Optimisation of the recovery of carotenoids from tomato processing wastes: application on textile dyeing and assessment of its antioxidant activity

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ABSTRACT
The present study has been focused on the extraction of natural pigments from tomato industry waste. At first, different solvents and solvents mixture were compared to determine which one is the best for extracting carotenoids compounds from tomato by-products. A mixture of hexane and acetone gave the highest carotenoids extraction yield among the others examined. The extraction conditions were optimised using a five-level–five-factor central composite design. Under optimal conditions, solvent solid ratio 90, hexane percentage in the solvent mixture 60, extraction duration 50, number of extractions 4 and extraction temperature 35 °C, the yield of carotenoids was 80.7 μg/g. The coloured extract of tomato by-products was applied on textile fabrics to investigate the dyeing characteristics and antioxidant activities. The results indicate that extract can be applied on textile fabrics (wool, silk and polyamide) to produce coloured clothing with acceptable antioxidant properties.

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1. Introduction

Plant material such as roots, barks, vegetables, leaves, fruits and berries has been used for textile dyeing over hundreds of years (Zhang et al. 2014). With the industrialisation and the invention of synthetic dyes, natural dyes disappeared almost entirely from the textile industry (Sinha et al. 2012). With their well-known structures, synthetic dyes became easier in handling, higher in process safety and better in reproducibility compared to natural dyes. Nevertheless, there is a reviving interest, in dyeing textiles with natural dyes considering their biodegradability, renewability and compatibility with the environment (Hou et al. 2013).

The high processing cost and the low availability of natural colouring substances are the most important reasons for preventing these products from being more popular. The attempts to overcome these problems and reduce prices have mainly focused on the discovery of newer natural colouring substances, especially the valorisation of several coloured plant wastes from industrial food and beverage production (Meksi et al. 2012; Baaka et al. 2015). Tomato is the second most important vegetable crop, with 100 million tons of fresh fruit produced annually in 144 countries. The industrial tomato processing generates huge amounts of residues, such as, tomato seeds and peels, representing 10–40% of total processed tomatoes (Topal et al. 2006).

Antioxidant activity is one of the most important properties of bioactive textiles. Several investigations reported the antioxidant activities of natural dyes extracted from plants (Guinot et al. 2007). Other studies investigated the antioxidant activities of textiles dyed with natural dyes (Sun et al. 2013; Zhou et al. 2015). The purpose of the present paper was to study the extraction yield of carotenoids from tomato waste with different solvents and solvent mixtures and to optimise the extraction conditions as regards the ratio of solvent mixture to tomato by-products, the hexane percentage in the solvent mixture, the extraction time, the number of extractions and the extraction temperature, using response surface methodology. The pigment extracted from tomato by-products was applied to wool, silk and nylon fabrics to investigate its dyeing properties and antioxidant activities.

2. Results and discussion

2.1. Selection of the extraction solvent

Carotenoids are liposoluble, and they are usually extracted from the plant sources with organic solvents such as hexane, acetone and ethyl acetate. To select the most suitable solvent for total carotenoid extraction from tomato waste, seven extraction solvents have been tested. The obtained results are presented in Table 1. From this table, it was clearly indicated that the combination of hexane with acetone, ethyl acetate or ethanol increased the total carotenoids yields compared with that obtained by any of the individual solvents. The highest carotenoid yield was obtained using a mixture of hexane/acetone (50:50, v/v).

This result may be explained by the fact that tomato waste contains polar carotenoids such as lutein and nonpolar carotenoids such as β-carotene and carotenoids ester. In fact, polar carotenoids are easily dissolved in polar solvent such as acetone while the nonpolar carotenoids are dissolved in nonpolar solvent, namely hexane (Strati & Oreopoulou 2011). Therefore, the combination of solvents improved the total carotenoids yield compared with that obtained by individual solvents.
2.2. Optimisation of the extraction process

In this study, the experiments were established based on a central composite design method with five factors and five levels. The extraction process performance was evaluated by analysing the carotenoid yield that is dependent on the input factors; the solvent/solid ratio \((X_1)\), the hexane percentage in the solvent mixture \((X_2)\), the extraction time \((X_3)\), the number of extractions \((X_4)\) and the extraction temperature \((X_5)\) (Gua et al. 2008; Strati & Oreopoulou 2011).

2.2.1. Model establishment

The formulated design matrix, shown in Table S1, was a response surface central composite design consisting in 32 sets of coded conditions.

Its regression analysis by a quadratic model leads to the following equation (Equation 1):

$$
\text{Carotenoids Yield} = 98.3 - 0.358 X_1 - 0.969 X_2 - 2.883 X_3 + 1.49 X_4 - 0.309 X_5
+ 0.011 X_1^2 + 0.011 X_2^2 + 0.056 X_3^2 - 0.775 X_4^2 + 0.018 X_5^2
- 0.012 X_1 X_2 - 0.014 X_1 X_3 + 0.007 X_1 X_4 + 0.004 X_1 X_5
+ 0.018 X_2 X_3 + 0.008 X_2 X_4 + 0.002 X_2 X_5
+ 0.312 X_3 X_4 - 0.032 X_3 X_5 - 0.106 X_4 X_5
$$

(1)

where \(X_1, X_2, X_3, X_4\) and \(X_5\) are the coded variables of solvent/solid ratio, hexane percentage in the solvent mixture, extraction time, number of extractions and extraction temperature, respectively. With \(R^2 = 0.994, R^2_{\text{adj}} = 0.983, R^2_{\text{pred}} = 0.874\)

The established model adequately described the observed data, explaining approximately 99.4% (due to \(R^2 = 0.994\)) of the variability of carotenoids yield.

2.2.2. Contour plots analysis

Contour plots were very useful to see interaction effects of the factors on the response. In this graph, the response was viewed as a two-dimensional plane where all points that have the same response are connected to produce contour lines of constant responses. The results are given in Figure S1. It shows the variations in carotenoids yield as a result of selecting different values of two variables while the values of the other variables are held constant.

The contour plots described in Figure S1 indicate that the highest carotenoid yield is obtained from average values of solvent/solid ratio, extraction duration and hexane percentage in the solvent mixture.

Table 1. Total carotenoid yield from tomato waste extracted with different solvents and solvent mixtures.

| Solvent/solvent mixture   | Carotenoids yield (μg/g dry extract) |
|---------------------------|-------------------------------------|
| Ethanol                   | 26.32                               |
| Hexane                    | 32.1                                |
| Ethyl acetate             | 35.84                               |
| Acetone                   | 43.5                                |
| Hexane–Acetone (50:50)    | 68.26                               |
| Hexane–Ethyl acetate (50:50) | 57.4                              |
| Hexane–Ethanol (50:50)    | 51.73                               |
2.2.3. **Optimisation of extraction parameters and validation of the model**

The optimal parameters for total carotenoids extraction from tomato waste were evaluated by response surface methodology, and a maximal carotenoids yield of 80.7 μg/g was achieved at the optimal conditions: solvent solid ratio 90:1 (v/w), hexane percentage in the solvent mixture 60%, extraction duration 50 min, number of extractions 4 and extraction temperature 35 °C. The accuracy of the model was validated with triplicate experiments. The experimental value of carotenoids yield was 79.8 μg/g, which agreed well with the predicted value (80.7 μg/g). The relative error between experimental value and predicted value was 0.9%.

2.3. **Characterisation of the tomato by-products optimised extract**

2.3.1. **Spectrophotometric analysis**

The spectrophotometric analysis gave a general view on the extract composition. In fact, the UV–visible absorption spectra (Figure S2) of natural pigments extracted in hexane/acetone mixture presented three bands with maximum absorption at 451, 478 and 508 nm. Those peaks are characteristics of carotenoids (Qiu et al. 2006; Aghel et al. 2011).

2.3.2. **FTIR characterisation**

FTIR spectral peaks of natural pigments extracted from tomato processing by-products with hexane/acetone mixture are shown in Figure S3. The spectra consist of different groups of absorption bands at wavenumbers ranging from 4000 to 400 cm⁻¹. It showed stretching OH at 3437.52 cm⁻¹. The C–H stretching symmetric bands were observed at 2929.04–2840.62 cm⁻¹. The sharp bands at 1728.62–1596.73 cm⁻¹ are assigned to carboxylate group vibration. Small peak assigned to deformation CH₃ cm⁻¹ was observed at 1385.32 cm⁻¹. The bands at 1190.82 and 1125.95 cm⁻¹ correspond to vibrations of –C–O–C glycoside ring bond, C–O stretching in COOH and O–H bending. We denote from this spectrum a common characteristic absorption bands of carotenoids structure (Salama et al. 2015; Grassino et al. 2016).

2.4. **Measurement of K/S, L* a* b* values**

The textile fabrics (wool, silk and polyamide) were dyed with tomato by-products extract. The obtained shades for different dyed fabrics are presented in Figure 1. The colorimetric data (K/S, L* a* b*) of dyed wool, silk and polyamide are given in Table 2.

![Figure 1. Photographs of dyed fabrics (wool, silk and polyamide) with tomato by-products extract.](image-url)
The dyeing of different fabrics (wool, silk and polyamide) with natural pigments extracted from tomato by-products gave reddish and yellowish shades (Figure 1). The obtained shades are verified by the results of $a^*$ and $b^*$ values.

### 2.5. Fastness of the dyed samples

The colour fastness of the dyed wool, polyamide and silk fabrics was evaluated, and the results are assessed and listed in Table 3. The fastness assessment of the dyed wool and polyamide fabrics was good for washing; this result is probably due to the high affinity of the natural carotenoids pigments to wool and polyamide fabrics. All the dyed fabrics presented good dry and wet rubbing fastness, indicating the good diffusion and penetration of the coloured pigment into find substrates. However, the light fastness properties of all the dyed fabrics were poor, with the grade 2 for wool and silk fabrics and 2–3 for polyamide fabrics dyed with tomato by-products extract. The poorer results of the light fastness for carotenoids dyestuff from tomato by-products could be interpreted by the high sensitivity of carotenoids compounds to photo-oxidation when exposed to light.

### 2.6. Antioxidant activity

Antioxidant activity represents an important characteristic property of functional textile fabrics. The bioactive fabrics with good antioxidant activity can deactivate highly reactive and harmful species such as active oxygen radicals (Sun et al. 2013). Because textile fabrics are in direct contact with body, its antioxidant activity is of great importance for developing healthy and hygienic textiles. Carotenoid compounds represent an important source of antioxidants and have good antioxidant activity. Figure 2 shows that undyed wool, silk and polyamide fabrics have an antioxidant activity about 22, 28, and 40%, respectively, revealing the poor radical scavenging ability of original fabrics. The three fabrics dyed with carotenoid pigments represent good antioxidant activities, which increased with increase in dye concentrations.
3. Experimental

3.1. Tomato by-products

The tomato processing residues (skin, peel and seeds) were collected from a tomato processing industry located in Kairouan region (latitude: 35° 40′, longitude: 10° 5′), Tunisia. The tomato was identified as *Solanum lycopersicon* L., variety Rio Grande (Petoseed, Saticoy, CA, USA) commonly grown in Tunisia. A voucher specimen (FSM-SL 2015) was deposited at the herbarium of the Faculty of Sciences of Monastir, Tunisia. Plant materials were dried at room temperature. Subsequently, the dried material was ground and a fine powder was obtained.

3.2. Carotenoids determination

The total carotenoids yield (μg/g dried biomass) was calculated according to the formula (Equation 2) determined in previous study (Chen et al. 2006):

\[
\text{Carotenoids yield (μg/g dried biomass)} = \frac{1000 \, \text{ADV}}{0.16 \, \text{W}}
\]

where A is the absorbance value of diluted extraction at 480 nm, D is the dilution ratio, V is the volume of solvent, W (g) is the weight of dried tomato waste and 0.16 is the extinction coefficient of carotenoids.

3.3. Colorimetric and fastness properties of dyed fabrics

Dyed fabrics processed in this study were subjected to the reflectance colour measurements using a SpectroFlash SF300 spectrophotometer. The following measurement conditions were selected: illuminant D65 and 10° standard observer. The colour measurements were analysed by considering the CIE L* a* b* or CIELAB colour system. The fastness properties of dyed
samples were tested according to ISO standard methods: colour fastness to washing (ISO 105-C06), to rubbing (ISO 105-X12) and to light (ISO 105-B02).

3.4. Antioxidant activity

The DPPH radical scavenging assay was used to evaluate the antioxidant activity of textile fabrics. A volume of 3 mL of DPPH solution in ethanol (0.1 mM) was mixed with 300 mg of fabric and 7 mL of ethanol (Jha & Matsuoka 2000). The samples were incubated for 30 min in dark at room temperature. The following equation (Equation 3) was used to calculate the DPPH scavenging activity:

\[
\text{Antioxidant activity(\%) } = 100 \times \frac{A_{\text{control}} - A_{\text{sample}}}{A_{\text{control}}}
\]

where \(A_{\text{control}}\) is the initial absorbance of the DPPH, \(A_{\text{sample}}\) is the absorbance of the DPPH solution in the presence of the fabric.

4. Conclusion

Response surface method has proved to be a powerful tool for the optimisation of total carotenoids extraction conditions from tomato industry waste. The conditions were optimised using a five-level–five-factor central composite design. Under optimal conditions (solvent solid ratio 90:1 (v/w), hexane percentage in the solvent mixture 60%, extraction time 50 min, number of extractions 4, extraction temperature 35 °C), the carotenoids yield was 80.7 μg/g. Natural pigments extracted from tomato by-products could be used for dyeing textile fabrics (wool, silk and polyamide) with reddish-yellowish shades and good fastness properties.

Dyed fabrics with tomato by-products extract were also found to have good antioxidant activity, which can greatly increase the interest of the consumers of green products by developing bioactive textile materials and clothing.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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