
PHYSICO-CHEMICAL STUDIES AND APPLICATION OF SOME NATURAL EXTRACTS AND ITS METALLIC MORDANT COMPLEXES AS DYES FOR TEXTILE FABRICS

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Abstract

The aim of this present study is to evaluate the performance and efficiency of dyeing of cotton, wool and polyamide **from dry skin Allium cepa and henna** fabrics with natural dyes obtained as extracts leaves.

In recent years, an upsurge of interest in natural dyes has been manifested as replacement of synthetic dyes for food and drugs' safety and so forth. Natural dyes have limitations of fastness, and brilliancy of shade. Therefore, in present work, use of metallic mordant was investigated to produce depth of shade, bright and fast colors. Natural dyes may chemically be classified as vat, direct, acid and/or pigment. Accordingly, efficiency and performance of dyeing were assessed on different natural and synthetic fibers. However, some good fast colors were obtained.

The preference of using easily, and cheaply, without any chemical processing, results in availability of materials for dyeing by conventional dyeing which lowers the cost of natural dyeing; this enhances resource productivity, and as a result, reduces solid wastes. This makes onion scale and henna leaves one of the easily available raw materials for natural dyeing industry. However, part (II) of present work compiles preparation , physico-chemical assessment, and application of some metallic mordant's (Cr^{+3} , Co^{+2} , Ni^{+2} , Cu^{+2}) of present natural dyes ,in a trial to obtain more chromaticity ,affinity and better fastness of colour.

1. Introduction

The colour reaction between metal ions and natural phenolic dyes (esp. quercetine) from onion skin and use of the colour reaction products in staining of natural and synthetic fibre materials, including nylon, wool, silk, kapok, polyesters has been demonstrated ^[1]. Several workers have used onion scales for wool dyeing^[2,3,4] However, we have shown the versatility of dyeing with allium skin extract for all the three types of natural fibers. In the present study onion scales have been used as natural dye source which has been developed scientifically for generating shades of light brown-dark brown for cotton, silk and wool dyed samples.

The name is also used for dye preparations derived from the plant. (Scientific classification: Kingdom: Plantae; Division: Magnoliophyta; Class: Magnoliopsida;

Order: Myrtales; Family: Lythraceae; Genus: Lawsonia a Species: *L. inermis*; Binomial name; *Lawsonia inermis* L). Henna (*Lawsonia inermis*, also called mignonette tree) is a flowering plant which has been used since the Bronze Age to dye skin (including body art), hair, fingernails, leather, silk and wool. The trivial name of this compound was hennotannic acid. Interesting from the chemists' point of view are the redox properties of naphtha quinones such as lawsone. Henna is commercially cultivated in Morocco, Yemen, Tunisia, Libya, Saudi Arabia, Egypt, Western India, Iran, Pakistan, Bangladesh, Afghanistan, Turkey, Somalia and Sudan. Henna's coloring properties are due to lawsone, a burgundy organic compound that has an affinity for bonding with protein. Lawsone is primarily concentrated in the leaves, especially in the petioles of the leaf. Henna, *Lawsonia inermis* produces a red orange dye molecule, "lawsone", also known as hennotannic acid. This molecule has an affinity for bonding with protein and has been used to dye skin, fingernails, hair, leather, silk and wool. [5]

Material and Experimental work

2.1. Extraction of Lawsone from henna leaves

Henna leaves were washed with distilled water and then dried at room temperature. The dried leaves were grounded to obtain particles of uniform size. [6] 100g dried powder sample was taken in saturated Na_2CO_3 solution for 24 hours at pH 8.5-9.2 at room temperature. The solution becomes reddish orange colour. Then percolated with Na_2CO_3 solutions until all of the colour has been removed and then filter again. The reddish orange colour was developed due to the presence of alkali. The alkali reddish orange colour solution was acidified with dilute hydrochloric acid at pH 4-5. After acidification the color of solution becomes orange. This colour is developed by the action of acid. The acidified colour solution was taken into separating funnel and shaken with successive portion of chloroform. The chloroform extract was dried with anhydrous sodium sulfate and filtered. The chloroform extract has an orange yellow colour, this solution kept away from light until all the chloroform were vaporized. [7]

2.1.1 Chemical review in henna leaves

The principal coloring matter of henna is Lawsone , 2- hydroxy-1, 4 naphthaquinone. Besides Lawsone other constituents present are Gallic acid, glucose, mannitol, fats, resin (2 %), mucilage and traces of an alkaloid. [8]

2.1.2. Physical Properties of lawsone

The dye component present in the leaves of henna is "Lawsone" which is identical with 2-hydroxyl, 4-naphthoquinone. It is an organic pigment, yellow crystal, m.p. 192-195°C. Lawsone has a very small molecule and exhibits a remarkable substantivity for wool, silk and also polyamide.^[9]

2.2. Extraction of quercetin from onion skin

Onion peels discarded from a food factory were collected and rinsed with water until the wash water was clear. After washing they were air-dried at room temperature.^[10]

Soxhlet apparatus was used to extract the dyestuff from the onion's skin. The Solvent (water) was evaporated. All of the solvents used during the experiment such as n-hexane and water were redistilled before use.^[11]

- 1- The dried onion skin (25 g) was left for 24 h in distilled n-hexane to separate terpens.
- 2- After decantation, the residue was extracted with 1000 ml of distilled water by using the Soxhlet apparatus.
- 3- 1000 ml of solution (dye-bath) was evaporated in oven, until all the solutions evaporate.
- 4- Recrystallization by methanol to remove any impurities.
- 5- Extract was subjected to silica gel column chromatography. The column was eluted with n-hexane/ethyl acetate (7:3) in (50 ml).^[11]

2.2.1. Chemical review in red onion skin

Preliminary phyto-chemical screening revealed the presence of Carbohydrate, terpens, Proteins, Phenolic compounds and Saponins.^[12]

2.2.2. physical properties of quercetine

The dye component present in the onion skin is quercetine which is identical with 3,3',4',5,7-Pentahydroxyflavone, it is an pale - yellow needles, Melting point: 316.5°C, boiling point, Sublimes. quercetine Slightly soluble in water and diethyl ether; soluble in ethanol and acetone. Despite the presence of five hydroxyl groups, the quercetine molecule has a lipophilic character.^[13]

2.3. Dyeing of cotton, wool and polyamide by onion and henna dyes

2.3.1. Dyeing of wool

Before dyeing the woolen yarn samples were soaked in water for 30 min. Water soaked woolen yarn samples without any mordant were drenched in extracted dye

solution keeping M:L ratio 1:40 and pH was adjusted at (4-4.5) with sodium acetate and acetic acid solution for dyeing with henna in bath. Temperatures of the dye baths were raised till simmering point (91–93 C⁰) and left at that temperature for 1 h with regular stirring. The dyed woolen yarn samples were washed with 5 g/L non-ionic detergent and then, rinsed with tap water.^[14]

2.3.2.Dyeing of cotton

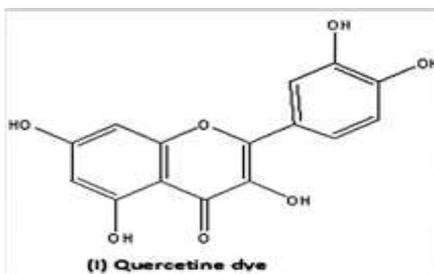
The knitted fabric samples were immersed in a dye bath composed of the natural dye (5% o.w.f); nonionic wetting agent (2g/L), salts (NaCl or Na₂SO₄) (10g/L), using the dye liquor ratio (1:40), at pH 4 using acetic acid. The dye bath temperature was gradually raised (about 1°C/min) up to 100°C, and was kept at this temperature for 60 min. The dye bath temperature was then allowed to cool to about 60 C⁰, then the dyed fabric samples were squeezed, rinsed thoroughly with hot and cold water.^[15]

2.3.3.dyeing of polyamide

The fabrics were dyed by the pad method with (5% o.w.f) dye in a bath containing (8 % o .w .f) sodium acetate and (4 % o.w.f) acetic acid, with a liquor ratio of 1:20. Firstly, salt and acid were added to water and the dyeing bath was warmed at 50°C, then the samples were immersed in the dyeing bath and the dyeing continued for 10 min., followed by adding the dye solution and the dyeing continued for 15 min., then the temperature was raised to boiling through 20 min, the dyeing was continued at this temperature for (45 min), Finally the dyeing was stopped and the dyeing bath was cooled. Dyed samples were thoroughly rinsed with running cold water, then soaped with a solution containing 5 g/L nonionic detergent and 1g/L Na₂CO₃ at 40°C for 15 min, Soaping were carried out for 4 times to ensure good washing fastness.^[16]

Results and discussion

3.1. Chemical and spectral assignment of quercetin dye



Spectroscopic analysis of the crude extract of onion skin and henna leaves was carried out mainly to find the chromophores present in the colorant of the extract and its extent of absorbance (Visible spectrum) and presence of functional group (FT-IR spectrum) which would help in understanding The chelation mode of the metal mordant effectively to the dye molecule. Hydroxy and Oxo groups present in the quercetine and lawsone structures have ability to form complexes with various metal ions. As the 3-hydroxy group (3-OH) and 4-oxo group (I) have more acidic protons, they are the first sites to be involved in the complexation processes.^[13]

UV-Visible spectrum of quercetine showed that the methanolic extract from onion shows λ_{max} at 256 nm and 370 nm in Fig (1), Which are characteristic for π - π^* (for π -bond electrons) and n- π^* (for lone pair) transitions, respectively.

FTIR spectrum of quercetine, fig(2) showed the characteristic -OH stretching vibration at 3270 cm^{-1} , and other bands appear at 1662 cm^{-1} for C=O ketone and ($1316, 1362$) cm^{-1} for C-O phenol and ($1562, 1610$) cm^{-1} for C=C in aromatic ring and other bands appear at ($1096, 1164$) cm^{-1} for C-O ether.

GC- Mass spectrum of quercetine dye fig. (3) Showed one peak for the Compound and molecular ion peak at m/e 302(1.52%), with base peak at m/e 111(100%) and other significant peak at m/e 65(66%).

3.2. Chemical and spectral assignment of the henna dye extract

UV spectrum of lawsone in CH_3OH showed λ_{max} at 244, 275 and 332 nm absorptions in fig (4). UV- visible spectra gave a band in the 240- 275 nm region corresponding to the intense benzene and quinone π - π^* electron transitions and the second band observed at 332 nm may be attributed to n- π^* transitions of carbonyl group in the quinone ring.^[17]

FT-IR spectrum of lawsone, fig (5) showed the characteristic -OH stretching vibration at 3154 cm^{-1} , and other bands appear at 1610 cm^{-1} for C=O ketone and 1386 cm^{-1} for C-O phenol and 1580 cm^{-1} for C=C in aromatic ring.

GC- Mass spectrum of lawsone dye fig. (6) Showed two peak for the compound and molecular ion peak at m/e 174(54%), with base peak at m/e 106(100%) and other significant peak at m/e 77(74.5%).

3.3. Assessment of extracted dyes.

3.3.1. U.V spectrum and behavior of extracted dyes in organic solvents.

The results obtained from the table (1) indicate that these dyes have limited solubility in water, as well as solubility in organic solvents. The spectra of some extracted dyes have been measured in organic solvents of different polarities; the results are presented in table (1).

Table (1):U. V Visible spectra of extracted dye in mixed organic solvents.

Dye name	Color in crystal	Colour		In mixed		Organic		solvent	
		Methanol		DMF		Water		Water\methanol	
lawsone	Dark orange	Color	λ_{max}	color	λ_{max}	color	λ_{max}	color	λ_{max}
		Yellow	465	Reddish orange	476	Orange yellow	456	Deep orange	453
Quercetin	yellow	Lemon Yellow	370	Greenish yellow	378	Light orange	322	lemon yellow	368

It is known that intermolecular interaction have an effect on the absorption spectrum of a molecule. Solvent solute interaction can have various influences on an absorption spectrum in case of natural dye it was found that variation in the polarity and also the solvating power of solvent leads to a noticeable shift as presented in fig (7, 8).At the same time, the formation of the hydrogen bonding with the solvent stabilizes the form. Increase in polarity of the solvent such as (CH₃OH or ETOH) shifts the equilibrium towards more polar structure.

3.4.Application of natural extracts as dyes for textile fibre

3.4.1.Exhaustion Isotherm

The extent of dye exhaustion was determined spectrophotometer ically, wherein the absorbance of dye bath solution before(A_0) and after(A_1) the dyeing process was recorded at the λ_{max} of the dye. The percentage dye exhaustion (%E) was calculated using equation (1).^[18]

$$\% \text{ Dye exhaustion} = [(A_0 - A_1) / A_0] \times 100 \text{ ----- (1).}$$

3.4.2. Kinetic and thermodynamic behavior of some extracted dye on polyamide.

3.3.2.1. Effect of dyeing time

It shown from figure (9) for quercetine and figure(10) for lawsone, that with the increase in dyeing time ,more colour strength is observed .the calculated data are showed in table (2),(3), that the % of lawsone exhaustion on wool and polyamide increased from 16 and 9.76 % at 10min. to 72 and 82.38% at 60min. respectively . the % exhaustion of lawsone on the some fibers also increased from 14.88 and 16.99% at 10 min. to 48.78 and 55.33% at 60min. respectively. The less strength might be due to incomplete dyeing when insoluble impurities compete with the colourant to sorbon to polyamide and wool fabric rather than colourant. As the time of dyeing increases from moderate to high, more and more colour strength is obtained even for 120 min dyeing. This might be because of the fact that the colourant significantly gets adsorbed and then absorbed. ^[5].

Table (2): % of exhaustion of quercetine dye by different fibre at different time.

time	% of exhaustion		
	polyamide	wool	cotton
0	0	0	0
10	20	16	9.76
20	49.25	37	17.4
40	63	56	24.2
60	82.38	72	31.4
80	96.6	88	35.4
100	98.6	88	41.4
120	98.6	88	41.4

Table (3) :% of exhaustion of Lawsone dye by different fibre at different time.

Time	% of exhaustion	
	Polyamide	wool
0	0	0
10	16.99	14.88
20	31.22	27.5
40	44.07	38.72
60	55.33	48.78
80	61.66	54.22
100	62.85	55.31
120	63.24	55.5

Table (4): Comparative study of efficiency for different dyes on different fibre.

Name of dye	Temperature dyeing C ^o	Equilibrium dye take up %	Half-time of dyeing t ^{1/2}	Type of fibre
Lawsone dye	100	55.5	22	Wool
Lawsone dye	100	55.31	28	Polyamide
Quercetine dye	100	41.4	35	Cotton
Quercetine dye	100	88	30	Wool
Quercetine dye	100	98.6	28	Polyamide

The obtained results for lawsone and quercetine dyes on polyamide, wool and cotton fibers from table (4) indicate that:

i)-in case of lawsone dye ,the maximum dye uptake (55%) and this indicate that good dye uptake by the fibre.

ii)-in case of quercetine dye, the maximum dye uptake range from (41-98.5%) and this indicate that very good dye uptake by the fiber.

iii)-the $T_{1/2}$ min for lawsone and quercetine dyes range from (22-35) and this indicate that good dyeing process on fibre.

3.4.2.2.Effect of temperature

Temperature also plays a significant role in dyeing too low temperature causes in complete dyeing while too high may causede gradation of components. Hence, dyeing should be done at moderate temperatures. The dyestuff is present in water as single molecules (ionized) as well as clusters of many molecules (aggregates). Aggregates are too large to enter the interior of fibers at a given temperature. Raising the temperature leads to the breaking down of aggregates. So, the number of single molecules existing in the solution increases. It is found that colour exhaustion of lawsone and quercetine on polyamide fibre increased with increasing temperatures. Figure (12) show that the exhaustion of lawsone increase from 32.21 to 64.09 % with increase of temperature from 30C^o to 100C^o,also ,the exhaustion of quercetine increase from 40.6 to 98.7 % with increase of temperature 30C^o to 100 C^o(fig(11)).

Table (5): - Exhaustion % of quercetine dye by polyamide at different temperature.

% of exhaustion for Quercetine dye				
time	Different Temperature			
	30 C ^o	60 C ^o	80 C ^o	100 C ^o
15	31.2	32	32.9	37.3
30	37.3	43.9	49.2	51.8
45	37.8	47.9	59.1	69.1
60	38.8	61.6	65.6	82.37
75	39.4	68.2	73.6	96.6
90	40	73.1	81.1	98.6
105	40.6	73.1	81.5	98.7

Table (6): - Exhaustion % of lawsone dye by polyamide at different temperature.

% of exhaustion for Lawsone dye				
time	Different Temperature			
	30 C ^o	60 C ^o	80 C ^o	100 C ^o
15	8.97	12.9	16.39	20.7
30	20.12	25.5	27.5	30.6
45	25.92	31	33	37.5
60	30.41	35	38.5	47.2
75	31.45	35.82	42	55.7
90	32.11	36.03	47.17	63.09
105	32.21	36.25	47.37	64.09

The increased dye uptake with increase of temperature of dyeing can be attributed to the need of the dye molecule for high thermal energy to overcome the energy barrier of the fibre water interface.^[19]

3.4.3. assessment of dyeing behavior and performance of extracted dyes applied as acid dye on polyamide fibre

3.4.3.1.Colour measurement

The colorimetric properties of the dyed fabric samples were obtained with Gretag Macbeth Color-Eye 7000 A Spectrophotometer in terms of CIEL ab color coordinates (L*, a*, b*, c*, h°) and color strength values (K/S). The Color strength value (K/S) in the visible region of the spectrum (350-700 nm) was calculated based on the Kubelka-Munk equation:

$$K/S = (1-R)/2R \text{ ----- (2)}$$

Where (K) is the absorption coefficient, (R) is the reflectance of the dyed sample and (S) is the scattering coefficient.

The color difference of dyed woolen yarn samples were obtained using following relationship:

$$\text{Color Difference (E)} = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \text{ ----- (3)}$$

L describes lightness (100 = white, 0 =black), (a) measures redness (+ve), greenness (-ve) and (b) measures yellowness (+ve), blueness (- ve).^[20]

Chroma (c*) and hue angles (H°) were calculated using the equations:
Chroma

$$(c^*) = (a^2 + b^2)^{1/2} \text{ ----- (4)}$$

$$\text{Hue angle (H}^\circ) = \tan^{-1} b/a \text{ ----- (5)}$$

The difference in exhaustion rates was because of difference in interaction between fiber- dyes.^[21]The hues of the dyed felts can be expressed in the L .a .b. notation as the ratio a \b. When a\b = 1, the hue is "pure" orange, and when a \b > 1, it is "reddish" orange, the red contribution increasing with increasing values of a\b .Similarly ,when a\b < 1, the hue is "yellowish" orange, the yellow contribution increasing with decreasing values of a\b. The a\b ratios of Felts dyed at various pH values are shown in Table I and indicate to movement from a predominantly red hue obtained in acid media to a slightly yellow hue in alkaline media, the opposite response to that observed with lawsone solutions.^[22]

3.4.3.2. Effect of Mordanting

Effect of postmordanting on L*, a*, b*, c* and h with copper, cobalt, nickel and chrome at optimized conditions is given in Table (7, 8). L* represents lightness value, the higher the lightness value represent lower the colour yield. a* and b* represent the tone of the colour, positive values of a* and b* represent redder and

yellowish tones while negative shows greener and bluer tones. c^* represents Chroma or purity of colour. H represents hue (shade) of colour. As can be noticed, the lightness of the dyeing increases in case of postmordanting with ($\text{Cu}^{+2}, \text{Ni}^{+2}, \text{Co}^{+2}, \text{Cr}^{+3}$) (% o.w.f.) at $60\text{ }^\circ\text{C}$ in case of lawsone dye while it decreases in case of quercetine dye. It can also be observed that there is huge change in hue in case of postmordanting with ($\text{Cu}^{+2}, \text{Ni}^{+2}, \text{Co}^{+2}, \text{Cr}^{+3}$), there is also a great deal of decrease in the Chroma or purity (c^*) of colour in case of M mordanting of lawsone and increase in the Chroma in case of quercetine dye.^[23] It is clear that the type of mordants has influence on the color strength, fixation ratio, hue as well as the fastness to wash and light by forming additional linkage with dye molecules compared to the silk samples dyed without any mordant. It is evident that the highest values of color strength and fixation, as well as fastness to wash and light were achieved with mordants.^[20] Further assessment of behavior, and efficiency of metal complex mordants, of present natural dyes, are compiled and discussed in part(II) of this paper (in-print).

Table (7): colour measurement of the dyed polyamide fabric by lawsone dye.

Type of colour	λ max	Visual Colour In fabric	L^*	a^*	b^*	C^*	H	ΔE	K\S
Control	375	Yellow	71.3	5.46	3.41	6.4	31.9	71.56	3.04
Mordant by copper	375	Pale brownish yellow	64.8	-3.31	49.06	49.2	86.1	81.31	10.16
Mordant by Cobalt	375	Pale brownish yellow	66.1	-2.92	49.72	49.8	86.6	82.79	23.8
Mordant by chrome	415	dark brownish yellow	50.9	5.80	47.62	48	83.1	69.94	16.50
Mordant by nickel	415	brownish yellow	45.8	11.3	39.64	41.2	74.1	61.59	18.30

Table (8): colour measurement of the dyed polyamide fabric by quercetine dye.

Type of colour	λ max	Visual Colour In fabric	L^*	a^*	b^*	C^*	H	ΔE	K\S
Control	460	Orange	63.3	16.5	27.61	32.2	59.1	71.3	2.30
Mordant by copper	460	Pale orange	73.9	3.11	9.23	9.74	71.4	74.50	0.5
Mordant by Cobalt	460	Reddish orange	69.2	7.81	10.06	12.7	52.2	70.38	0.75
Mordant by chrome	460	Pale orange	68.9	9.08	17.15	19.4	62.1	71.63	1.02
Mordant by nickel	460	Pale orange	71.3	5.46	3.41	6.44	32	71.56	0.48

3.5. Fastness properties of the dyed fabric.

The fastness ratings of polyamide fabric dyed with or without mordants are presented in Table (9). The control sample exhibited poor fastness properties and mordanted samples showed improved fastness properties with reference to light, and washing. The reason attributed is metal complex content of the dye which may help in fixation of the dye with the fiber. [20].

Table (9): Colour fastness properties of polyamide fabric dyed with quercetin and lawsone dye.

Type of dye	Dyeing methods	Light fastness	Washing fastness
Quercetin in Red onion Skin	Polyamide (control)	4	4
	Mordant by copper	4-5	4-5
	Mordant by Cobalt	4	4-5
	Mordant by chrome	5	5
	Mordant by nickel	4	4-5
Lawsone in Henna leaves	Polyamide (control)	1-2	3-4
	Mordant by copper	2	4
	Mordant by Cobalt	2-3	4
	Mordant by chrome	2	4
	Mordant by nickel	2	4

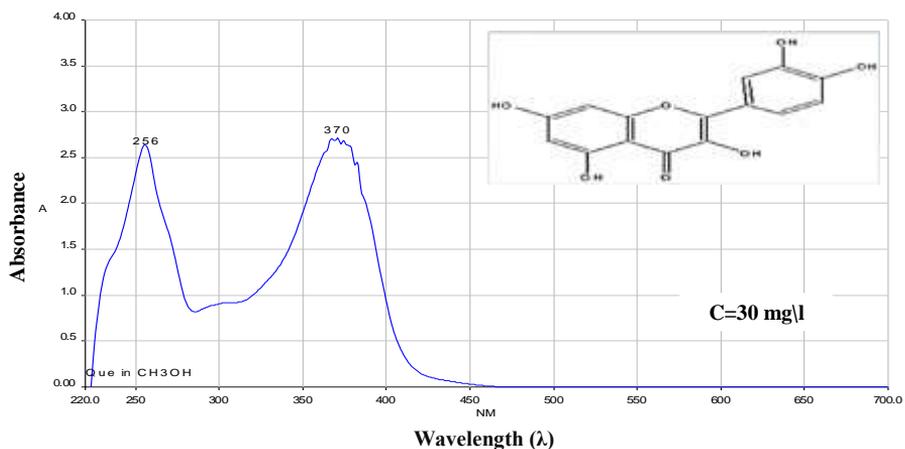
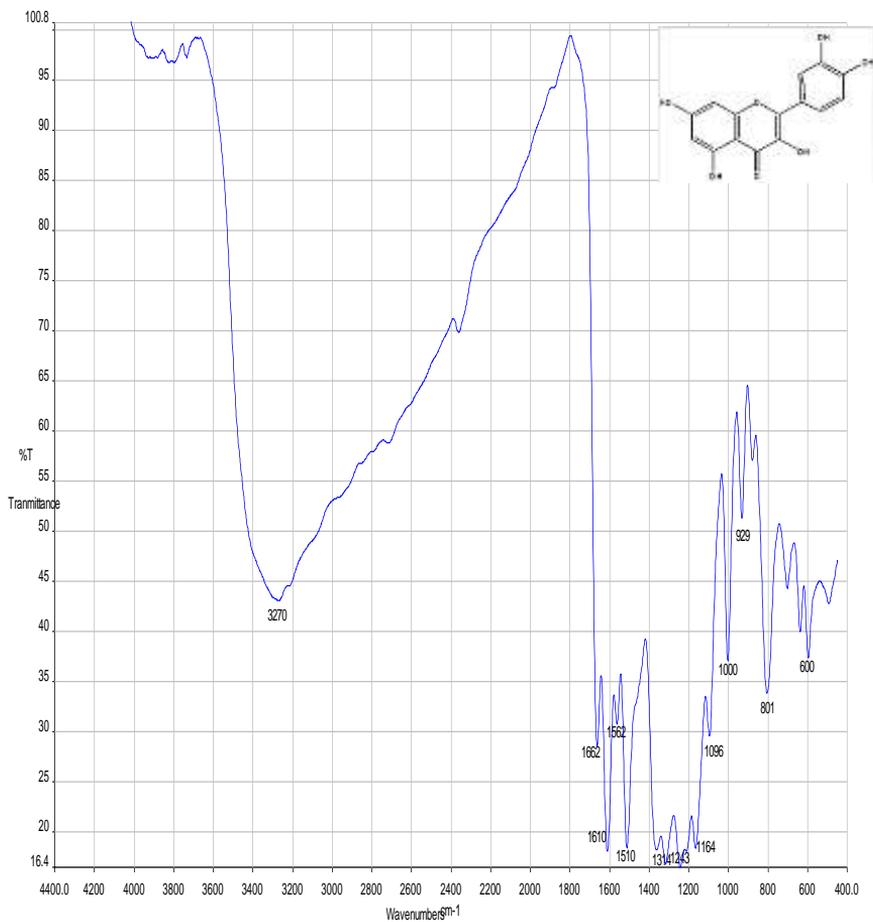


Fig (1): UV\Vis absorption spectra of quercetin dye in Methanol solvent



Fig(2):IR Spectrum of quercetin dye

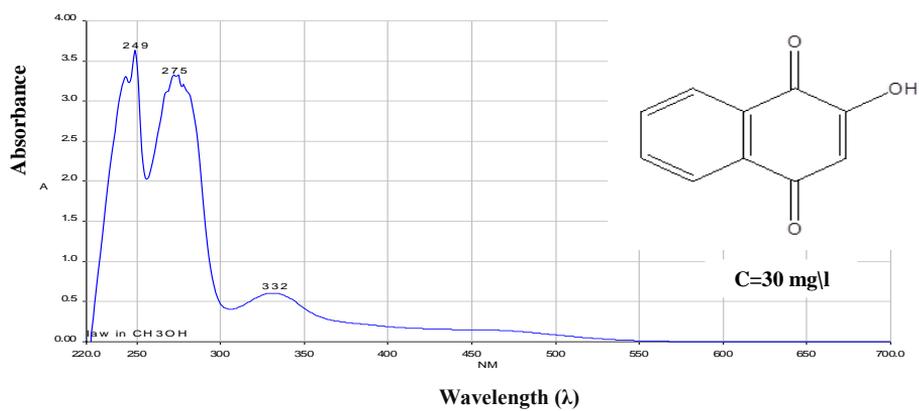
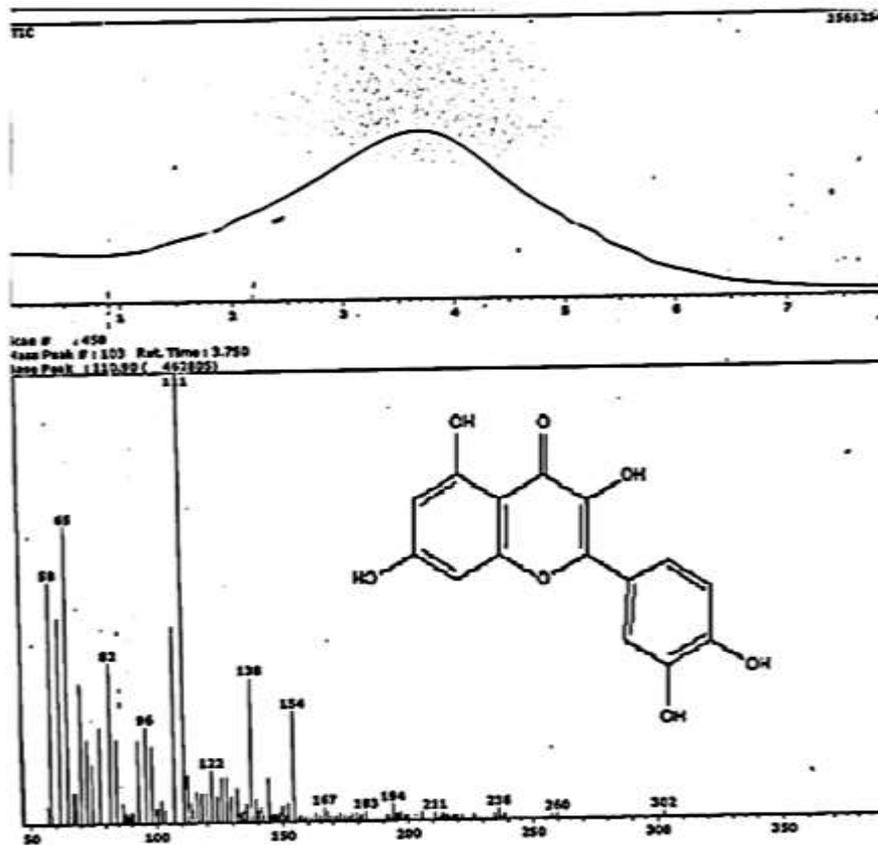


Fig (2):UV\Vis absorption spectra of lawsone dye in Methanol solvent**fig(3):mass spectrum of quercetine dye extracted powder**

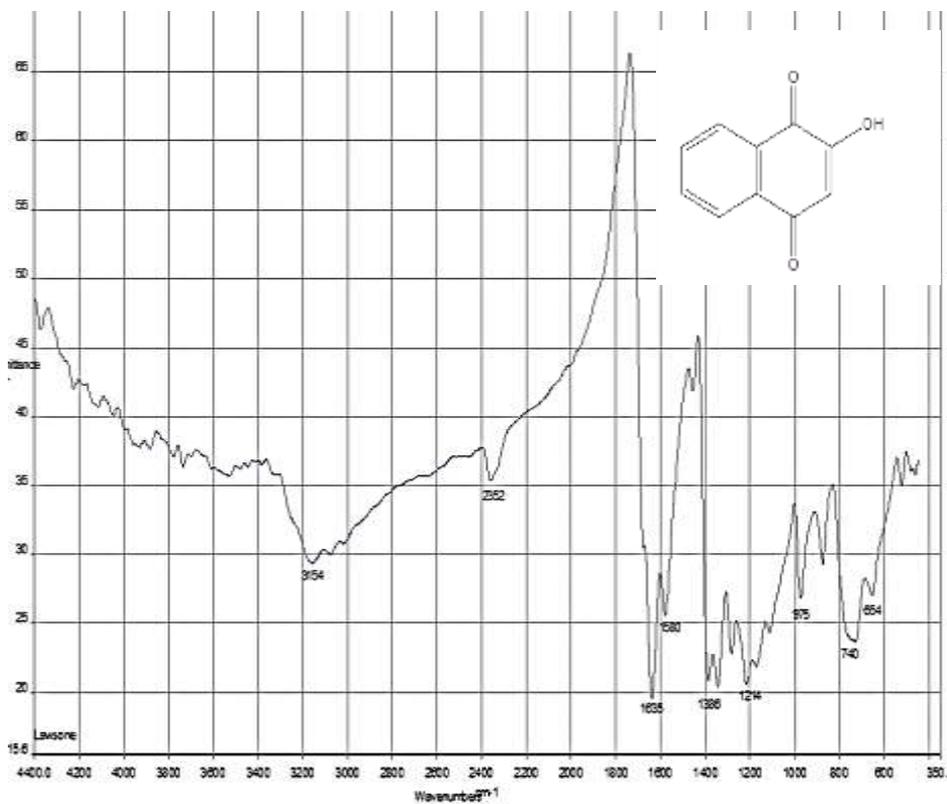
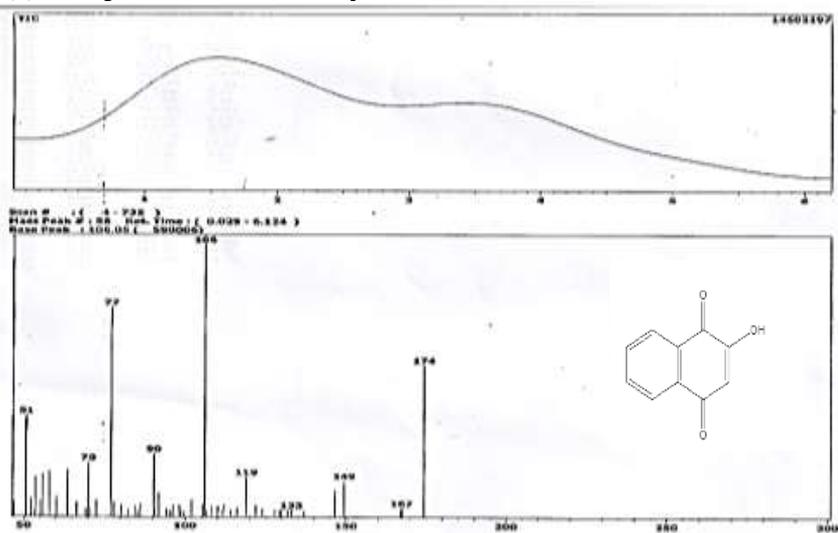


Fig (5): IR Spectrum of lawsone dye



Fig(6):Mass spectrum of lawsone dye

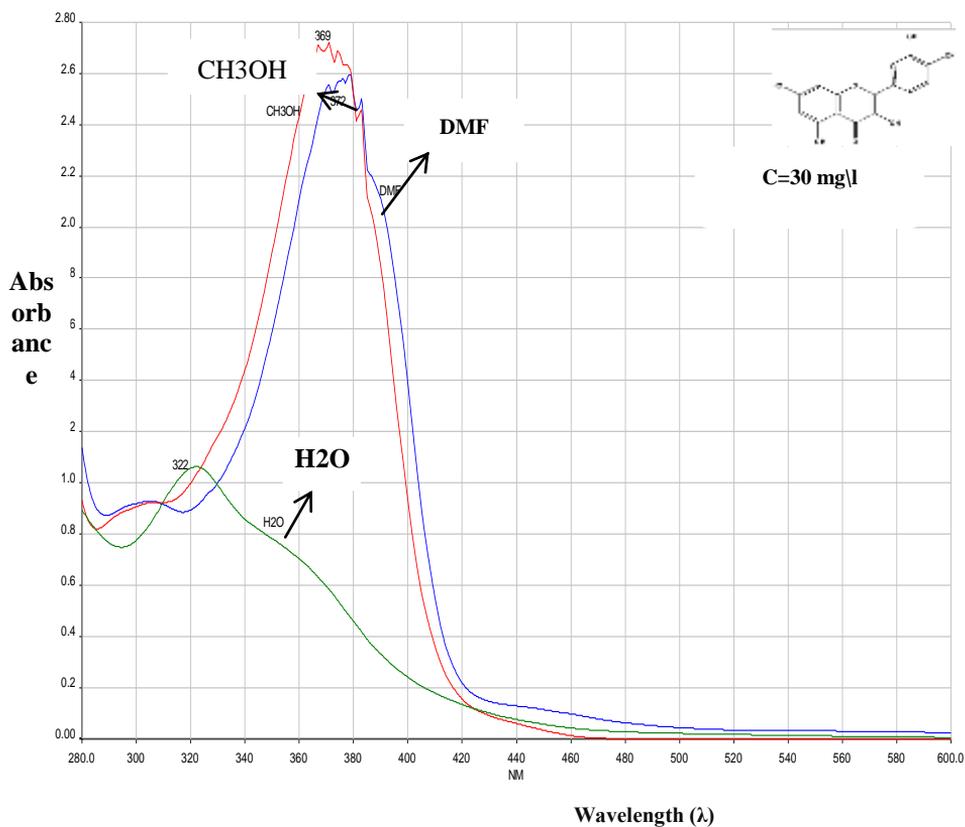


Fig (7):UV\Vis absorption spectra of quercetine in different solvents.

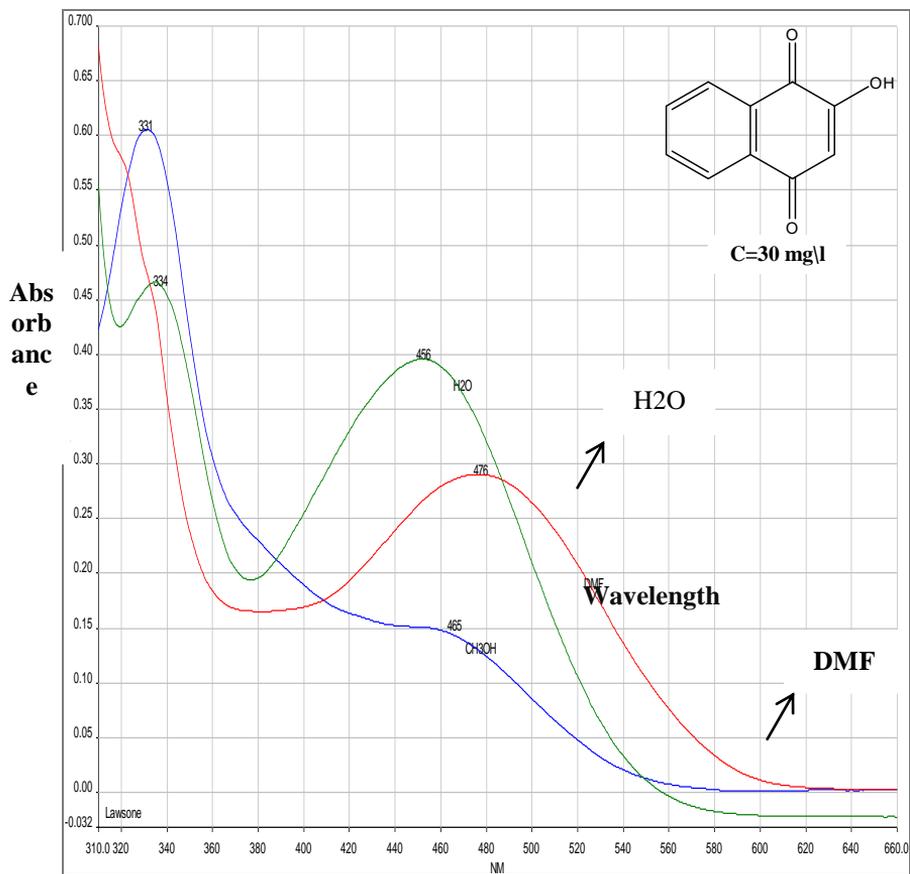


Fig (8):UV\Vis absorption spectra of lawsone in different solvents

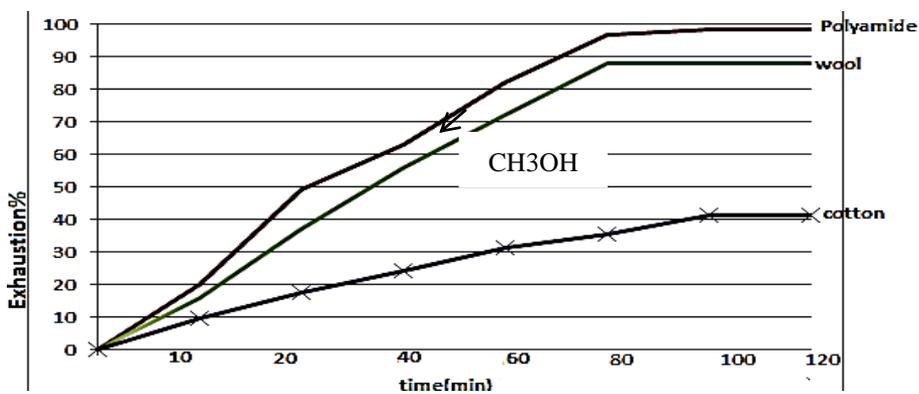


Figure (9): dyeing performance of quercetin dye on different fibers (wool, cotton and polyamide) in water: methanol solvent.

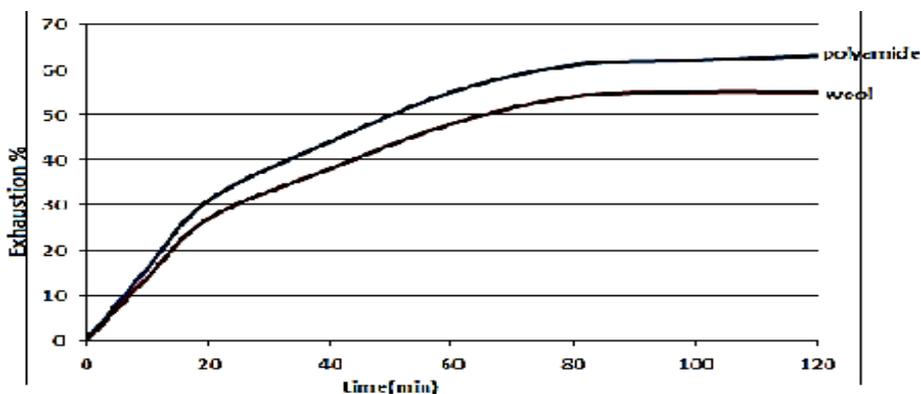


Figure (10):dyeing performance of lawsone dye on different fibers (wool and polyamide)in water: methanol solvent.

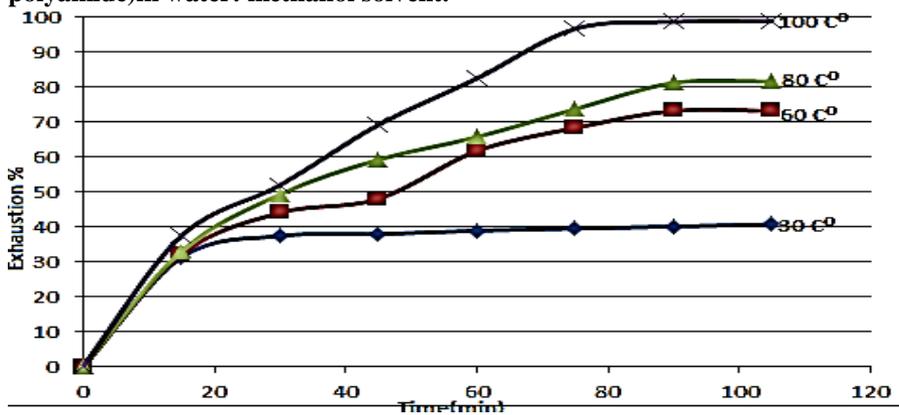


Fig (11): Exhaustion curves on polyamide fibre of quercetine dye at different Temperature in water: methanol solvent.

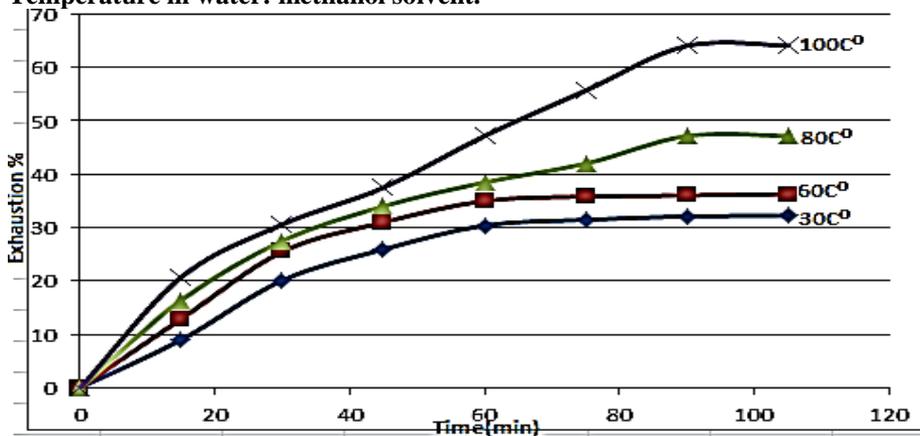


Fig (12): Exhaustion curves on polyamide fibre of Lawsone dye at different Temperature in water: methanol solvent.

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