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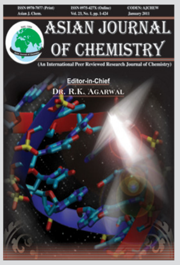

Extraction and Identification of Dye from Walnut Green Husks for Silk Dyeing

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This paper introduces an analytical method for identifying the colour base extracted from the walnut shell (*Juglans regia* L.) which is based on the extraction of colourant from walnut shell through a solvent using Soxhlet apparatus. Here, the main colour bases of samples were isolated and analyzed by column chromatography, thin layer chromatography, infrared, nuclear magnetic resonance and mass spectrometry. The method easily allows the identification of several colour bases by detecting the molecular structure and finally the separation of chemical structures from this plant. The absorbability of the extracted dye using ethanol solvent has been compared to that of the dye from the raw plant in order to determine the dyeing efficiency rate through dyeing silk fibers. The results show that the exhaustion rate for the extracted dye increases by 54 % compared to the raw dye. This per self leads to a considerable decrease in the amount of the extracted dye used to reach the same desired results.

Key Words: Walnut shell, Extraction, Silk, Diethyl ether, Chromatography.

INTRODUCTION

Natural dyes comprise colourants that are obtained from animal or vegetable matter without any chemical processing. Increasing awareness of the environmental and health hazards associated with the synthesis, processing and use of synthetic dyes has created a worldwide interest in textiles dyed with natural dyes. During the last decade, the use of natural dyes has gained momentum due to the increased demand for these dyes by the food, pharmaceutical, cosmetic as well as the textile colouration industry.

Textile processing industry is one of the major environmental polluters. In order to process a ton of textile, one might have to use as much as 230 to 270 tons of water. The effluent generated so much water pollute the environment as it may contain a heavy load of chemicals used during textile processing. There are two main ways to limit the environmental impact of textile processing. One is to construct sufficiently large and highly effective effluent treatment plants and the other way is to make use of dyes and chemicals that are environment friendly.

Recently, several studies reported the dyeing of natural fiber such as cotton, jute, flax, wool and silk with natural dyes[1-7]. Natural dyes are mostly eco-friendly, biodegradable, less toxic and less allergenic as compared to synthetic dyes. Most of the natural dyes are safe and some even have curative effects *e.g.*, walnut has antibacterial properties[8-11]. Walnut (*Juglans regia* L.) is one of the most important fruit crops grown in parts of the Kurdistan, Azarbayejan and Mazandaran provinces, in north of Iran[12,13].

The walnut shell belongs to the group of nutshells, a class of highly insoluble species. The presence of extensive cross-linking polymeric structures in these species makes structural elucidation of the components of the walnut shell difficult. Since the walnut shells are used in a variety of industries, knowledge of its chemical structure is important in order to improve its additive effects and also find new areas of application. Till date, only methods based on wet chemistry are used to study the content of nutshells, which involves solvent extraction, followed by elemental analysis and/or ^{13}C NMR spectral analysis. So far, only the characterization of an antimicrobial quinone derivative, juglone, ascorbic acid and furfural has been reported[14].

The aim of this study is the detection and identification of chemical components present in the extracts of walnut shell dye. In this study, colourant was extracted from walnut shell by the different solvent and in order to distinguish the number of spots on silica sheet, each of these samples was tested by thin layer chromatography method. Finally, the different functional groups of these samples were identified by infrared, nuclear magnetic resonance and mass spectrometry methods and after that extract dye was beside raw walnut shell dye used for silk dyeing.

EXPERIMENTAL

The chemical solvents were provided by Merck Co. used for identification purposes; chloroform, ethanol, silicagel, petroleum ether, diethyl ether and acetone were purchased from Merck. NMR spectra were obtained by ^{1}H NMR 300 MHz, spectrophotometer ($CDCl_3$), infrared taken by Shimadzu 470, mass spectrometry (MS) taken by Quattro LC (Micromass, Manchester, UK), TLC method by aluminum sheet, silica gel 60_{F25u} was done. UV-Vis spectroscopic analyses were performed on a Varian-Carry 100 spectrophotometer. Ahiba Polymat dyeing machinery was used for dyeing the samples.

Chromatography: At first, we employed the Soxhlet apparatus for extracting colourant from walnut shell (*Juglans regia* L.) by ethanol solvent. The dissolved colourant in ethanol was collected by means of rotary evaporator and the collected extract was mixed with silicagel (silicagel 60_{F25u}) in order to convert it to colourant powder.

The colourant powder was immersed into column chromatographer and then washed by different mixed solvents from non-polar to polar *i.e.*,petroleum ether, petroleum ether/diethyl ether, diethyl ether, diethyl ether/chloroform, chloroform, chloroform/ethanol, ethanol and acetone.

The total number of samples used at this stage was 36 pieces and in order to distinguish the number of spots on silica sheet (2.0 cm × 4.5 cm), each of these samples was tested by thin layer chromatography (TLC) method. Samples with similar and equal spots, were mixed together and numbered (Table-1).

TABLE-1
SOLVENTS USED FOR COLUMN CHROMATOGRAPHY

Number of sample	Solvent
4	*n*-Hexane/Petroleum ether (95:5, v/v)
5	Petroleum ether /Diethyl ether (50:50, v/v)
6-10	Petroleum ether /Diethyl ether (55:45, v/v)
11-16	*n*-Hexane/Petroleum ether (90:10, v/v)
17-23	Petroleum

To separate and analyze the numbered colourant samples, they were set like spots on a line on a silica sheet. The spotted silica sheet was then immersed in a TLC tank and the sheet was washed by a suitable predetermined solvent. This caused the separation of different colour bases from the main line and the formation of different thin bands. Then the R_f for each band was calculated (Table-2).

TABLE-2
COMPARISON R_f OF SOME BASE COLOR IN THE WALNUT SHELL DYE

Sample	Solvent	R_f
4	*n*-Hexane/Petroleum ether (95:5, v/v)	0.61
6	Petroleum ether /Diethyl ether (50:50,v/v)	0.89, 0.79, 0.74, 0.68, 0.22, 0.50
6-10	Petroleum ether /Diethyl ether (55:45, v/v)	0.76, 0.64, 0.29, 0.18, 0.08
11-16	*n*-Hexane/Petroleum ether (90:10, v/v)	0.42, 0.32, 0.21, 0.11
17-23	Petroleum	0.47, 0.12

In order to separate the colourant from the silica sheet, the thin bands were cut and put into the acetone or methanol solvent and then they were filtered. To ensure that the samples (dye liquor) contain the same product, the samples were tested by TLC again [petroleum ether/chloroform (95:5 v/v)]. Thin layer chromatography experiments showed that some of these samples still contained several spots that were again separated.

Finally, the different functional groups of these samples were identified by IR, NMR and MS methods.

Dyeing: The absorbability of the extracted dye using ethanol solvent has been compared to that of the dye from the raw plant in order to determine the dyeing efficiency rate through dyeing silk fibers.

The silk fibers were dyed in an AHIBA dyeing system with extracted dye using ethanol solvent and raw dye. The dye bath was comprised of 2 % dye, 1 % acetic acid and 3 % potash alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12(H_2O)$]. The liquor ratio was kept at 40:1, the bath temperature was set at 60 ºC for 5 min. Then the temperature was raised to100 ºC by a thermal gradient of 2 ºC/min and dyeing operation continued for 40 min. At the end of the dyeing operation, the dye concentration of each bath dyeing and washing bath was measured by the absorption spectrophotometer technique.

λ_{max} of the walnut shell dye adsorption extracted by ethanol and boiling water as pure dye in 360 nm to 780 nm in blank solution of water was calculated by adsorbing spectrophotometer. The calibration graph of the above dye was also calculated in λ_{max} by preparing the standard solution.

All measurements were done at room temperature and the following relation calculated the exhaustion per cent:

$$E\,(\%) = \left(A - \frac{(B+C)}{A} \right) \times 100$$

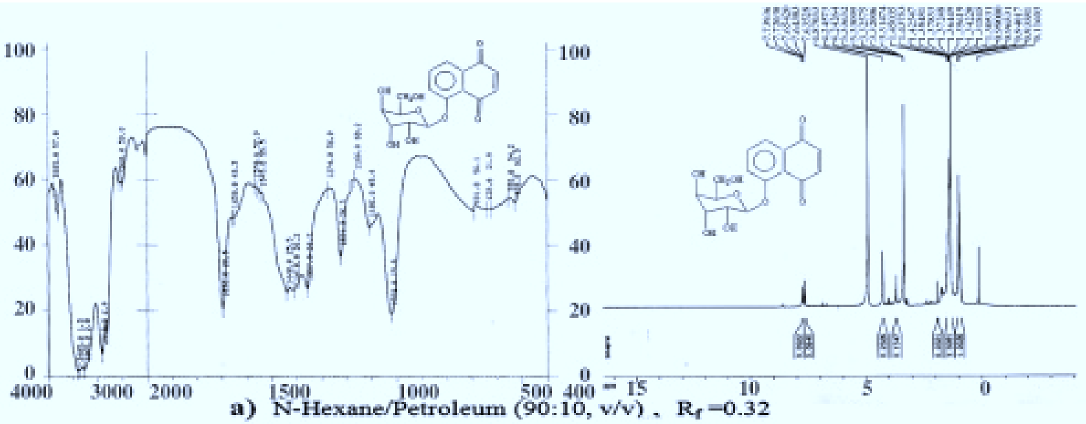
where, E is the exhaustion per cent, A the total dye concentration in bath dying, B the dye concentration that is removed in bath dying and C the dye concentration in bath washing.

Fastness testing: Washing fastness of the dyed samples was tested according to the ISO 105-CO3 method. The samples were washed in a standard soap solution at 60 ºC for 0.5 h, keeping liquor to material ratio as 1:50. Light fastness was tested according to the ISO 105-BO2 method. The dyeing were exposed to xenon arc lamp for 24 h at standard testing conditions[15].

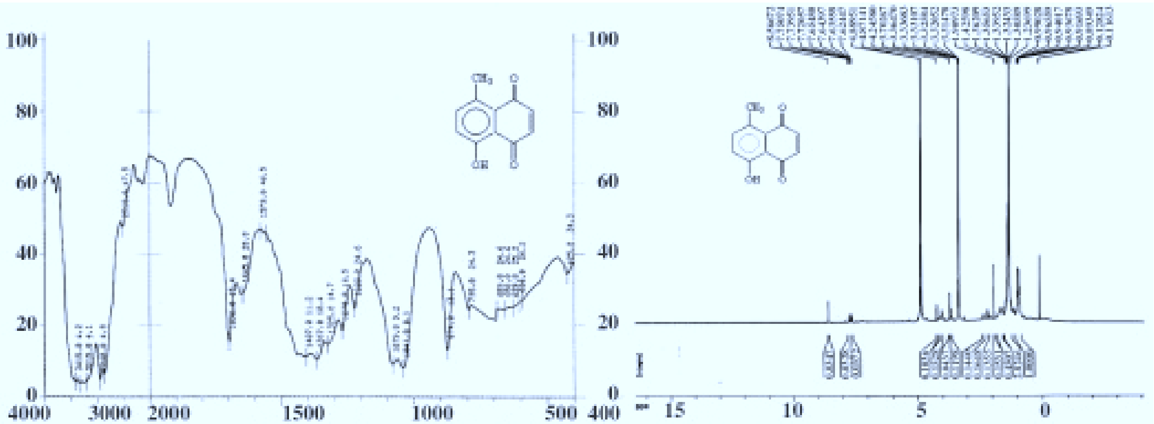
RESULTS AND DISCUSSION

Identification of colouring compounds: Considering the results from IR and NMR spectra, shown in Fig. 1, when the extracted colour bases from the walnut shell by ethanol solvent were purified with the mentioned methods, the following items were produced (Fig. 2, Table-3).

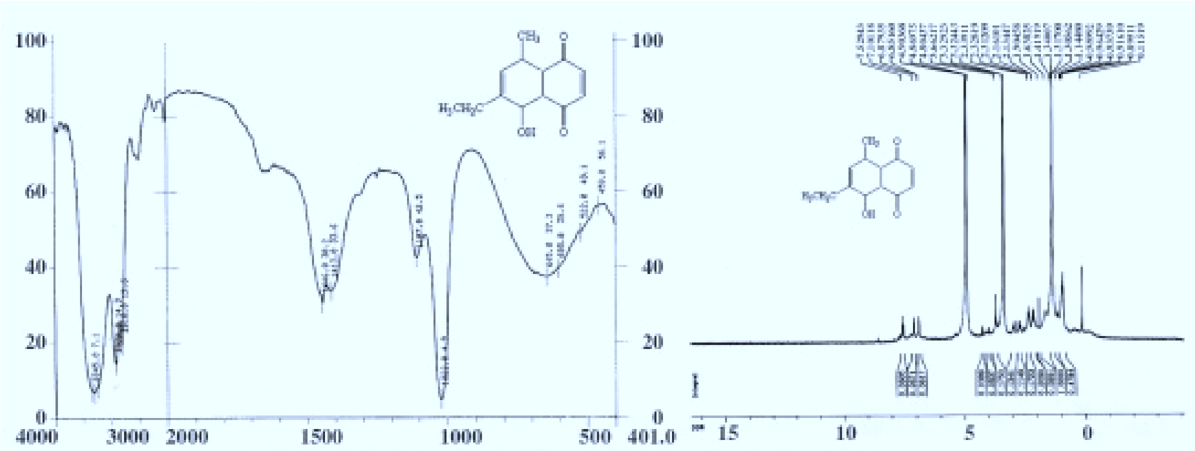
MS spectrophotometry: Mass spectroscopy was used to identify the compound of the extracted the walnut shell dye by ethanol. As shown in Figs. 3 and 4, mass spectra were presented as per cent of ion frequency (m/z).



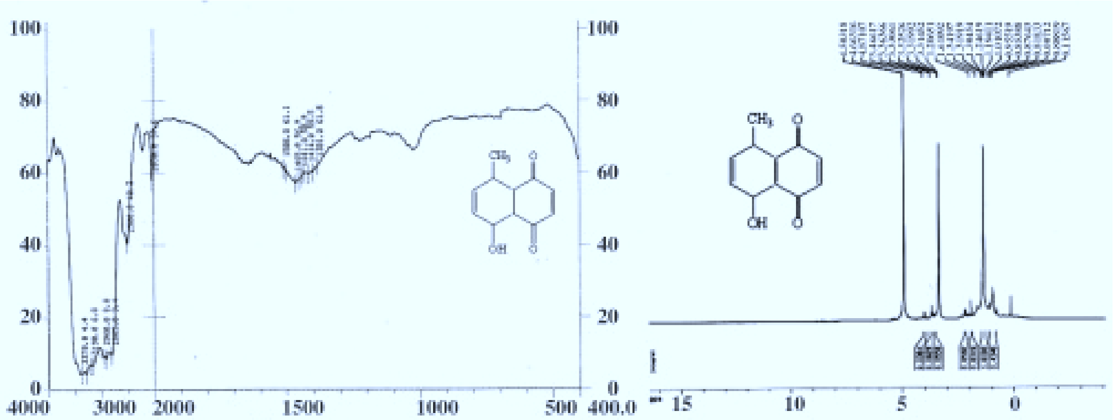
a) N-Hexane/Petroleum (90:10, v/v) , R_f =0.32



b) Petroleum/Diethyl Ether (50:50,v/v), R_f =0.68



c) Petroleum/Diethyl Ether (55:45, v/v), R_f =0.29



d) Petroleum/Diethyl Ether (50:50.v/v), R_f =0.50

Fig. 1. IR and NMR spectra from the Walnut shell (a) chloroform, (b) chloroform/ethanol (50:50), (c) chloroform/ethanol (80:20)

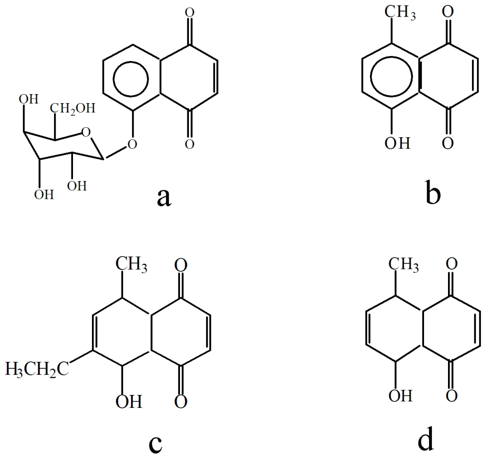


Fig. 2. Chemical structures of extracted color bases from the walnut shell with different solvents (a) *n*-hexane/petroleum ether (90:10, v/v), R_f = 0.32; (b) petroleum ether/diethyl ether (50:50,v/v), R_f = 0.68; (c) petroleum ether/eiethyl ether (55:45, v/v), R_f = 0.29; (d) petroleum ether/diethyl ether (50:50,v/v), R_f = 0.50

TABLE-3
SPECIFICATION OF THE WALNUT SHELL DYE EXTRACTED SPECTRA IN ETHANOL AND BOILING WATER

Dye	λ_{max}	Colour equation
Walnut shell dye extracted by ethanol	360	Abs. = 14.20033 × Conc.
Walnut shell dye extracted by boiling water	360	Abs. = 7.200390 × Conc.

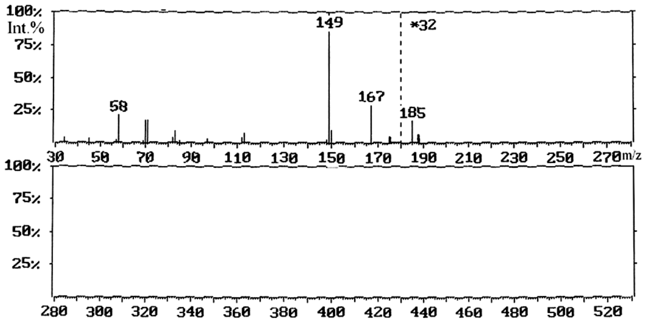


Fig. 3. MS graph of the walnut shell dye extracted by ethanol (code b)

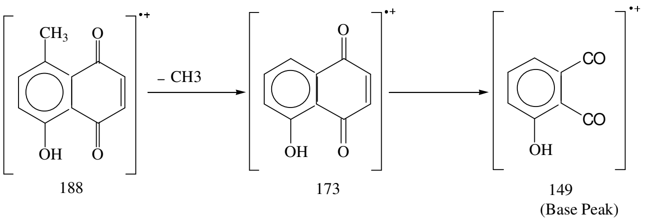


Fig. 4. Base molecular bound breaking and creating the walnut shell by molecular ion (code b)

Most compound ions in the ionization place have a highest peak in value spectra which is called "the base peak", while the other peaks in spectra are observed to be the main peak. With regard to the walnut shell mass spectra, by breaking the base molecular of dye and converting it into molecular ions, the molecular compound and the molecular weight can be obtained. As observed in the present graphs, this can introduce the molecular bound breaking mechanism (Figs. 5 and 6).

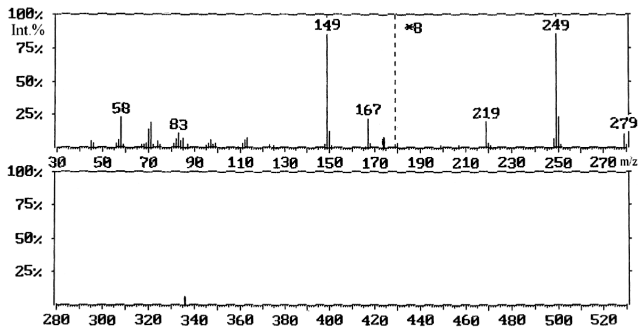


Fig. 5. MS graph of the walnut shell dye extracted by ethanol (code a)

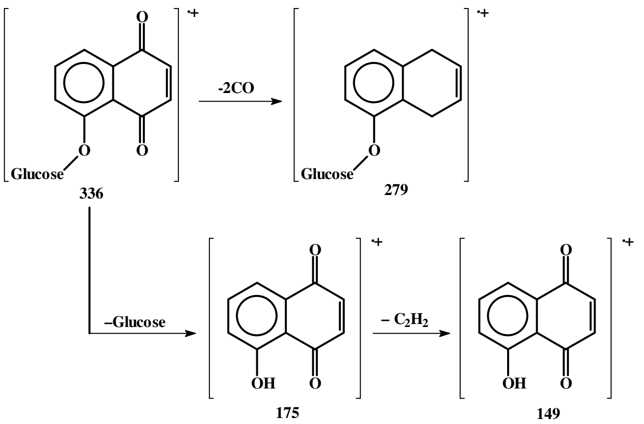


Fig. 6. Base molecular bound breaking and creating the walnut shell by molecular ion (code a)

Dyeing condition: λ_{max} of the walnut shell dye extracted in ethanol solution and boiling water and also the calibration graph of those dyes are shown in Table-3.

Extracted dye has more exhaustion per cent as compared to the raw walnut shell dye. The results from dying treatment are given in Table-4.

TABLE-4
EXHAUSTION OF DYED SILK FIBERS WITH WALNUT SHELL DYE EXTRACTED BY ETHANOL AND BOILING WATER

Dye	Dye concentration in bath (g/L)		Exhaustion (%)
	Dying	Washing	
Extracted dye (Walnut shell)	0.0093	0.0007	99
Raw dye (Walnut shell)	0.0750	0.0780	45

The obtained results from colour exhaustion show that the colour extracted from both plants by ethanol solvent enjoys a high absorbability.

In the meantime, this high exhaustion was resulted from only 10 g of raw plant and by ethanol solvent, whereas in comparison with the boiling water, 100 g of raw plant was needed to obtain the same result. On the other hand, using the dye solution obtained from 10 g of raw plant by boiling water resulted in 54 % exhaustion for the Walnut shell.

Fastness properties: Table-5 shows the fastness properties of the silk samples dyed with the extracted dye and the raw dye with the metachrome method. As can be seen, there was no change in washing and light fastness properties of dyes. However, the results show that the dyed samples extracted by

TABLE-5
FASTNESS PROPERTIES OF DYED SILK FIBER WITH WALNUT SHELL DYE EXTRACTED BY ETHANOL AND BOILING WATER

Dye	Washing fastness	Staining test on silk	Light fastness
Walnut dye extracted by ethanol	5	4-5	6
Walnut dye extracted by boiling water	4-5	4-5	5

ethanol and boiling water, have high fastness and this is because of groups such as C=C, C=O in natural dye, that because of its bounds and non-saturation properties, adsorb by fiber and increase washing fastness.

Conclusion

In this work, we separated eight colour bases from the walnut shell plant and identified the different functional groups by spectrophotometric methods. All of these purified products belong to flavonoid groups.

The dyeing results reveal that the exhaustion rate for the extracted dye increases by 54 % compared to the raw dye. This per self leads to a considerable decrease in the amount of the extracted dye used to reach the same desired results.

It is concluded that the obtained results are because of the high polarity of ethanol and that the colour bases extracted from the walnut shell were more effective in comparison with the boiling water. The colour bases extracted from this plant by ethanol contained oxochromic groups, which because of their high polarity increased the absorption and colour intensity.

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