

ECO-FRIENDLY DYEING TEXTILES WITH NEEM HERB FOR MULTIFUNCTIONAL FABRICS. PART 1: EXTRACTION STANDARDIZATION

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Abstract— Textile industries produce huge amounts of polluted effluents, whereby over 80% of textile dyes are constituted of Benzedrine based dyes or aromatic hazardous substances azo groups that are normally discharged to surface and ground water aquifers. Through the scientific awareness to reach an eco-friendly system, this research part deals on the optimum extraction condition of the new neem natural dye, where the optimization parameters have technical and commercial importance on cost and color yield. This has been carried out using water and different concentrations of water-acetone and water ethanol mixtures at different temperatures, pH values and time intervals. Data observed that the optimum extraction condition was achieved with 50% (v/v) acetone, 18% (w/v) neem amount at pH 9 at 70oC for 60 min where 50% (v/v) water-acetone exhibited 60 % absorbance percentage compared to (31 and 9) % of 40% (v/v) water-ethanol and water respectively. The absorbance values are influenced by the properties of solvents such as, the dipole moment, dielectric constant, and refractive index values. Aqueous extraction gave less amount of pigment and was time consuming, promoting the degradation of color compounds while the other co-solvents increased the extract solubility, giving high extraction capacity. pH 9 increased the diffusion coefficients of color component and the temperature at 70oC for 60 min enhanced the de-aggregation of its molecules. Finally, FTIR analysis investigated the presence of mainly yield quercetin (flavonoid) compounds in neem extract which is known to have antibacterial and antifungal properties giving chance to be applied for antimicrobial textile dyeing in the second part of this study.

Key words— Neem, extraction, solvents, natural dyes, environmental technology.

I. INTRODUCTION

An aspect of the return to use natural dyes is the search for novel natural dyes from various plant materials. This is because the use of synthetic dye has recently been banned not only due to the carcinogenic nature of the intermediates used in the preparation of these dyes, but also the effluent coming from their industries are the major cause of environmental pollution [1].

There are several plants parts that provide natural dyes which might be used in the textile industry. However, their common drawback is the lack of scientific information on the chemistry of extraction and dyeing [2].

Extraction of color component from natural sources is an important step for dyeing any textile substrate in order to evaluate their dyeing characteristics and maximize the color yield on textile fabrics [3, 4].

Moreover, standardization of extraction process and optimizing the extraction variables both, have technical and commercial importance on color yield and cost of extraction process as well as dyeing cost [5]. Commonly, conventional aqueous extraction methods give less amount of coloring component for coloring textiles. Thus these methods are, in general, time and solvent consuming and may promote the degradation of these compounds. To overcome these drawbacks conditions popular common solvents such as acetone, ethanol, and methanol have been successfully used to obtain natural dyes and pigment-rich extracts [6, 7].

Use of organic solvents might give rise to extract which are not completely water-soluble. It was reported that the solvent gave high extraction capacity, had quite low boiling temperature and latent heat of vaporization. As a result, lead to extract the dye at low temperatures with minimum energy consumption and insignificant reactivity with pigments to avoid any loss in the color quality [8].

The Neem plant (*Azadirachta indica*) of family meliaceae is also named Margosa and Indian Lilac. It is well known since the ancient times, it is an aboriginal tree found in tropical and semi-tropical countries like Burma and India. It has been declared non-toxic to humans having variety of medicinal and germicidal properties that attributed to leaves, bark, seeds and other parts of the plant and each part of the tree. So it is used as an active ingredient in different industries ranging from cosmetics to agriculture [9]. Its seeds and leaves have been in use not only to treat a number of human ailments such as anti-inflammatory, anxiolytic, anti-androgenic, anti-stress, humoral and cell-mediated immune stimulant, anti-hyperglycemic, liver-stimulant, anti-viral and anti-malarial activities [10], but also as a household pesticide [11-13], but also was used as a promoting adsorbent for dyes in aqueous solutions. At the same time its bark contains tannin, so it is useful in tanning and dyeing a number of products [9]. Few years ago; neem leaves was extracted by grinding into fine powders and followed by mixing with methanol at room temperature then was left closed for 3 days [14]. So this method is time consuming and might promote the degradation of color compounds.

The present investigation, therefore, was aimed at identifying the most appropriate leaching solvent for neem pigments to produce an optimum concentrated extract with high extraction capacity avoiding any loss in the color quality and time consuming. This has been carried out using water in addition to the co-solvents of water-acetone and water ethanol mixtures at different concentrations, temperatures, pH values and time intervals, where the color components and chemical

constituents were isolated and established based on spectroscopic investigations.

II. MATERIALS AND METHODS

A. Material

- The air dried leaves of neem plants (*Azadiracta indica*), collected from Jeddah, KSA were washed under flowing water repeatedly to remove dust particles and soluble impurities and were allowed to dry at ambient temperature (24-25 °C) till the leaves became crisp, then were crushed into a fine powder in an electrically grinder.
- Distilled water, acetone, ethanol, sodium hydroxide and acetic acid were all of analytical grade.

B. Pigment leaching and estimation of extraction yields

To select the best extraction variable parameters, different amount of neem powder from (1-21) % (w/v) were dissolved in distilled water and other co-solvents as water-acetone and water ethanol mixtures were tested at different concentrations ranged from (5-75) % (v/v), at (25-70) °C, for (15-120) min, at pH values of (3, 5, 7 and 9). This was carried out using a liquor ratio of 1:50 to determine the standardization method of extraction.

C. Spectral analysis

The absorption spectra were recorded for the determination of absorbance on Pharmacia Biotech Ultrospec 3000 UV/Vis spectrophotometer in the wavelength range 300-800 nm. Infrared spectra of the compounds were recorded on a PerkinElmer FTIR spectrum (version 10, 03.08) in the frequency range 4000-450 cm^{-1} .

III. RESULTS & DISCUSSION

The color capacity of neem extract was evaluated by the absorption values in the wavelength range 300-800 nm, giving maximum absorbance at (550-600) λ_{max} where its molecules are complex organic molecules which might carry charge centers which are thus prone to absorption changes in various media [15].

As shown in Figure 1. When dissolving 10% (w/v) neem powder in pure distilled water and different concentrations of water – acetone and water methanol mixtures with different concentrations of (5-75) % (v/v) at 70 °C and pH 9 for 60 min using liquor ration of 1:50.

It was denoted that, the maximum absorbance was achieved with 50% (v/v) water acetone, followed by 40% (v/v) water-ethanol then pure distilled water. On the other hand; as shown in Figure 2. 50% (v/v) water- acetone co-solvent exhibited 60 % absorbance percentage compared to (31 & 9) % in case of 40% (v/v) water- ethanol co-solvent and pure distilled water respectively.

Absorbance values were influenced by influenced by the properties of solvents such as, the dipole moment, dielectric constant, and refractive index values, thus the change in values can be noted as a probe for various types of interactions between the neem powder and the solvent where the solvent polarity can change the position of the absorption or emission band of molecules. By the way, dye molecules are complex organic molecules which might carry charge centers and are

thus prone to absorption changes in various media [15, 16]. As a result, as a result; it was denoted from figs 1 and 2 that the absorbance values of neem extract was affected by the solvent type and the change in values can be noted as a probe for various types of interactions between the solute and the solvent.

Acetone acts as the non-hydrogen-bond donating solvents also called as non-HBD type of solvents that contain a large multiple bond between carbon and either oxygen or nitrogen e.g. C-O double bond, while water and ethanol are the hydrogen-bond donating solvents, also called as HBD type solvents where their polarity stems from the bond dipole of the O-H bond, whereas the large difference in the electro-negativities of the oxygen and hydrogen atom, combined with the small size of the hydrogen atom, warrant separating the neem molecules that contain the OH groups from those polar compounds that do not. On the other hand, although water has the highest dielectric constant among ethanol and acetone solvents, its extraction demonstrated the lowest value of absorbency due to the formation of strong hydrogen bond between the dyes extract and water molecules. [16, 17].

In case water-acetone co-solvent, the salvation of extract is non-HBD type of solvent mainly occurs through charge-dipole type of interaction, whereas in HBD type of solvent, the interaction also occurs by hydrogen bonding besides the usual ion-dipole interaction. In this situation, the methyl groups of acetone are responsible for the solvation of the neem powder. Thus, decreasing the amount of non-HBD acetone solvent “concentration” increasing the amount of HBD solvent (water) shall break these interactions with the neem molecule, thereby decreasing the value of absorbance [15, 16].

In case of water-ethanol mixtures, it belongs to HBD type of solvents where neem powder is preferentially solvated by the alcoholic component in all mole fractions in aqueous mixtures with ethanol [15, 16].

Water makes strong hydrogen-bonded nets in the water-rich region, which are not easily disrupted by the co-solvent explaining the strong preferential salvation by the alcoholic component in this region. Since water preferentially interacts with itself rather than with neem powder, the alcohol molecules are freer to interact with neem molecules where their nets formed by hydrogen bonds are weaker than in water. In this situation, the alcohol molecules can, to a greater or lesser extent, interact with water through hydrogen bonding by solvating a solute molecule or any other molecular species introduced into the solvent matrix [15, 17].

Increasing the concentration of acetone or ethanol in water rather than (50 and 40) % (v/v) respectively breaks these interactions with the neem molecule; thereby decrease the extract absorbance value [16]. While decreasing the concentrations brings an increase of the other compounds concomitant extraction which lowers the neem pigment concentrations and lead to a lesser absorbance [18].

As shown in Fig. 3, it was denoted that, more concentrated extract resulted in an increase in absorbance values where the maximum value was achieved with 18% w/v. This can be explained by the diffusion of high amount of neem solvated in the solvent.

The pH of the plant extraction plays an important role in controlling the absorbance capacity into the extract solution. Neem molecules are complex organic molecules which carry charge centers and are thus prone to absorption changes in

various media [15]. These changes are important to understand various physical- organic reactions of these macromolecules which have become important in plant extraction. As shown in Figure 4, it was recorded that the maximum absorbance was achieved at pH 9 due to the increased solubility and diffusion coefficients of neem extract, while the decrease of absorbance at pH values 3, 5 and 7 was due to the possible degradation of pigment compounds caused by hydrolysis and polymerizations [19].

Extraction temperature and time are important parameters influenced the absorbance values as shown in Figures 5 and 6. It was recorded that the standard parameter of extraction time was achieved after 60 min 70o C. The absorbance values increased with the increase in temperature and time otherwise a decline was achieved with prolong extraction.

Generally, the increase in extract absorbency may be explained by the de-aggregation of neem molecules in the extract bath, while the decline in the absorbance value may be not only attributed to the hydrolytic decomposition of the extract molecules during prolonged extraction rather than 60 min. [20], but also the loss of solvent by evaporation [21].

Neem leaves yield quercetin (polyphenolic flavonoid) and nimbosterol (β - sitosterol) as well as number of liminoids (nimbin and its derivatives) as shown in Figure 7. [22]

This was confirmed from the FTIR spectrum (version 10, 03.08) in the frequency range 4000-450 cm^{-1} as shown in Fig 8. It was recorded that the number of peaks lying between 3429.10 cm^{-1} , 2925.55 cm^{-1} , 2335.72 cm^{-1} , 1607.23 cm^{-1} , 1404.91 cm^{-1} , 1261.28 cm^{-1} , 1073.05 cm^{-1} , 800.97 cm^{-1} and 600.72 cm^{-1} .

The broad band (3600-3000) corresponds to hydroxyl group (bonded). Band around 2900 cm^{-1} could be attributed to aliphatic CH_3 and CH_2 . The bands from 2800 to 2000 cm^{-1} are normally void of other absorptions, so the presence of alkyne or nitrile groups can be easily seen. The bands from (1638-1484) cm^{-1} may be attributed to $\text{C}=\text{C}$ group of an aromatic ring. Bands at (1433-1368) cm^{-1} due to the CH_3 and CH_2 , bending, and the present bands at (1300-1000) cm^{-1} indicated C-O group, while the bands below 900 cm^{-1} indicated the existence of C-H deformation of an aromatic proton. This confirmed the presence of flavonoid compounds in the neem extract so that the bands in the 1650-1050 cm^{-1} range are represented the flavonoid skeleton [23].

IV. CONCLUSION

Use of organic solvents gave rise to neem extract which are not completely water-soluble provided extremely high capacity for neem pigments to avoid any loss in the color quality present in its material at quite latent heat of vaporization to allow its separation at low temperatures with minimum energy consumption. The absorption maxima of neem dye extract are dependent on solvent polarity; in non-hydrogen-bond donating solvents, solvation of dye molecules probably occurs via dipole-dipole interactions, whereas in hydrogen-bond donating solvents the phenomenon is more hydrogen bonding in nature. The alkaline extraction at pH 9 increased solubility and diffusion coefficients while the increase of extraction time and temperature till 70oC for 60 min lead to an increase in the absorbency due to the de-aggregation of neem molecules in the extract bath and any decline in the absorbance value might be not only attributed to the hydrolytic decomposition of the

extract molecules but also might be potentially increased the loss of solvent by evaporation. Finally, FTIR analysis investigated the presence of mainly yield quercetin (flavonoid) compounds in neem extract which is known to have antibacterial and antifungal properties giving chance to be applied for antimicrobial textile dyeing in the second part of this study to approach the demands of economic and ecological viewpoints.

V. ACKNOWLEDGEMENT

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VI. LIST OF FIGURES

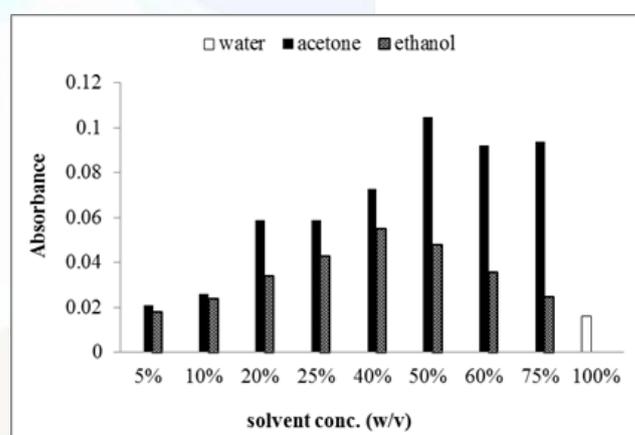


Figure1: Effect of solvent type and concentrations on the absorbance of 10% (w/v) neem powder extracted at 70o C and pH 9 for 60 min using L:R of 1:50

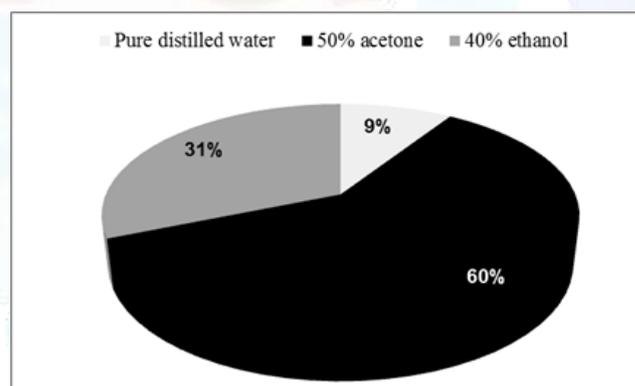


Figure 2: Efficiency of the optimum solvents concentrations on the absorbance percentage of 10% (w/v) neem powder extracted at 70o C and pH 9 for 60min using L:R of 1:50

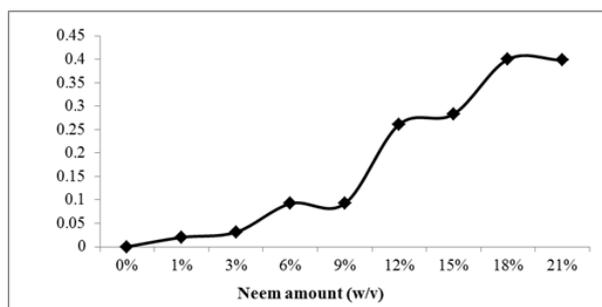


Figure 3: Effect of neem powder amount (w/v) on the absorbance when extracted with 50 % (v/v) water-acetone at 70o C and pH 9 for 60 min using L:R of 1:50

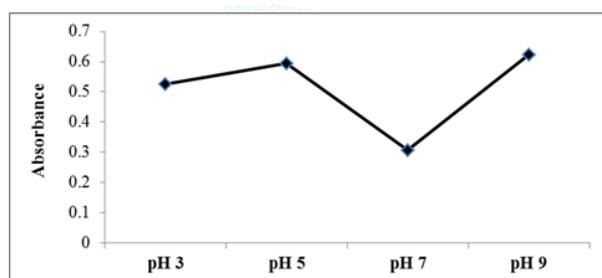


Fig. 4. Effect of pH values on the absorbance of extracting 18% (w/v) neem powder with 50 % (v/v) water-acetone at 70o C for 60 min using L:R of 1:50

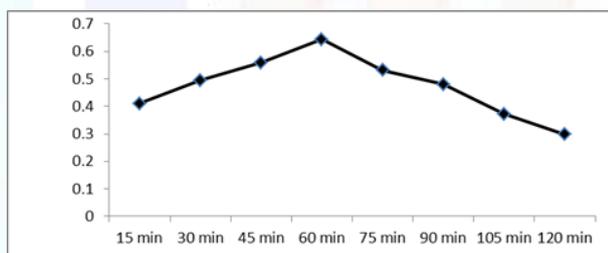


Figure 5: Effect of extraction bath time on the absorbance of extracting 18% (w/v) neem powder with 50 % (v/v) water-acetone at 70o C and pH 9 using L:R of 1:50

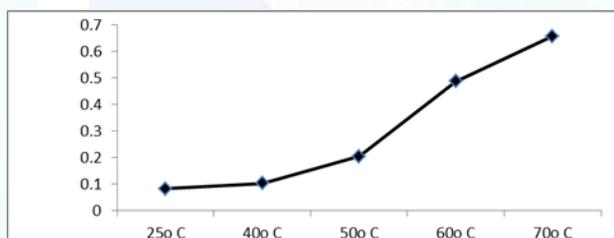


Figure 6: Effect of extraction temperature on the absorbance of extracting 18% (w/v) neem powder with 50 % (v/v) water-acetone at pH 9 for 60 min using L: R of 1:50

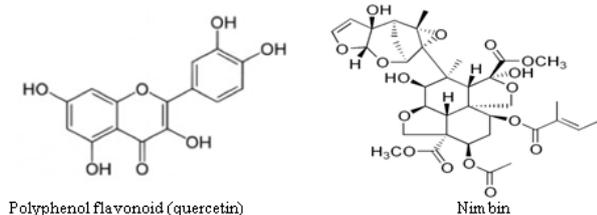


Figure 7: Chemical structure of neem

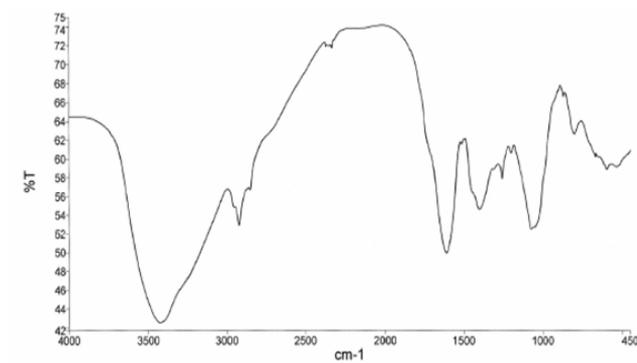


Figure 8: FTIR spectrum of the standardize neem extract using 50 % (v/v) water-acetone, 18% (w/v) neem amount at pH 9 and 70oC for 60 min using L:R of 1:50.

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