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Chemical analysis of the characteristics of Tunisian *Juglans regia L.* fractions: Antibacterial potential, gas chromatography–mass spectroscopy and a full investigation of their dyeing properties

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ABSTRACT

The current report deals with the assessment of the characteristics of Tunisian *Juglans regia* L. (Walnut) fractions. First, prepared stem and leaves methanolic extracts were chemically characterized. The Total Phenolic Contents (TPC), Total Flavanoid Contents (TFC) and the concentration required to scavenge 50% of DPPH* (IC50) were determined. The ability of walnut fractions to quench reactive species was measured through 1,1-diphenyl-1-picrylhydrazyl (DPPH*) radical scavenging activity assay. The highest values of TPC and TFC were achieved using leaves fraction whereas the maximum value of IC50 was reached using stem part. The main constituents of this latter were analyzed using Gas Chromatography–Mass Spectroscopy (GC–MS) and its antibacterial activities against pathogenic strains of *Aspergillus Niger, Aeoromonas hydrophila, Pseudomonas Fluorescens, Salmonella arizonae 2, Listeria monocytogenes, Staphylococcus aureus, Salmonella arizonae1, Orchi Epididymite and Escherichia Coli* were reported. Results reveal that *Aspergillus Niger* and *Salmonella arizonae 1* are the most sensitive microorganisms exhibiting the largest inhibition zones ($18 < d < 20$ mm). The dyeing properties of stem, leaves and their mixture with various arrangements were performed on wool, cotton and polyamide. The effect of the mode of dyeing, p*H* value, extract concentration, temperature and agitation speed were studied and the dyeing performances of samples were determined. For example, compared to the dyeing properties using leaves extract at optimum conditions, the improvement of color in the leaves-stem mixture is about 1.7 times. The resulting data from rub, light, wash and perspiration fastness assays exhibited fair to excellent grades.

1. Introduction

Historically, natural products resulting from flora and fauna are recognized as a common practice over the world. Indeed, natural dyes, extracted from roots, stems, berries, leaves, and flowers of a range of plants, remains as green ecological substitutes to usual synthetic dyes (Islam et al., 2013; Yusuf et al., 2012; Teli et al., 2000; El-Zawahry and Kamel, 2001; Paul et al., 2005). Hence, their non-toxic effect and biodegradable nature can be explained based on the activity of some extracts that they enclose such as essential oils, flavonoids, etc. Besides, their numerous functional finishing properties could justify the continuous progress of their valorization in many fields (Specos et al., 2010; Rather et al., 2015; Islam and Mohammad, 2015).

Thus biomass could be seen as one environmentally friendly renewable resource from which various useful chemicals and fuels can be produced (Fernando et al., 2006) and the use of vegetable biomass to exploit its main components have also proved to be of great interest (Villaverde et al., 2016). Additionally, the knowledge of the problems that extractives show for pulp and paper could contribute to prevent eventual pitch problems and chemical consumption/costs, caused by the accumulation of lipophilic compounds in pulping and bleaching processes (Gutierrez and del Rıo, 2005; Villaverde et al., 2009).

Among the large numbers of plants grown over the world, walnut, which is cultivated throughout southern Europe, northern Africa, eastern Asia, USA and western South America, has been mainly studied (Nael and Mohammed, 2011). Indeed, it has been found to exhibit interesting antibacterial properties (Oliveira et al., 2008; Pereira et al., 2006, 2007; Fernandez-Agullo et al., 2013). Many works have been concentrated on the use of different walnut fractions such as leaves, bark and husk. For example, the studies of Upadhyay et al. (2010a,b,c)

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dealt with the antifungal activity and preliminary phytochemical analysis of stem bark extracts. In the investigation of Emira et al. (2011), the antibacterial and the antioxidant activities of Salvadora persica and walnut extracts were evaluated. The works of Ismet et al. (2013) reported the antimicrobial properties of two different extracts *of* walnut tree bark. Moreover, some dyeing experiments were conducted on cotton using walnut bark dye in the presence of mordants such as alum, $CuSO_4$ and $FeSO_4$ (Anshu and Ekta, 2011). Mohammad and Loghman (2013) studied the extraction and the characterization of natural dye from green Walnut shells and its use in polyamide dyeing. The green husks were analyzed for their antioxidant potential and antimicrobial activity (Oliveira et al., 2008). Shahmoradi et al. (2012) analyzed the effect of mordant salts on antibacterial activity of wool fabric dyed with pomegranate and walnut shell extracts. Recently, the dyeability of wool fabrics with walnut leaves extract have been investigated in the presence of various acids including acetic acid, citric acid, maleic acid, oxalic acid, and formic acid (Eser et al., 2015). Mirjalili et al. (2011) studied the identification of dye from walnut green husks for silk dyeing.

Indeed, these important numbers of published studies that have been found, and as globally observed, were concentrated on the use of some fractions of walnut in restraint concerns. As a consequence, the absent data about the valorization of both stem and leaves fractions from walnut in dyeing field, encourage us to chemically analyze and compare the dyeing performance of the two fractions, for the first time, and extend their use in single and in mixture for the dyeing of different structure of textiles. Here in, the current report was devoted to analysis the characteristics of Tunisian walnut methanolic fractions and to assess their dyeing properties considering color strength and color fastness grades. Extracts were chemically characterized and the ability of the fractions to quench reactive species was measured through the DPPH radical scavenging activity assay. TPC, TFC and IC50 values were determined. The antibacterial activities of stem fraction against nine pathogen bacteria were obtained from the disc diffusion method. The dyeing properties were investigated using stem, leaves fractions and their mixture for wool, cotton and polyamide. The influence of the experimental parameters and the fastness to rub, light, wash and perspiration were carried out.

2. Experiment

2.1. Chemicals, reagents and materials

The vegetable leaves and stem fractions from walnut were collected throughout the region of Ain Drahem (Tabarka, Tunisia). Stem part was harvested during the month of March. Whereas, the leaves were harvested during the month of April. Then, fractions were air dried, before they were applied to extraction experiments. The Chemicals such as Folin-Ciocalteu's reagent, gallic acid and 1,1-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich. All other solvents and chemicals [Dimethylsulfoxyde (DMSO, purity = 99%), Methanol (purity = 99.5%), Acetic acid (purity = 98%), Sodium hydroxide, etc.] used in this study were of analytical grade.

Three sorts of samples were checked for the dyeing experiments. Each one was subjected to be purified using conventional method of pretreatment. Briefly, cotton (a twill fabric, weight = 356 g/m^2) was pre-treated according to a process described in our previous work (Mahjoub et al., 2011). Polyamide sample (a plain fabric, weight = 164.8 g/m^2) was subjected to a washing bath containing 2 g/L of a non-ionic detergent at 80 °C for 30 min. The p*H* was adjusted to 9 using Na_2CO_3. Then, it was rinsed with CH_3COOH until neutral conditions. Wool sample (a knitted jersey, weight = 476 g/m^2) was bleached in a bath containing 30 mL/L H_2O_2, 2 g/L of sodium pyrophosphate, 1 g/L trisodique phosphate and 0.5 mL/NH_4OH for 120 min at 50 °C. Then, it was rinsed with hot water and cold water and finally air dried.

2.2. Functionalization of cotton samples

In order to impart additional functional groups on the surface of the cellulose fibers, cotton samples were subjected to a series of bath treatment containing different doses (0.05–5%) of the cationic reagent PolyDimethy-Diallyl-Ammonium-Chloride-Diallylamin-co-polymer (PDDACD). The functionalization of cotton with PDDACD was performed in aqueous NaOH solution (2%, 1 M) at 50 °C for a period of 30 min, then neutralized, cold rinsed and air dried.

2.3. Preparation of the walnut fractions extracts

Both water and pure methanol were checked as solvents for stem and leaves walnut fractions to assess the effect of the solvent on the extraction yield. Vegetable leaves and stems fractions of walnut with weighted dry mass were extracted with water and methanol for 72 h at room temperature. After filtration, the fraction was evaporated using vacuum evaporator® and the extracted fraction was weighed to determine TPC, TFC and IC50 measurements and then stored at +4 °C for further analysis. The extracts were, later, diluted in distilled water and kept for dyeing experiments in single or binary system.

2.4. Determination of TPC value

The TPC of the methanolic walnut fractions extracts were determined according to the method described by Bursal and Gülçin (2011) with modifications. Briefly, 10 µL of methanolic extract (1 mg/mL) or standard gallic acid (0.06–1 mg/mL) was mixed with of a volume of Folin-Ciocalteu's reagent (100 µL). To the above mixture, after 5 min, 90 µL of Na_2CO_3 (10%) was added and the resulting mixture was incubated at room temperature for 40 min. The absorbance of the resulting blue color was measured at 765 nm. The TPC was reported as the mean value of triplicate assays and it is expressed as mg of Gallic Acid Equivalent (GAE) per gram of dry methanolic extract.

2.5. Determination of TFC value

The TFC value of the methanolic extracts was determined based on the method described in the studies of Sun et al. (2011) with some modifications. Briefly, 20 µL of the methanolic extract (1 mg/mL) or quercetin (0.6–1 mg/mL) was mixed with 30 µL of $NaNO_2$ (5%). After 6 min, 50 µL of $AlCl_3$ (10%) was added and the resulting mixture was allowed to be kept for another 5 min. To the above mixture, 100 µL of NaOH (10%) was added and it has been incubated at room temperature for 15 min. The absorbance was measured at 510 nm and TFC value was expressed as Quercetin Equivalents (QE).

2.6. Free radical scavenging activity

The radical scavenging assay 1,1-diphenyl-2-picrylhydrazyl (DPPH) was carried out similar to the method described by Yu et al. (2008). Indeed, a volume of 1 mL of the methanolic extract with different concentrations was mixed with 1 mL of DPPH solution (0.1 mM in ethanol). This mixture was incubated at room temperature for 30 min, and the absorbance was measured at 517 nm. The concentration required to scavenge 50% of DPPH* was determined based on the ascorbic acid calibration curve.

2.7. FT-IR spectroscopic investigations

Fourier Transform Infra Red (FT-IR) spectra were recorded on a Perkin Elmer Spectrum Two ATR-FTIR using UATR-unit (diamond) in the 4000–400 cm^{-1} region in order to determine the different functions or groups present in the structure of leaves and stem walnut fractions extracts or along their interaction in mixture system with different arrangements.