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UPCYCLING: TURNING AGRICULTURE WASTE INTO SUSTAINABLE DYED TEXTILES

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ABSTRACT

Recently, we have started taking a different view on waste and we are finding ways to use it in creating new products. The concept of upcycling has received great attention from numerous fields. The aim of this work is to identify if upcycling of agriculture by-product is possible with textile industry through the use of pomegranate peel for dyeing. HPLC analysis of the methanolic extract obtained from the pomegranate peel powder showed that various phenolic compounds were identified. Effects of dyeing conditions including pH values and temperature on the colour of dyed polyamide fabrics were studied. The best conditions for dyeing were pH of 3 and temperature of 100°C. The dyeing properties were evaluated by measuring K/S values. Fastness properties have been also evaluated. They were ranging between excellent for rubbing and fair for light.

KEYWORDS

Pomegranate peel; Dyeing; Polyamide; Flavonoids; Fastness

1. INTRODUCTION

The massive agriculture waste creates an economical and environmental problem. It is useless and requires costly disposal. Throughout the world, agriculture generates 140 billion metric tons of biomass every year (Dtie, 2009). This waste has substantial economic costs related to its management (Papargyropoulou et al., 2014). For exemple, landfill costs in the USA reach up to 25 millions of dollars per year (Kollikkathara et al., 2010). Recycling is one of the most effective ways to overcome this. Numerous recycling methods are applied for agriculture waste such as composting, refeeding, land application and incineration. Generally, the value of the recycled product is less than or equal to the value of the original product (Vats, Rissanen, 2016). Upcycling is considered as the process in which wastes and by-products are converted into new higher value added product. It covers many different areas such as plastics and metals (Dubreuil et al., 2010; Pol, 2010). In recent years, upcycling of agriculture waste has expanded to textile field. Many researchers have investigated for textile dyeing (Guesmi et al., 2016; Haddar et al., 2015; Meksi et al., 2012). During this work, we report a study to dye polyamide fabrics with pomegranate peels considered as an important agriculture waste.

The pomegranate is one of the oldest edible fruits in the world. It is widely spread in many countries and it is well adapted to Mediterranean climate and arid zones (Ozgen et al., 2008). In Tunisia, it grows in many regions of the country. The main production regions are the oasis of Gabes and Gafsa, Cap Bon, the region of Bizerte and Sousse (Mansour et al., 2013). The peel of the pomegranate presents about 50% of the total weight (Sreekumar et al., 2014). Many authors have reported the use of natural dyes for polyamide dyeing. Lokhande and Dorugade studied the polyamide dyeing using Onion (*Allium cepa*), Lac (*Laccifer Lacca*) and Turmeric (*Curcuma longa*). They found higher dye uptake under acidic conditions and good washing,

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sublimation and light fastness while dyeing using mordants (Lokhande, Dorugade, 1999). Gulrajani et al investigated the methanolic extract of Annato tree (*Bixa orellana*) to dye nylon fabric. They showed that the carotenoid-based dye (bixin) has high affinity for the fiber and yields to good washing fastness (Gulrajani et al., 1999). Gupta et al reported that the dyeing of polyamide with purpurin corresponds to the Nernst isotherm as linear isotherms were obtained. In addition, the dye was found to be sensitive to pH and high temperature. (Gupta et al., 2001). The literature review indicates that there have been relatively few works dealing with polyamide dyeing using pomegranate peel extract. In the current study, we aim the extraction of natural dye from pomegranate peel powder, the characterization of the extracted dye and its use for polyamide dyeing.

2. MATERIAL AND METHODS

2. 1. Materials

Pomegranates (*Punica granatum*) were obtained from local markets in Gabes. The peels were manually removed, sun-dried for 6 hours, cut in small pieces and powdered by electronic grinder, sifted and stored in dark. Fabric of 100% polyamide 6.6 was procured commercially. Chemical reagents were all of analytical grade and were used without further purification: methanol (MeOH), acetonitrile and sulphuric acid (purity nearing > 99.8%) were obtained from Sigma-Aldrich Chemie GmbH (Steinheim, Germany).

2.2. Extraction and CHARACTERIZATION

Pomegranate peel powder was extracted with a Soxhlet extractor using MeOH as solvent. The extract was filtered through a filter paper, evaporated in rotary evaporator and then concentrated under vacuum at 40°C. Visible absorption spectrum was determined using an UV-visible spectrophotometer (Shimadzu, UV-2401).

The presence of phenolic compounds in the extract was studied by reversed phase HPLC analysis using a binary gradient elution. The phenolic compounds analysis was carried out using an Agilent Technologies 1100 series liquid chromatography (HPLC, Palo Alto, CA) coupled with an UV–vis multi-wavelength detector. The separation was carried out on a 250mm × 8mm, particle size 5µm Eurospher-100C18 reversed phase column at ambient temperature. The mobile phase consisted of acetonitrile (solvent A) and water with 0.2% sulphuric acid (solvent B). Using acetonitirle is suitable for high-sensitive analysis in the UV short-wavelength range and results in less noise in detection. Organic solvent is mixed with water to give higher elution capacity. The pH value of the mobile phase is adjusted with sulfuric acid in order to improve constituent separation.

The flow rate was kept at 0.5 $mL.min^{-1}$. The separation was accomplished by gradient elution, as follows: 15% A/85% B 0-12min, 40% A/60% B 12-14min, 60% A/40% B 14-18min, 80% A/20% B 18-20min, 90% A/10% B 20-24min, 100% A 24-28min. The injection volume was 20µL, and peaks were monitored at 280nm since phenolic compounds have a strong absorption peak between 270 and 280nm during spectrophotometric detection (conventional UV-vis detector). Samples were filtered through a 0.45µm membrane filter before injection. Peaks of phenolic compounds were identified based on their relative retention times compared to those of authentic standards analyzed in the same conditions.

2.3. Dyeing procedure

The fabrics were dyed at a liquor ratio (LR) of 1:40. Polyamide dyeing was performed at different pH values. The temperature was raised to different levels. The dyeing was carried out in laboratory dyeing machine (Ahiba Data colour International, USA). Then, the dyed fabrics were rinsed in followed with cold water in a bath of liquor ratio 1:50, squeezed and dried at room temperature.

2.4. Testing of colour strength

The spectral reflectance of dyed samples was measured using spectrophotometer (Data Colour 650®, USA) under illuminant D65, with a 10° standard observer. The colour yield (K/S) values were calculated using the Kubelka-Munk equation (1):

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

Where, R is the reflectance, K the absorption coefficient and S the scattering coefficient.
Integ values were used in this study, and were calculated according to equation (2):

$$Integ = \sum_{\lambda=400}^{700} \left[\left(\frac{K}{S}\right)_{\lambda} E_{\lambda}(\overline{x_{\lambda}} + \overline{y_{\lambda}} + \overline{z_{\lambda}})\right] \qquad (2)$$

Where λ represents the wavelength, E_{λ} is the spectral power distribution of the illuminant,$\overline{x_{\lambda}}$ and $\overline{y_{\lambda}}$, and $\overline{z_{\lambda}}$ are the standard observer functions. Integ is the integration of the Kubelka–Munk constant K/S weighted by spectral power distribution of D65 illuminant and the standard observer functions.

2.5. Fastness properties measurements

The dyed samples were tested for fastness properties according to standard methods: Washing colour fastness (ISO 105-C02), rubbing fastness (ISO 105-X12) and light colour fastness (ISO 105-B02).
Washing fastness of the dyed samples was tested according to the ISO 105-CO2 method. The samples were washed in a standard soap solution. Light fastness was tested according to the ISO 105-BO2 method. The dyed samples were exposed to xenon arc lamp for 24 h at standard testing conditions. Rubbing fastness was evaluated according to the ISO 105-X12. Fading and staining of samples in colour were evaluated using grey and blue scales.

3. RESULTS AND DISCUSSION

3.1. Extraction and characterization

The UV-visible spectrum of pomegranate peel extract is shown in Figure 1. The crude extract showed two spectral bands with maxima absorptions at 292nm and 370nm. The first band peaking is attributed to the presence of aromatic ring(s), and is detected in the spectra of all phenolics. The other band is situated in the 300-400nm range and it is attributed to the presence of flavonoids. Generally, the UV-VIS spectrum of flavonoids shows a first band at 210-290 nm region, which is due to the absorption of the benzoyl system (A-ring), and a second band in the 300-400 nm region, which is associated with the cinnamoyl system (rings B and C)(Mabry et al., 1970)(Figure 2). By increasing conjugation the absorbance shifts towards higher wavelengths (Halbwirth, 2010).

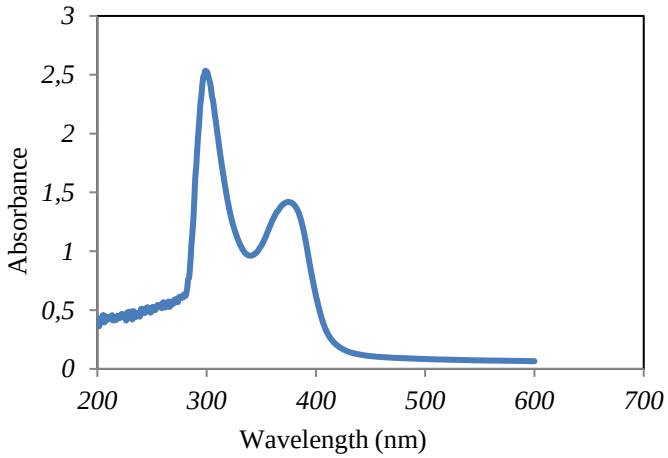

Figure 1: UV-visible spectrum of the extract in aqueous solution

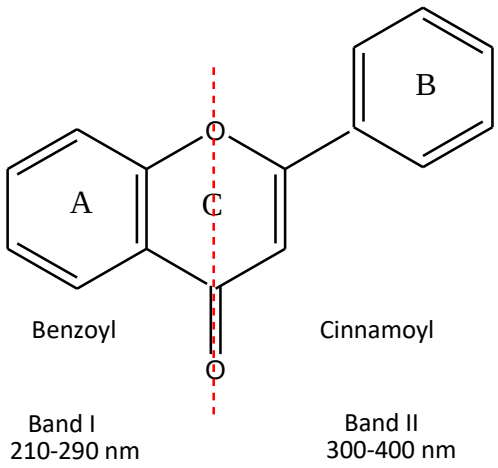

Figure 2: Structural base for flavonoid light absorbance. (Halbwirth, 2010)

HPLC chromatogram of methanol extract is shown in Figure 3. It can be observed the presence of numerous compounds. According to the retention time in reversed phase chromatography, only three peaks were identified as **(1)** catechin, **(2)** caffeic acid and **(3)** Luteolin-7 -Glucoside. The above result was in agreement with literature findings since the identified compounds belong to the main families present in Tunisian pomegranate peel such as flavonoids and hydrolysable tannins (Mansour et al., 2013). Due to the unavailability of authentic standards, many compounds were not identified.

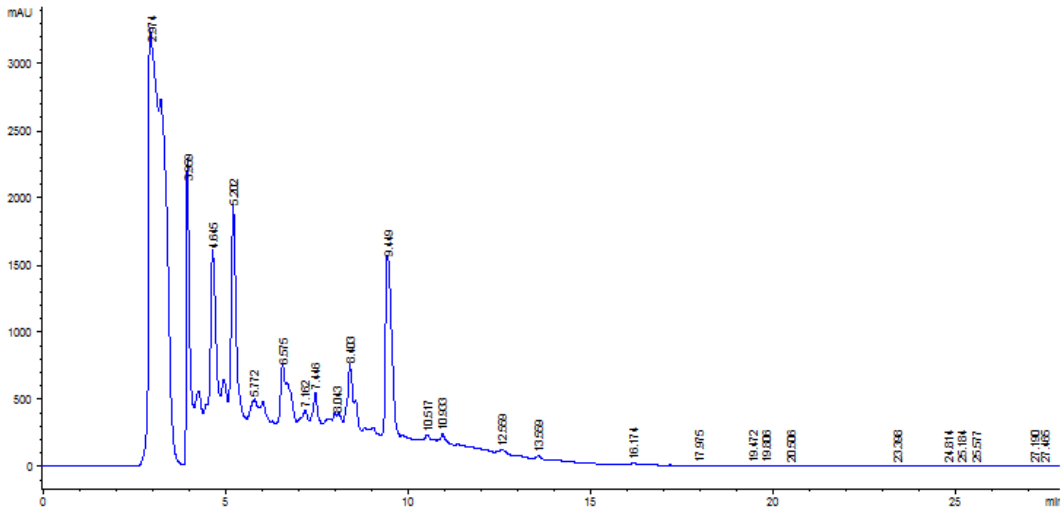

Figure 3: HPLC profile of methanol extract at 280nm wavelength

After the peaks have been identified, quantification was realized using peak areas to determine the concentration of each compound in the extract. The calculated contents of identified compounds are summarized in table 1. The results indicated that the quantity of each compound in the methanolic extract was small. In addition, there was notable difference among the concentration of different compounds. There are some possible factors, such as volatile components and the quality of herbal materials which lead to the variance of concentrations. Due to the complexity of chemical composition in plant extracts, the desired colour probably results from a cooperative action of all compounds.

Table1. Identified compounds (retention times and concentrations)

Retention time (min)	Compound	Concentration (mg/kg)
6.575	Catechin	443.11
8.043	Caffeic acid	276.69
9.449	Luteolin-7-Glucoside	711.48

According to above results, the identification of flavonoids in the pomegranate peel extract confirms that the high dyeing power of this extract is related to the presence of various flavonoids. Luteolin-7-Glucoside was the major flavonoid compound detected in the extract. The luteolin compounds are known to give yellow colour when applied to textiles. They were identified in historical textiles (Valianou et al., 2009) and they are recently used to dye textiles such as wool fabrics and cotton yarn (Cristea, Vilarem, 2006; Mirjalili et al., 2011).

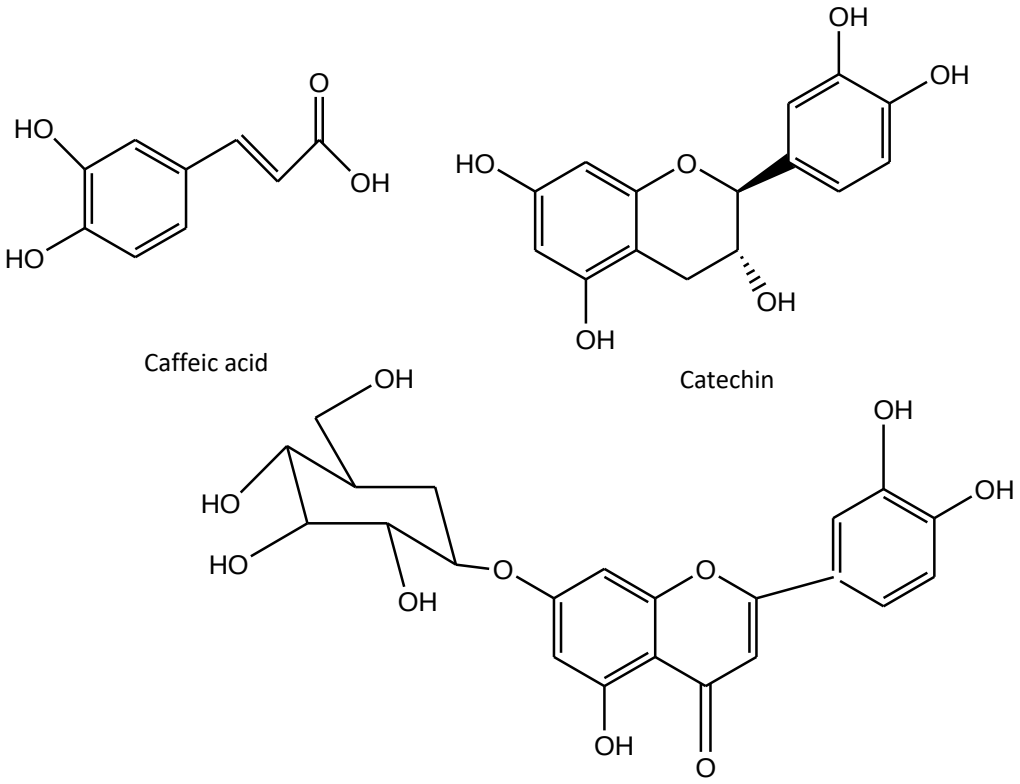

Figure 4: Chemical Structures of identified compounds

3.2. Determination of total phenolic content

Determination of total phenol content was carried out with an UV/Vis spectrophotometer at 760 nm using the Folin-Ciocalteau reagent and gallic acid as standard. Results were reported as mg Gallic Acid Equivalent (GAE) per g of dry weight (DW) (Scalbert et al., 1989). Results revealed the highest amount of total phenols: 210 ± 18mg (GAE).g^{-1}(DW).

3.3. Dyeing

3.3.1. Effect of dyeing pH

The effect of the dye bath pH on the dyeability of polyamide fabrics with the pomegranate peel extract was conducted at different pH (3-12). As shown in Figure 5, the colour yield (K/S) of the dyed fabrics is inversely proportional with the pH values. The dyeability decreased while increasing pH values. The number of ionized amino groups and carboxylic acid groups give rise to the dyeing properties of polyamide fiber. In aqueous solution and based on the pH value, terminal groups (attached to the polyamide fiber back bone PA) will be ionized to a greater or lesser extent as shown bellow (Soleimani-Gorgani, Taylor, 2006):

$$NH_2 - PA - COO^- \xleftrightarrow{H^+} NH_2 - PA - COOH \xleftrightarrow{H^+} NH_3^+ - PA - COOH$$

As it can be observed, polyamide is essentially anionic at high pH. Therefore, an electrostatic repulsion occurs between the anionic natural dye and the fiber. At acidic pH, ionization of amino groups prevails on the carboxylic acid ones. In consequence, the deduced increase in colour strength can be attributed to an

ion-ion attractive interaction occurring between the fiber and the dye. This result is in agreement with previous studies which have shown that at acidic pH, terminal amino groups of polyamide are protonated enhancing dyeability by improving the interaction between the fiber and the flavonoids (Haddar et al., 2015).

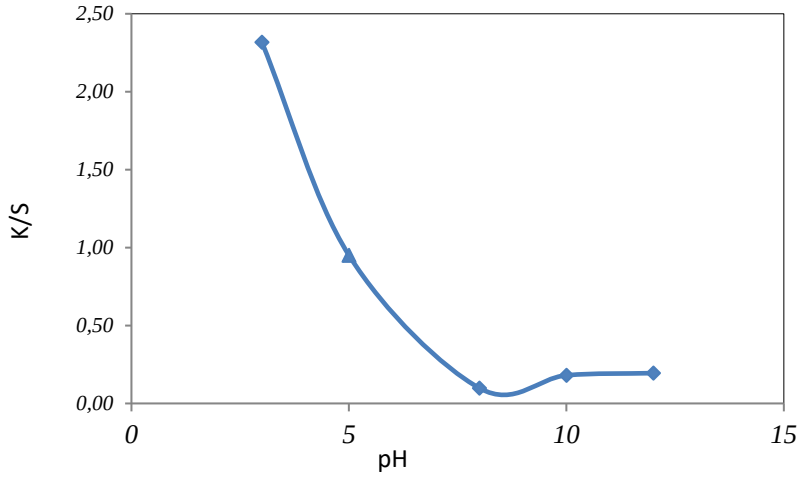

Figure 5: Effect of dye bath pH on the colour strength of dyed polyamide fabrics
Dyeing conditions: dye concentration 0.5g/100ml, 45min, LR 40:1 and T=90°C.

3.3.2. Effect of dyeing temperature

As shown in Figure 6, colour strength of dyed samples increases as the temperature increases. This finding can be explained by the fact that heating increases the fiber swelling, and leads to a more dye dispersion and solubility (Haddar et al., 2015). Generally, synthetic fibers are dyed at high temperature because of their crystalline structure. Increasing the temperature leads to the diffusion of the dye into the fibers (El-Shishtawy et al., 2009). As the temperature increases, the molecular structure becomes open which facilitate the dye uptake and therefore the higher colour strength values are obtained. In addition, at high temperature, the rate of dye adsorption into the fabric will be fast because the rate of reaction of dye molecules increases due to their fast movement. However, at low temperature, the adsorption rate is slow. The movement of dye molecules is slow down. Chemical interactions diminish at low temperature giving rise to the scarce adsorption and final fixation of the dye.

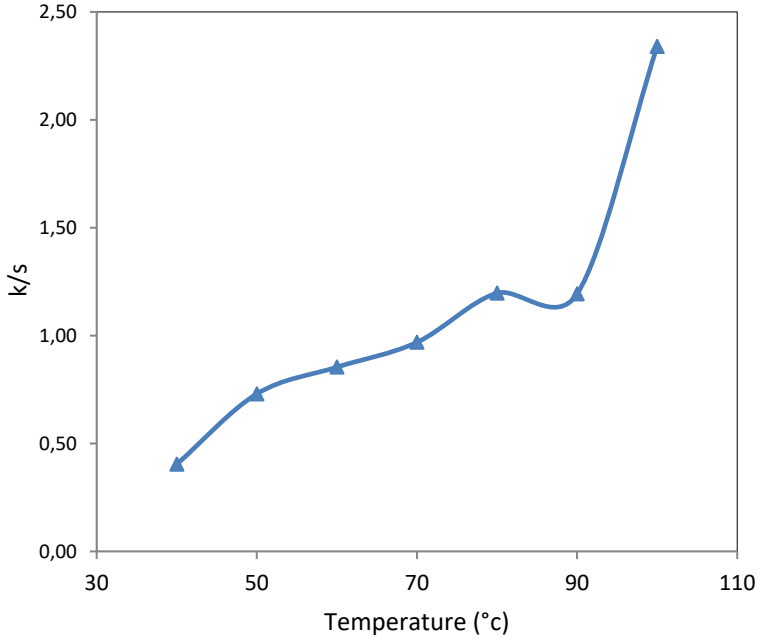

Figure 6: Effect of dye bath Temperature on the colour strength of dyed polyamide fabrics.
Dyeing conditions: dye concentration 0.5g/100ml, 45min, LR 40:1 and pH=3.

3.3.3. Colour fastness

An important condition for further application of dyed fabrics is related to the colour fastness. To evaluate the fixing rate of the natural dye, a visual assessment of change in colour of samples was operated after realizing tests according to different ISO standards. On the grey scale, a value of 1 indicates poor wash fastness whereas a value of 5 corresponds to virtually no colour change. On the blue scale, a value of 1 indicates poor light fastness and a value of 8 indicates excellent light fastness. The fastness tests (washing, rubbing and light fastness) of polyamide fabrics dyed with *pomeg*ranate peel extract are shown in Table 2. The results indicate fair to excellent fastness properties of the dyed samples. It was found that rubbing fastness showed excellent properties. However, washing fastness was relatively good and light fastness was fair.

Table 2: Colour fastness

Dry rubbing fastness	Wet rubbing fastness	Washing fastness	Light fastness
5	5	3-4	2

4. CONCLUSION

The present work study the possibility of dyeing polyamide fibers with pomegranate peel extract. Extraction was conducted using soxhlet apparatus and methanol as solvent. HPLC analyses demonstrate the presence of flavonoids such as luteolin which gives the yellow colour while dyeing. Other phenolic compounds are also identified such as caffeic acid. Furthermore, The study of the effect of dyeing conditions on the colour yield values showed that better colour yield (K/S) are obtained at acidic pH and high heating temperature. The best conditions for dyeing of polyamide fabric with pomegranate peel extract were pH of 3 and temperature of 100°C. The wash, rubbing, and light fastness of the dyed samples were ranging between excellent for rubbing and fair for light. The use of pomegranate peel for dyeing seems to be a promising way to create functional textiles since flavonoids present particular biological activities.

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