behavior in comparison with the color constants, a^* and b^* . The observed decrease in the whiteness index, W , values and the results of the color scales, C^* and H , as well as color difference, ΔE , indicated that variations in color difference between the fabrics and the neem dyed were occurred due to the presence of different neem concentration and/or exposure to artificial day light.

As noticed from Table 3, the observed changes in the values of the color parameters by increasing neem concentration and/or exposure to artificial day light for 160 h may be due to the change in the physical bonds and then changes in the molecular configuration of the fabric which may lead to formation of new color centers. In addition, the obtained results of the color parameters were of great importance for the improvement of the optical properties of the fabrics.

3.3. Wash Fastness Test

Table 4 shows the wash fastness properties of the undyed and neem dyed silk fabrics with different dye bath concentrations. It was noticed that as the dye concentration increase, the samples give excellent rating. Other samples give rating good to very good. This is because the ionic bonds between dye molecules and the carboxyl groups in the silk fiber are strong. Also, in this natural dye there are chemical groups such as $C=C$ and $C=O$ which adsorb in the fiber and increase washing fastness due to its saturation properties.

Table 3. The color parameters for undyed as well as neem dyed silk fabrics with different dye bath concentrations before and after exposure to artificial day light for 160 h

Color parameters	Concentration of neem (g/L)						
	0	40	80	120	160	200	240
L*							
Before exposure	75.75	58.74	57.00	58.71	56.63	54.58	50.85
After exposure	67.98	60.88	58.99	59.22	57.23	55.07	51.67
a*							
Before exposure	-0.09	2.30	2.82	2.43	2.69	2.83	4.86
After exposure	0.15	1.50	3.09	2.86	4.17	3.39	5.06
b*							
Before exposure	-0.86	20.29	22.28	22.28	23.46	24.43	26.23
After exposure	0.74	17.99	21.58	19.77	20.76	23.62	25.50
W							
Before exposure	-	-107.06	-125.20	-121.50	-135.30	-147.30	-169.60
After exposure	33.50	-87.90	-114.7	-102.6	-113.9	-139.5	-161.80
$\Delta E^{(1)}$	-	22.95	25.52	24.69	26.59	28.43	32.16
$\Delta E^{(2)}$	1.44	3.11	2.12	3.53	4.45	1.66	1.11
$\Delta E^{(3)}$	-	4.16	2.78	4.66	5.45	2.66	2.66
C*							
Before exposure	0.80	20.42	22.46	22.29	23.47	24.51	26.68
After exposure	0.80	18.05	21.80	19.98	21.17	23.76	26.00
H							
Before exposure	101.50	83.52	82.80	88.90	88.31	85.26	79.50
After exposure	101.46	85.23	81.85	81.77	78.64	81.83	78.78
T							
Before exposure		-17.70	-20.70	-13.50	-15.30	-20.40	-31.90
After exposure	0.00	-13.70	-20.50	-18.80	-23.70	-23.90	-31.70

1) Variation in ΔE^* due to different neem dye bath concentrations

2) Variation in ΔE^* due to exposure to artificial day light for 160 h

3) Variation in ΔE^* due to due to different neem dye bath concentrations after exposure to artificial day light for 160 h

Table 4. Wash fastness rating for undyed as well as neem dyed silk fabrics with different dye bath concentrations

Concentration of neem (g/L)	Wash fastness		
	Assessment of change in color	Assessment of staining	
		Silk	Cotton
Undyed fabric	4	4-5	4-5
40	4	4-5	4-5
80	4	4-5	4-5
120	4-5	5	4-5
160	4-5	5	5
200	4-5	5	5
240	5	5	5

4. CONCLUSIONS

The present study was planned, to be looked out for safer alternative for dyeing with natural dyes. Leaves of neem can be used as dye for coloring textiles. It was found that neem dye can be successfully used for dyeing of silk fabric to obtain wide range for soft hell shades. The process of extraction was simple and environmental friendly. The natural colorant obtained from neem leaves has been successfully used as an eco-friendly dye to obtain different shades of yellow.

It was concluded that the absorption coefficient, extinction coefficient, color strength, tristimulus values and color parameters values were found to be influenced by either the concentration of the neem dyeing bath and/or exposure to artificial day light for 160 h with respect to the chemical structure of the used dye. Moreover, the dye-ability of silk fabrics was investigated. The increase in the dye-ability may be due to: the enhanced desorption of the dye, the greater availability of the dye molecules in the vicinity of the fiber, and the increase in diffusion due to the increase in the amorphousity of the fiber. Broad variations in shade and color depth were achieved, which indicate that the dye is environmentally and ecological acceptable for dyeing technology. Moreover, neem plant shows good shade reproducibility with significant fastness properties.

It was mentioned that, it is the first time that Egyptian silk fabrics were dyed with neem dyed extract. Also, it is the first time this search was investigated by optical technique.

REFERENCES

1. Da Eun Chung, Hyung Hwan Kim, Moo Kon Kim, Ki Hoon Lee, Young Hwan Park, In Chul Um. Effects of different Bombyx mori silkworm varieties on the structural characteristics and properties of silk. International Journal of Biological Macromolecules 2015;79:943-51.
2. Guan J, Yang ChQ, Chen G. Formaldehyde-free flame retardant finishing of silk using a hydroxyl-functional organophosphorus oligomer. Polymer Degradation and Stability 2009;94:450-5.
3. Koh L-D, Cheng Y, Teng C-P, Khin Y-W, Loh X-J, Tee S-Y, Low M, Ye E, Yu H-D, Zhang Y-W, Han M-Y. Structures, mechanical properties and applications of silk fibroin materials. Progress in Polymer Science 2015;46:86-110.
4. Kaplan D, Adms WW, Farmer B, Viney C. Silk Polymer Material Science and Biotechnology, American Chemical Society; Washington; Chapter 1; 1993.
5. Hojo N. Structure of Silk Yarns, Science Publisher, Inc.; 2000.
6. Skeikh MRK, Farouqi FI, Moak PR, Hoque MDA, Yasmin ZJ. Dyeing of Rajshahi silk with basic dyes: Effect of modification on dyeing properties. Journal of the Textile Institute 2006;97:295-300.
7. Ahmad Khan S, Ibrahim Khan M, Yusuf M, Shahid M, Mohamed F, Ali Khan A. Natural dyes shades on woollen yarn dyed with Kamala (*Mallotus philippinesis*) using eco friendly metal mordants and their combination. Colourage 2011;58:38-44.
8. Shaoyong Chen, Lan Cheng, Huiming Huang, Fengzhu Zou, Hong-Ping Zhao. Fabrication and properties of poly(butylene succinate) biocomposites reinforced by waste silkworm silk fabric. Composites: Part A 2017;95:125-31.
9. Li G, Liu H, Li T, Wang J. Surface modification and functionalization of silk fibroin fibers/fabric toward high performance applications. Materials Science and Engineering: C 2012;32:627-36.
10. El-Nagar K, Sanad SH, Mohamed AS, Ramadan A. Mechanical properties and stability to light exposure for dyed Egyptian cotton fabric with natural and synthetic dyes. Polymer-plastics Technology and Engineering 2005;44:1269-79.
11. Iqbal MJ, Ashiq MN. Adsorption of dyes from aqueous solutions on activated charcoal. Journal of Hazardous Materials 2007; 139:57-66.
12. Gulrajani ML. Present status of natural dyes. Indian Journal of Fiber and Textile Research 2001;26:191-201.

13. Kumaresan M. Comparison of properties of eco-friendly natural dyed cotton fabric. *Der Pharma Chemica* 2015;7:257-60.
14. Nattadon Rungruangkitkrai Rattanaphol Mongkholrattanasit, RMUTP, International Conference: Textiles and Fashion July 3-4, Bangkok Thailand; 2012.
15. Alam MM, Rahman MI, Haque MZ. Extraction of Henna leaf dye and its dyeing effects on textile fibers. *Journal of Science and Industrial Research* 2007;42:217-22.
16. Chengaiah B, Mallikarjuana Rao K, Mahesh Kumer K, Alagusundaram M, Madhusudhana chetty C. Medicinal Importance of natural Dyes - A review. *International Journal of Pharm Tech Research* 2010;2:144-54.
17. Makkar P, Singh SS, Rose N. Colour fastness Properties of tesu dyed silk. *Research Journal of Family, Community and Consumer Science* 2013;1:1-5.
18. Shahid-ul-Islam M Shahid, Mohammad F. Perspectives for natural product based agents derived from industrial plants in textile applications: a review. *Journal of Cleaner Production* 2013;57:2-18.
19. Shahid-ul-Islam M Shahid, Mohammad F. Recent advancements in natural dye applications: a review. *Journal of Cleaner Production* 2013;53:310-31.
20. Bakhru HK. *Herbs that Heal*, Orient Paper Books; New Delhi; 1992.
21. Patel BH. Dyeing and antimicrobial finishing of polyurethane fibre with Neem leaves extract. *Man-Made Textiles in India* 2009;52:112-6.
22. Kokate CK, Purohit AP, Gokhale SB. *Pharmacognosy*, 12th Edn., Pune; Nirali Prakashane, 1990.
23. Grover GS, Rao JT. Investigation on the antimicrobial efficiency of essential oils *Ocimum sanctum* and *Ocimum gratissimum*. *Perfume and Kosmet* 1979;56:50-2.
24. Schmutterer H. The Tree and its Characteristics. In: *The Neem Tree Azadirachta indica* A. Juss and other Meliaceous Plants: Sources of Unique Natural Products for Integrated Pest Management, Medicine, Industry and Other Purposes, ed. H. Schmutterer, VCH Weinheim, Germany; 1995.
25. Eppler A. The Neem Tree *Azadirachta indica* A. Juss and other Meliaceous plants, ed. H. Schmutterer, VCH Weinheim, Germany; 1995.
26. Manjinder Singh Khehra, Harvinder Singh Saini, Deepak Kumar Sharma, Bhupinder Singh Chadha and Swapandeep Singh Chimni, Biodegradation of Azo Dye C.I. Acid Red 88 by an anoxic-aerobic sequential bioreactor. *Dyes and Pigments* 2006;70:1-7.
27. Guirguis OW, Moselhey MTH. Optical study of poly(vinyl alcohol)/hydroxypropyl methylcellulose blends. *Journal of Materials Science* 2011;46:5775-89.
28. Maradulin AA, Montroll EW, Weiss GH. *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic Press, New York, USA; 1963.
29. Tintu R, Saurav K, Sulakshna K, Nampoori VPN, Radhakrishnan P, Sheemu Thomas. $\text{Ge}_{28}\text{Se}_{60}\text{Sb}_{12}/\text{PVA}$ composite films for photonic applications. *Journal of Non-oxide Glasses* 2010;2:167-74.
30. Mott NF, Davis EA. *Electronic Processes in Non-Crystalline Materials*. Oxford: Clarendon; 1979.
31. Wood DL, Tauc J. Weak absorption tails in amorphous semiconductors. *Physical Review B* 1972;5:3144-50.
32. Judd DB, Wyszzecki G. *Color in Business Science and Industry*, 3rd Edition, John Wiley & sons, Inc. New York; 1975.
33. CIE Recommendations on Colorimetry; CIE Publ. No: 15.2. Central Bureau of the CIE, Vienna; 1986.
34. CIE Recommendations on Uniform Color Spaces, Color Difference Equations, Psychometric Color Terms, Suppl. No. 2 of CIE Publ. No. 15 (E-1.3.1), Paris; 1971;1978.
35. Christi RM, Mather RR, Wardman RH. *The Chemistry of Colour Application*. 1st Edition, John Wiley & Sons Ltd, Blackwell Science Ltd, Oxford, UK; 2000.
36. Kubelka P. New contributions to the optics of intensely light-scattering materials. Part I. *Journal of the Optical Society of America* 1947;38:448-57.
37. Kubelka P. New contributions to the optics of intensely light-scattering materials. Part II, Nonhomogenous Layers. *Journal of the Optical Society of America* 1954;44:330-5.
38. Tera Light Fastness Tester, Egypt, Patent No. 15182; 1981.
39. Al-Amoudy ES, El-Ebissy AA. Optical studies of cotton fabrics dyed with a natural dye, *British Journal of Applied Science & Technology* 2015;9:159-71.

40. Robertson SM. Dyes from Plants. Van Nostrand Reinhold Company, New York, Toronto, London; 1973.
41. Miller A. Handbook of Optics, Vol. 1, McGraw-Hill, New York, USA; 1994.
42. Chikwenze RA, Nnabuchi MN. Effect of deposition medium on the optical and solid state properties of chemical bath deposited CdSe thin films. Chalcogenide Letters 2010;7:389-96.
43. Abd El-Kader FH, Gafer SA, Basha AF, Bannan SI, Basha MAF. Thermal and optical properties of gelatin/poly(vinyl alcohol) blends. Journal of Applied Polymer Science 2010;118:413-20.
44. Lever ABP. Organic Electronic Spectroscopy, Elsevier, Amsterdam, Netherland; 1968.
45. Pankove JI. Optical Process in Semiconductors, Devers Publication, New York, USA; 1975.
46. Mansour HF, Haroun AA. 6th International Conference of Textile Research Division, National Research Center, Cairo, Egypt; 2009.
47. Al-Amoudy ES, Osman EM. Optimization of dyeing performance of an eco-friendly natural dye "Vervain Barks" applied to silk fabrics at different pH values. Research Journal of Textile and Apparel 2009;13:34-45.
48. Ebtsam S. Al-Amoudy, Extraction and application of novel eco-friendly natural dye obtained from leaves of sanamicky on silk fabric. British Journal of Applied Science & Technology 2016;14:1-12.