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Isolation, identification and dyeing studies of betanin on modified acrylic fabrics

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ABSTRACT

Mature red fruits of *Opuntia ficus-indica* contain two soluble pigment, betanin and indicaxanthin. The optimal conditions for dye extraction were to mix 50 g of juice from cactus pears with 100 mL of acidified water as solvent for dye extraction. Two main dyes were purified from the pigment extract by chromatography and identified by UV–vis, HPLC and LC–MS techniques as indicaxanthin (15 mg per 100 g) and betanin (280 mg per 100 g). The effect of dye bath pH, salt concentration, dyeing time and temperature was studied. The optimal conditions for dyeing modified acrylic fabrics with betanin dye were carried out at 50 °C for 45 min at pH 5. Un-mordanted samples have good properties of water and washing fastness. Mordant $CoSO_4$ was found to give good light fastness (rating 5).

1. Introduction

Opuntia ficus-indica belongs to the family Cactaceae, and is originating from Mexico. It is known for rapid growth, good adaptation to poor soils and low requirement for water (Mohamed-Yasseen et al., 1995). Its fruit is a berry, varying in colour, it has been developed green and change colour with its maturity state to orange-yellow and then to reddish purple. Fruit has been used to treat diabetes, hypertension, asthma, oedema and indigestion (Hegwood, 1990). Also, it was also used as a natural food colourant (Moßhammer et al., 2005). Mature red fruits of *O. ficus-indica* were selected as the topic of the present study because of their higher growth in Tunisia. Betanin is the most prevalent betalain in red fruits, which typically contain large quantities of it. The use of betanin in the food industry seems to have been known (Diego et al., 2008) but it's not well known in the field of textile (Henry, 1996). The objective of this study was to investigate the dyeing of modified acrylic fabric using betanin as a natural dye. The dyeing conditions such as the concentration of the dye, the dye bath pH, the salt concentration, the dyeing temperature, the dyeing time, and the effect of the mordants and the overall fastness properties were investigated.

2. Experimental

2.1. Materials

2.1.1. Textile materials

Plain 1/1 woven acrylic fiber was used (43 × 38 threads/inch, metric count 16, weft and warp and 562 den). The fabric was soaped with 2 g/L non-ionic detergent at 60 °C for 30 min, thoroughly rinsed and air dried.

2.1.2. Plant materiel

Reddish purple fruits of *O. ficus-indica* were used in this investigation. Mature fruit samples were harvested on August 2010 and taken immediately to the laboratory where they were manually peeled and subjected to the dye extraction.

2.1.3. Chemicals used

The chemicals used in this study included hydroxylamine hydrochloride, ammonium acetate, alum ($KAl(SO_4)_2{\cdot}12H_2O$, M_W: 342.15, Aldrich), Cobalt sulfate heptahydrate ($CoSO_4{\cdot}7H_2O$, M_W: 281.1, Aldrich), manganese sulfate monohydrate ($MnSO_4{\cdot}H_2O$, M_W: 169.02, Aldrich), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$, M_W: 287.54, Aldrich), and iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, M_W: 278.03, Aldrich). Thin layer chromatography was performed on silica gel 254 plates (Merck) with UV (254 nm) visualisation whereas chromatographic separations were conducted on C_{18} Sep-Pak cartridge column.

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2.2. Methods

2.2.1. Extraction of colourants

50 g of juice from cactus pears was mix with 100 mL of acidified water [water/HCl, v/v ratio 99:1] as solvent for dye extraction. Indeed, slight acidification of the extraction medium enhances betacyanin stability (Schliemann et al., 1999; Strack et al., 2003). To enhance betalain extraction efficiency, extraction was performed by ultrasound (80 W). The ultrasound bath temperature was maintained at around 45 °C in order to prevent potential heat damage to the plant material (Rosario et al., 2003).

The solution was separated from the plant tissue on a Büchner funnel with a filter paper. To achieve complete discolouration of the plant material, the filter residue was rinsed with the extraction solution.

2.2.2. Photometric quantification of betalains

All determinations were performed using a Philips model PU UV/visible spectrophotometer. Measurements were performed in triplicate, and the betalain content (BC) was calculated according to (Stintzing et al., 2003) with a slight modification: BC [mg/L] = $[(A \times DF \times M_W \times 1000/\varepsilon \times L)]$ where A is the absorption value at the absorption maximum, DF is the dilution factor and L is the path-length (1 cm) of the cuvette. The molecular weight (M_W) and molar extinction coefficient (ε) of betanin {M_W = 550 g/mol; ε = 60,000 L/(mol cm) in H_2O} were applied in order to quantify the betacyanins. Quantitative equivalents of indicaxanthin were determined by applying the mean molar extinction coefficient {M_W = 308 g/mol; ε = 48,000 L/(mol cm) in H_2O} (Kugler et al., 2004).

2.2.3. Thermal stability of dyes

Thermal stability studies were performed at pH values of 3–7. Thermal stability was assayed at 50 and 90 °C. Samples were withdrawn at different time intervals and spectrophotometrically analysed. Pigment content and colour retention were determined in triplicate for each sample. The thermal stability was expressed in terms of half-life time ($t_{1/2}$) calculated assuming first-order deactivation kinetics vs temperature exposition time.

2.2.4. HPLC analysis

The HPLC system (Merck) was equipped with an L-7200 autosampler, a D-7000 interface module, an L-7100 pump, an L-7350 column oven with Peltier cooling module, and an L-7450A diode array detector. Reverse phase chromatography was performed with a Kromasil C_8 5 μm column (150 mm × 4.6 mm). HPLC conditions were as follows: Solvent A was H_2O with 0.05% TFA, and solvent B was composed of methanol with 0.05% TFA. A linear gradient was performed over 21 min from 5 to 35% B. The flow rate was 1 mL/min, operated at 25 °C. The injection volume was 20 μL. Elutions were monitored at 475 (indicaxanthin) and 538 nm (betanin).

2.2.5. Mass spectrometry (MS)

Positive ion electrospray mass spectra were recorded on ThermoFinnigan LCQ Advantage (electrospray voltage: 4.5 kV; capillary: 200 °C; sheath gas: N_2). Helium was used to improve trapping efficiency and as the collision gas for CID experiments.

2.2.6. Desalting and separation of betalains

Filtrate was evaporated in vacuo at 40 °C. The concentrate was applied to a C_{18} Sep-Pak cartridge column. The C_{18} cartridge was activated with 3 volumes of 100% methanol and then rinsed with 3 volumes of acidified water (pH 3). For fractionation, the indicaxanthin part was eluted with 100% ethanol while the betanin part remained adsorbed until eluted with acidified ethanol [95:5, ethanol/acidified water (pH 2), v/v] (Guesmi et al., in press).

2.2.7. Pre-treatment and dyeing

2.2.7.1. Pre-treatment. Following a previously published method (El-Shishtawy and Ahmed, 2005), a known weight of acrylic fibre was pretreated with hydroxylamine hydrochloride (10 g/L) using aqueous solutions of ammonium acetate (20 g/L) at a liquor-to-goods ratio of 50:1 at 85 °C for 1 h. The pretreated samples were thoroughly rinsed with water and air dried.

2.2.7.2. Dyeing procedure. In a dye bath containing different amounts of sodium chloride (0–15 g/L) and a dye concentration of 30 mg/L with liquor ratio 40:1, modified acrylic fabric was dyed using conventional heating (CH) at different pH values (1–7) for different durations (30–120 min) and at different temperatures (40–90 °C). The dyed samples were rinsed with cold water and finally dried at ambient temperature. The pH values were recorded with Hanna pH meter, the dye bath was acidic (pH 4.5). To work at pH values superiors at 4.5, the pH values were adjusted with dilute solutions of sodium carbonate and to work at pH values inferiors at 4.5, the pH values were adjusted with dilute solutions of hydrochloric acid.

In case of mordanting, pre-mordanting was chosen as the most suitable process. Modified acrylic fabrics were pre-mordanted at 40 °C for 60 min using various aqueous mordant solutions (0.01 M) with liquor ratio 1:100. Then the samples were removed, squeezed, and air dried (Young and Han, 2004).

2.2.8. Colour strength and colour depth measurements

The colour yield of samples was evaluated by light reflectance measurements using SF 300 spectrophotometer. Relative colour strengths (K/S values) were determined using the Kubelka–Munk equation (Judd and Wysezcki, 1975):

$$\frac{K}{S} = \frac{1 - R^2}{2R}$$

2.2.9. Colour fastness test

The dyed samples were tested for fastness properties according to standard methods, the specific tests were for colour fastness to washing ISO 105-C02:1989, colour fastness to rubbing ISO 105-X12:1987, colour fastness to water ISO 105-E01:1989 and colour fastness to light ISO 105-B02:1988 (carbon arc).

3. Results and discussion

3.1. Extraction and spectroscopic analysis of dyes

Fig. 1 shows the visible absorption spectra of the aqueous extract of reddish purple fruits of *O. ficus-indica*. The spectrum shows two peaks, one at 475 nm corresponding to indicaxanthin and the other at 538 nm corresponding to betanin (José et al., 2001).

The presence of a slight peak at 475 nm would indicate that in these fruits indicaxanthin is to be found in a very lower level than betanin which is present in a much higher concentration. The concentration of pigments was estimated about 300 mg of betanin per 100 g of fresh pulp, and about 20 mg of indicaxanthin per 100 g.

3.2. Effect of pH on the thermal stability of reddish purple fruits of *O. ficus-indica* extracts

To ascertain the effect of pH on the colourant capacity of *O. ficus-indica*, aqueous extracts at different pH values (3–7) were obtained.

The colourant capacity, expressed as a percentage of the maximum absorbance at 538 nm, is shown in Table 1. The maximum