

Recovery of antioxidant compounds from mango peel by green extraction processes

^{1,2}Souza, M. E. A. O., ^{1,3}Mezzomo, N., ⁴Correa, L. C., ²Lima, M. S., ²Azevêdo, L. C. and ^{1*}Ferreira, S. R. S.

¹Chemical and Food Engineering Department - Federal University of Santa Catarina - EQA/UFSC - C.P. 476, CEP 88.040 - 900, Florianópolis, SC, Brazil

²Food Technology Department - Federal Institute of Sertão Pernambucano, CEP 56.314 - 520, Petrolina, PE, Brazil

³Catarinense Federal Institute - Campus Brusque/SC, R. Hercilio Luz, 63, CEP 88.350 - 300, Brusque, SC, Brazil

⁴Brazilian Agricultural Research Corporation - Embrapa Semiárido, BR 428, Km 152, CEP, 56302 - 970, Petrolina, PE, Brazil

Article history

Received: 17 January, 2019

Received in revised form:

19 June, 2019

Accepted: 17 October, 2019

Abstract

The present work shows that mango peel is an agro-industrial residue with high nutraceutical value, and a suitable separation process was evaluated for the best extraction of its bioactive content. The objective of the present work was to analyse the phenolic profile and *in vitro* antioxidant activity (AOX) of extracts from mango peel obtained by low pressure methods using organic solvents and by supercritical fluid extraction (SFE). Soxhlet extraction procedure with ethanol provided the highest extraction yield and the highest *in vitro* AOX. Extracts recovered by SFE exhibited better antioxidant potential according to β -carotene bleaching method, while extracts obtained with polar solvents using low pressure methods resulted in higher AOX according to DPPH method. Several phenolic compounds detected in the extracts obtained with organic solvents were quantified, namely kaempferol 3-glucoside, quercetin piranoside, quercetin 3-glucoside, isorhamnetin, myricetin, and rutin, which was the major compound found in all extracts, confirming the presence of valuable components in this bio-waste.

© All Rights Reserved

Keywords

SFE

Bioactive compounds

Bio-residue valorisation

Green processes

Introduction

Mango (*Mangifera indica* L.) is recognised as one of the most important tropical and subtropical fruits in the world (Castro-Vargas *et al.*, 2019). Brazilian mango production in the semi-arid region in the São Francisco River Valley has been increasing by about 3% annually, due mostly to the use of improved postharvest technologies associated with favourable climate and irrigation conditions. As a result, mango was the leading exported fruit in 2016, and Brazil is one of the largest mango producing countries in the world (Carvalho, 2017).

Tommy Atkins mango cultivar, present in many regions of America and Asia, is recognised for its large size and common use in the food industry

(Castro-Vargas *et al.*, 2019). According to Coelho *et al.* (2019), the Tommy Atkins variety is appreciated for its attractive colour, distinctive appealing flavour, and various health-promoting nutrients, such as flavonoids and carotenoids, and as bioactive compounds with potential antioxidant activities (Lerma-Torres *et al.*, 2019). Besides that, recent studies have demonstrated that mango leaves are also important sources of polyphenols with antioxidant and pharmaceutical properties (Fernández-Ponce *et al.*, 2016). The mango processing generates a large amount of agro-industrial residues consisting of seed and peel, which may cause significant environmental impacts (Siddiq *et al.*, 2017). Mango peel represents from 15 to 20% and seed around 20% of the total fruit weight (Kim *et al.*, 2012). Mango and its by-

*Corresponding author.

Email: s.ferreira@ufsc.br

products are reported to have functional constituents, mostly flavonols such as mangiferin, catechins, quercetin, and gallic acid, which are associated with the antioxidant capacity of mango pulp and peel (Dembitsky *et al.*, 2011; Ribeiro da Silva *et al.*, 2014; Jahurul *et al.*, 2015). These compounds are associated with the prevention of degenerative diseases, including cancers, cardiovascular diseases, and diabetes (Masibo and He, 2009; Sellamuthu *et al.*, 2013).

Mango peels are important industrial by-products, scarcely used as processed foods, but with high potential for recovery of functional ingredients (López-Cobo *et al.*, 2017). The phytochemical profile of mango peel contains polyphenols, carotenoids, and vitamins, with several health benefits mainly associated to its antioxidant activities (Garcia-Mendoza *et al.*, 2015). Various polyphenolic compounds, such as gallates, gallatannins, flavonoids, xanthones, benzophenones, gallic acid, and derivatives, were detected from mango peel extract samples (Dorta *et al.*, 2014). According to Liu *et al.* (2013), mango peels contain a considerable concentration of bioactive compounds, and they suggest that the rational use of these residues provides, in addition to the nutritional benefits, reduction in environmental impacts. The utilisation of mango by-products, such as peel and seeds, can enable the recovery of functional natural products for food and pharmaceutical industries and reduce problems of waste disposal of mango agro-industries (Castro-Vargas *et al.*, 2019). Therefore, industrial units should adjust their manufacturing processes to efficiently and ecologically recover from their bio-residues as it is a valuable substance with promising applications (Martins and Ferreira, 2017).

According to Sogi *et al.* (2013), different drying procedures (freeze drying, hot air drying, vacuum drying, and infrared drying) applied to Tommy Atkins mango peel show comparable ascorbic acid contents, while carotenoids and phenolic components are affected by the high temperature of the drying methods. Based on this, the present work was aimed at evaluating the influence of the pre-treatment (drying procedures) on the extraction yield obtained by different low pressure separation processes.

Soxhlet, maceration, and ultrasound processes are extensively applied as methods for extraction of several raw materials. Some of the commonly used organic solvents are ethanol, hexane, and ethyl acetate. Although these processes and solvents are commonly used, they are associated with high temperatures and extensive solvent use, causing

chemical and/or thermal damages to the resulting extract (Pourmortazavi and Hajimirsadegui, 2007; da Silva *et al.*, 2016b). Alternatively, supercritical fluid extraction (SFE) has been considered as an option for extraction and fractionation of several natural raw materials, with carbon dioxide as the most common high-pressure solvent. SFE enables the use of a “green” solvent (carbon dioxide), provides a fast and selective extraction with low thermal degradation, produces solvent-free extracts, and allows an easy control of selectivity— aspects that are relevant for high quality products (Khajeh *et al.*, 2004; Straccia *et al.*, 2012).

Fernández-Ponce *et al.* (2012; 2016) compared SFE, pressurised liquid extraction (PLE), subcritical water extraction (SWE), and enhanced solvent extraction (ESE) for the recovery of extracts from mango leaves, with a good SFE and PLE performance due to high pressure effects on solubility and desorption of active compounds (Fernández-Ponce *et al.*, 2016). Ruiz-Montañez *et al.* (2014) studied the extraction of bioactive compounds, such as mangiferin and lupeol from mango peels using ultrasonic assisted extraction and hydrostatic high pressure extraction. According to Garcia-Mendoza *et al.* (2015), pressurised solvents are an interesting alternative for the extraction of bioactives from mango peel. Lerma-Torres *et al.* (2019) obtained mangiferin and lupeol from leaves and bark of the Ataulfo and Autochthonous mango tree varieties using maceration, Soxhlet, ultrasound, and microwave techniques. Pereira and Meireles (2007) obtained mango leaves extract with antioxidant activity and phenolic compounds using supercritical CO₂, while Garcia-Mendoza *et al.* (2015) used the same method to recover extracts from mango peel.

Although studies on the extraction of bioactive compounds from Tommy Atkins peel have been reported, limited number of phenolic compounds was identified in those studies, mostly catechin, procyanidin A2, B1 and B2, kaempferol, quercetin, rutin, cinnamic and benzoic acids, and resveratrol. Therefore, given that the bioactive potential of the recovered extracts is highly related to the diversity of their components, the objective of the present work was to evaluate the phenolic profile of Tommy Atkins peel extracts recovered by SFE, with CO₂ under pressure conditions set at 100, 200 and 300 bar and temperatures of 40, 50 and 60°C; and compare it with the results of low pressure extraction methods (Soxhlet, maceration, and ultrasound-assisted extraction) using ethanol, hexane, and ethyl acetate as solvents.

Materials and methods

Chemicals

Trolox (6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid) and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium persulphate, ethanol, acetone, sodium carbonate, and Folin-Ciocalteu were purchased from Merck (Darmstadt, Germany). Methanol and acetonitrile (both HPLC grade) and ortho-phosphoric acid were supplied by Vetec Química Fina Ltda. (Rio de Janeiro, Brazil), JT Baker (Phillipsburg, NJ) and Fluka (Switzerland), respectively. Water was purified by Elga PURELAB option-Q (USA) purification system. The standards of ferulic, syringic, cinnamic, *ortho*-coumaric, and benzoic acids were purchased from Chem Service (West Chester, USA). The *para*-coumaric and gallic acids were purchased from Sigma-Aldrich (St. Louis, MO, USA). Kaempferol-3-O-glucoside, isorhamnetin, quercetin 3-piranoside, quercetin 3-glucoside, (+)-catechin, (-)-epicatechin, rutin, (-)-gallate, epicatechin, (-)-epigallocatechin gallate, procyanidin A2, procyanidin B1, procyanidin B2, and trans-resveratrol were purchased from Extrasynthese (Genay, France).

Sample preparation

“Tommy Atkins” variety mangoes were provided by fruit producers from São Francisco River Valley (Petrolina, PE, Brazil), latitude 9° 34’ south, longitude 40° 26’ west and 375 m altitude. The mango peel was manually removed from the washed fruits by using a stainless steel kitchen knife. The peels were cut into thick strips of 2.7 ± 0.9 mm, measured by an electronic outside micrometer, and then dried by: (a) air-drying at 23 to 36°C, relative humidity of between 30 and 80%, in atmospheric pressure for 8 d; and (b) forced-drying in an oven with forced air circulation (Pardal, PE 30, 900 W) at $40 \pm 2^\circ\text{C}$ for 24 h. following drying, the peels were ground in a knife mill and stored in plastic bags in a domestic freezer at -18°C . The low-pressure extractions methods were applied for both dried raw materials, whereas the supercritical fluid extraction was performed for forced dried mango peel samples. Since forced-drying allows control of process variables such as temperature and providing homogeneous dry materials, this method was selected to provide samples for the supercritical fluid extraction process.

Low pressure procedures

Low pressure extraction methods (Soxhlet, maceration, ultrasound assisted extraction) were

performed at least in duplicate, using the solvents *n*-hexane, ethyl acetate, and ethanol (Nuclear, CAQ Ind. e Com. LTDA., Brazil), with increasing polarity from 0 to 5.2 (Reichardt, 2003).

Soxhlet extraction (SOX)

The SOX extraction was performed following the procedure described in the 920.39C method of AOAC (2012) using 5 g of dry and ground sample, packed inside a cartridge and placed in a 250 mL Soxhlet apparatus. The extractions run for 6 h with 150 mL of solvent at boiling point.

Maceration extraction (MAC)

Maceration was conducted following the procedure described by Sachindra *et al.* (2006) with 25 g of sample and 100 mL of solvent, protected from light for 5 d at room temperature with manual stirring once daily. The resulting mixture was vacuum-filtered using a Büchner funnel with filter paper, and the filtrate was collected in a Kitasato apparatus.

Ultrasound-assisted extraction (UAE)

The ultrasound-assisted extraction was conducted following the procedure described by Gu *et al.* (2008) in an ultrasonic cleaner bath (Unique Ultracleaner, USC - 700) at 55 kHz and 100 W by placing 5 g of pre-treated sample and 150 mL of solvent into a covered glass balloon at room temperature for 60 min.

Supercritical fluid extraction (SFE)

SFE of mango peel was performed in a dynamic extraction unit (Zetzl *et al.*, 2003). A co-solvent pump (Constametric, 3200, EUA) was connected to supply the modifier (co-solvent) at a preset flow rate. The extractions, conducted according to Michelin *et al.* (2005), used 15 g of sample (forced dried and ground mango peel). The extract was collected in amber flasks after 3.5 h (210 min) and weighed on an analytical balance (OHAUS, Model AS200S - NJ - USA). The SFE assays were performed at least in duplicate for two groups: (a) CO₂ assays, at pressure conditions of 100, 200 and 300 bar, temperatures of 40, 50 and 60°C, and constant solvent flow rate of 8.3 ± 0.8 g/min; (b) co-solvent assays, where ethanol was mixed with CO₂, at concentrations of 2.5, 5.0, and 7.5% (w/w). The co-solvent assays were conducted at 50°C and 300 bar, criteria chosen based on the high yield obtained with CO₂. The SFE assays were performed with 99.9% purity CO₂ (White Martins, Brazil), with specific weights for each operating condition, determined according to Angus *et al.* (1976).

Separation of the mixture extract/solvent

The residual solvent from the extracts (SOX, MAC, UAE, and SFE with co-solvent) was eliminated by rotary evaporator (Fisatom, 802, Brazil), supplied with cooling and vacuum controllers, and the extracts were stored in amber flasks at -18°C. The extraction yield, for all methods, was calculated using to Eq. 1, which considers mass of extract (m) and mass of raw material on a dry basis (M). The results were presented as average ± standard deviation.

$$X = \frac{m}{M} \times 100 \quad (\text{Eq. 1})$$

Phenolic compounds profile by RP-HPLC/DAD/FD

The phenolic compounds of mango peel extracts were determined by Reversed-Phase High Performance Liquid Chromatography (RP-HPLC) (Waters systems - model Alliance e2695) coupled to diode-array-detection (DAD) and fluorescence-detection (FD). The analysis followed the methodology described by da Silva *et al.* (2016a). The Empower™ 2 software (Milford, EUA) was used for data processing. Briefly, the analysis consisted of identifying and quantifying 16 phenolic compounds, which represent the phenolic compounds profile. Diode-array-detector (DAD), at a wavelength of 280 nm, was used to detect syringic acid, at 320 nm for the stilbene trans-resveratrol and three phenolic acids (cinnamic, ortho-coumaric, and para-coumaric); at 360 nm for the flavonols kaempferol 3-O-glucoside, quercetin 3-glucoside, quercetin piranoside, rutin, and isorhamnetin. Otherwise, fluorescence detection (FD), excitation at a wavelength of 280 nm and emission at a wavelength of 320 nm, was used to identify and quantify benzoic acid and the phenolic flavanols catechin, epicatechin, and procyanidin B1 and B2. The furnace temperature was maintained at 40°C, the flow rate was 0.6 mL/min and the total run time was 65 min. The elution gradient used was 0 min 100% A; 18 min 87.5% A, 2.5% B, 10.0% C; 30 min 83.5% A, 3.2% B, 13.3% C; 36 min 75.0% A, 5.0% B, 20.0% C; 48.5 min 65.0% A, 8.3% B, 26.7% C; 50 min 65.0% A, 8.3% B, 26.7% C and 65 min 100% A. The mobile phase consisted of 25 mmol/L potassium dihydrogen phosphate solution, pH adjusted to 2.05 using phosphoric acid as solvent A, methanol as solvent B and acetonitrile as solvent C.

Total phenolic content and in vitro antioxidant activity

Total phenolic content (TPC) was determined following the Folin-Ciocalteu spectrophotometric method (Peschel *et al.*, 2006). The TPC value was calculated based on the standard curve of gallic acid (Nuclear, CAQ Ind. e Com. Ltda.). The analysis was performed in triplicate and values expressed as milligrams of gallic acid equivalent (GAE) per gram of the extract (mg GAE/g). The antioxidant potential of all extracts was estimated by the spectrophotometric methods described as follows:

DPPH free radical scavenging assay: The DPPH (1,1-diphenyl-2-picrylhydrazyl) analysis of mango peel extracts followed the method described by Mensor *et al.* (2001). Briefly, the extract was mixed with DPPH ethanol solution (0.3 mM), to concentrations of 5, 10, 25, 50, 125, 250, and 500 µg per mL of extract. Absorbance at 517 nm was measured after 30 min at room temperature, showing the percentage of antioxidant potential (% AP). The results were also represented as effective concentration 50% (EC₅₀), i.e., the concentration of a compound required to reduce the absorbance by 50% in test organisms, compared to blank solution (expressed in µg of extract/mL).

β-carotene bleaching method: The antioxidant activity of mango peel extracts by β-carotene / linoleic acid system was determined following the method described by Matthäus (2002) and Kang *et al.* (2006). Briefly, 5 mL of β-carotene / linoleic acid (40 mg linoleic acid, 400 mg Tween-20, 3.34 mg β-carotene / 100 mL distilled water) was added to 0.2 mL ethanolic mango peel extract (1,667 mg/mL), immediately submitted to absorbance measured at 470 nm, and compared against blank emulsion (without β-carotene). The tested tubes were placed in a water bath at 50°C for 120 min and the absorbance was measured at 470 nm. The β-carotene bleaching rate was determined by the difference between the absorbance values measured at 0 min and at 120 min (mean of experiments performed in triplicate) and converted into percentage of antioxidant activity (% AA). The results were expressed as mean ± standard deviation of assays performed in triplicate.

Statistical analysis

The results were statistically evaluated by one-way analysis of variance (ANOVA) using SPSS Software 17.0. The results showed extraction yield (X₀), TPC, EC₅₀ and AP%. The differences, with a significance level set at 5% (p < 0.05), were analysed by Tukey's test (Montgomery, 2005).

Results and discussion

Drying effect on extraction yield

Low pressure extraction methods

Mango peel samples [in natura (untreated), air-dried (sun-dried), and forced-dried (at 40°C)] showed moisture content values of $26.2 \pm 0.3\%$, $3.20 \pm 0.02\%$ and $7.9 \pm 0.4\%$ (d.b.), respectively. The air-dried sample reached the lowest moisture content, albeit with a drying time of 168 h, as compared to the forced drying procedure of 24 h, at similar temperatures (35 - 40°C: air-drying and 40°C: forced-drying).

The drying effect was evaluated by comparing the extraction yields (X_0) from SOX, MAC, and UAE methods using different solvents, as shown in Table 1. The results show that for low-pressure extractions with different solvents, the drying pre-treatments did not influence the yield results, probably because the extraction method and the solvent type are more relevant to the yield than the drying treatments used. This result differs from that reported by Sogi *et al.* (2013), who detected a significant influence of the drying procedure on extraction yield, when comparing four different drying procedures and one extraction method and solvent type.

The results from Table 1 show that SOX with ethanol gave the highest yield, probably due to the high temperature, solvent recycling and polarity, and the solvent / solute interactions, which contribute to an enhanced solubilisation of the raw material components (maximum X_0). The lowest yield was obtained by UAE with hexane for both air-dried ($1.5 \pm 0.5\%$) and forced-dried ($1.5 \pm 0.1\%$) samples. The low efficiency of UAE may be related to the short extraction time (60 min) as compared to other methods, which reduced the solubilisation of the compounds and the diffusion of solvent in the raw material. In addition, hexane is a non-polar solvent with low efficiency to solubilise polar compounds. Therefore, the high performance of ethanol (polar solvent) suggests the presence of polar substance in mango peel because solvent polarity defines the ability to interact with similar polarity molecules (Barwick, 1997).

Supercritical fluid extraction (SFE)

The X_0 results of SFE at different conditions show a maximum yield of $3.8 \pm 0.7\%$ (w/w), obtained at 50°C and 300 bar, with a solvent specific mass of $0.871 \text{ g CO}_2/\text{cm}^3$, while the lowest yield was $0.50 \pm 0.02\%$ (w/w) at 60°C and 100 bar, with a solvent specific mass of $0.295 \text{ g CO}_2/\text{cm}^3$. Most SFE results are within the hexane performance range for low

pressure methods (Table 1), both of which are equally non-polar solvents. This poor yield performance confirms the presence of polar components in the raw material. Therefore, ethanol was applied as co-solvent at concentrations of 2.5, 5.0, and 7.5%, at 50°C and 300 bar. Co-solvent had almost no effect in terms of extraction yield in the concentration range used. In addition, the SFE yields obtained with CO₂ at 300 bar and at all temperatures or with CO₂ plus 5% ethanol at 50°C and 300 bar were statistically equal. These results were similar to data obtained by Soxhlet using hexane as solvent. This behaviour may be explained by the non-polar characteristic of both solvents (CO₂ and hexane).

As can be seen from Table 1, X_0 decreased (from 0.8 ± 0.1 to $0.5 \pm 0.02\%$) when temperature increased from 40 to 60°C, at 100 bar due to solvent specific mass reduction (from 0.629 to 0.295 g/cm^3). The same behaviour was observed at 200 bar. On the other hand, at very high pressures (300 bar), temperature rise enhanced yield due to increased solute vapour pressure combined with temperature, which was more significant than the reduction in solvent specific mass, resulting in a higher overall extraction yield. Although no statistical differences in yield were observed when comparing pre-treatments, extraction procedures, and solvent types, the influence of these process variables can be better observed on product quality, described as follows.

Total phenolic content (TPC)

TPC from low pressure extraction methods

The TPC results from mango peel extracts obtained by the low pressure method are also shown in Table 1. The highest TPC values were obtained by MAC-Et-Ad (maceration-ethanol-air drying sample) and UAE-Et-Ad (ultrasound-ethanol-air drying), with values of 63 ± 2 and $62 \pm 4 \text{ mg GAE/g}$, respectively, with no significant difference. This behaviour is explained by the polar characteristic of ethanol, which enhances extraction of phenolic acid compounds. These data were followed by MAC-EA-Fd (maceration-ethyl acetate-forced drying), with values of $54 \pm 3 \text{ mg GAE/g}$, a solvent with intermediate polarity. High TPC values were also obtained by MAC-Et-Fd ($45 \pm 4 \text{ mg GAE/g}$) and by MAC-EA-Ad ($43 \pm 2 \text{ mg GAE/g}$), which suggests that maceration can be a good method for phenolic extraction, probably due to the low temperatures used, reducing the thermal degradation of the extracts. Drying procedures, such as pre-treatment for low pressure extractions, showed no clear effect on phenolic recovery (TPC values), probably because

Table 1. Extraction yield (X_0) and TPC of mango peel extract obtained by different extraction methods and solvents.

| Low pressure extractions | | | | | |
|--|-----------------------|--|--------------------------------------|--------------------------------------|--------------------------|
| Techniques | Drying ⁽¹⁾ | Solvents | SPI ⁽²⁾ | Total yield X_0 (%) ⁽³⁾ | TPC (mg EAG/g) |
| Soxhlet extraction | Air | Ethanol | 5.2 | 37.1 ± 0.7 ^a | 25.0 ± 2.0 ^c |
| | | Hexane | 0.0 | 2.5 ± 0.4 ^d | 2.3 ± 0.3 ^f |
| | | Ethyl Acetate | 4.4 | 4.5 ± 0.2 ^d | 21.0 ± 3.0 ^{cd} |
| | Forced | Ethanol | 5.2 | 36.3 ± 0.7 ^a | 10.0 ± 1.0 ^{dc} |
| | | Hexane | 0.0 | 2.4 ± 0.5 ^{dc} | 18.0 ± 2.0 ^d |
| | | Ethyl Acetate | 4.4 | 4.3 ± 0.2 ^d | 30.0 ± 1.0 ^c |
| Maceration | Air | Ethanol | 5.2 | 18.7 ± 1.8 ^b | 63.0 ± 2.0 ^a |
| | | Hexane | 0.0 | 2.3 ± 0.4 ^d | 1.2 ± 0.3 ^f |
| | | Ethyl Acetate | 4.4 | 4.5 ± 0.3 ^d | 43.0 ± 2.0 ^b |
| | Forced | Ethanol | 5.2 | 19.0 ± 2.0 ^b | 45.0 ± 4.0 ^b |
| | | Hexane | 0.0 | 2.3 ± 0.5 ^{dc} | 5.6 ± 0.3 ^c |
| | | Ethyl Acetate | 4.4 | 4.3 ± 0.1 ^d | 54.0 ± 3.0 ^b |
| Ultrasound assisted extraction | Air | Ethanol | 5.2 | 11.6 ± 0.6 ^c | 20.0 ± 2.0 ^d |
| | | Hexane | 0.0 | 1.5 ± 0.5 ^d | 8.0 ± 1.0 ^c |
| | | Ethyl Acetate | 4.4 | 2.7 ± 0.5 ^d | 11.0 ± 1.0 ^c |
| | Forced | Ethanol | 5.2 | 14.3 ± 0.5 ^c | 62.0 ± 4.0 ^a |
| | | Hexane | 0.0 | 1.5 ± 0.1 ^{dc} | 6.0 ± 2.0 ^c |
| | | Ethyl Acetate | 4.4 | 2.0 ± 0.0 ^{dc} | 5.0 ± 1.0 ^c |
| SFE with CO ₂ - Forced dried samples | | | | | |
| Pressure (bar) | Temperature (°C) | CO ₂ specific mass ⁽⁴⁾ | Total yield X_0 (%) ⁽³⁾ | TPC (mg EAG/g) | |
| 100 | 40 | 0.629 g/cm ³ | 0.8 ± 0.1 ^{bc} | 15.4 ± 0.6 ^c | |
| 100 | 50 | 0.385 g/cm ³ | 0.71 ± 0.02 ^{bc} | 6.8 ± 0.7 ^c | |
| 100 | 60 | 0.295 g/cm ³ | 0.50 ± 0.01 ^{bc} | 0.5 ± 0.0 ^f | |
| 200 | 40 | 0.840 g/cm ³ | 2.4 ± 0.1 ^{ab} | 17.5 ± 0.4 ^b | |
| 200 | 50 | 0.785 g/cm ³ | 1.4 ± 0.1 ^{bc} | 11.9 ± 0.6 ^d | |
| 200 | 60 | 0.724 g/cm ³ | 1.4 ± 0.1 ^{bc} | 12.7 ± 0.3 ^d | |
| 300 | 40 | 0.911 g/cm ³ | 2.7 ± 0.8 ^{ab} | 27.4 ± 0.8 ^a | |
| 300 | 50 | 0.871 g/cm ³ | 3.8 ± 0.7 ^a | 15.5 ± 0.3 ^c | |
| 300 | 60 | 0.830 g/cm ³ | 2.60 ± 0.01 ^{ab} | 7.0 ± 0.0 ^c | |
| SFE with co-solvent (ethanol) - Forced dried samples | | | | | |
| Pressure (bar) | Temperature (°C) | Co-solvent conc. | Total yield X_0 (%) ⁽³⁾ | TPC (mg EAG/g) | |
| 300 | 50 | CO ₂ + 2.5% ethanol | 3.7 ± 0.1 ^b | 12.0 ± 1.0 ^d | |
| 300 | 50 | CO ₂ + 5.0% ethanol | 4.0 ± 0.1 ^a | 16.6 ± 0.3 ^c | |
| 300 | 50 | CO ₂ + 7.5% ethanol | 3.7 ± 0.1 ^b | 7.8 ± 0.3 ^c | |

⁽¹⁾Air drying: 23 - 36°C, 30 - 80% relative humidity, at atmospherical pressure for 8 d; forced drying: in an oven with forced air circulation at 40 ± 2°C for 24 h; ⁽²⁾SPI = solvent polarity index (Reichardt, 2003); ⁽³⁾Different letters indicate significant difference at $p < 0.05$; ⁽⁴⁾CO₂ specific mass according to Angus *et al.* (1976).

the drying effect was lower than the influence of the extraction method (Soxhlet, maceration, and ultrasound) and the type of solvent (ethanol, hexane, and ethyl acetate) on the TPC results.

TPC from supercritical fluid extraction

The TPC results from mango peel extracts obtained by the high pressure method are also shown in Table 1. As expected, SFE provided low TPC values as compared to ethanolic extracts due to CO₂ non-polar character. Therefore, the TPC results from

high pressure extracts were more like the results from extracts obtained by hexane and by ethyl acetate. The TPC values showed a tendency to decrease with the increase in the SFE temperature. The lowest TPC value was observed from SFE at 100 bar and 60°C (0.62 ± 0.21 mg GAE/g), while the highest TPC value was obtained at 300 bar and 40°C (26.6 ± 1.6 mg GAE/g). Even SFE with ethanol as co-solvent did not affect the TPC result; reaching 16.6 ± 0.3 mg GAE/g for the extract obtained with 5% ethanol at 300 bar / 50°C.

Ajila *et al.* (2007) determined the polyphenols in two varieties of Indian mango peel (Badami and Raspuri) at different maturation stages (green and ripe). Polyphenols quantification was carried out using the Folin-Ciocalteu reagent. The values obtained by these authors when using ethanol and acetone as solvents were respectively: 37.9 ± 0.9 and 90.2 ± 0.6 mg GAE/g for green Badami; 33 ± 1 and 55 ± 2 mg GAE/g for ripe Badami; 73.9 ± 0.4 and 109.7 ± 0.8 mg GAE/g for green Raspuri; and 46 ± 4 and 100 ± 2 mg GAE/g for ripe Raspuri. Sogi *et al.* (2013) determined the TPC from Tommy Atkins mango peel extracts obtained by different technologies (combining extraction methods and drying times). The values obtained were: 31.85 mg GAE/g using 11 h lyophilisation; 23.20 mg GAE/g from 4 h oven-dried peels; 20.32 mg GAE/g using 7 h vacuum drying; and 30.49 mg GAE/g from 2 h infrared drying.

The results of the present work were similar to the data found in the literature, with an even higher performance for low-pressure extraction methods and with ethanol as solvent. In general, TPC results for the SFE extract (up to 26.6 ± 1.6 mg GAE/g) and for low pressure extracts with ethanol (up to 58 ± 10 mg GAE/g) and with ethyl acetate (up to 54 ± 3 mg GAE/g) were superior than the results found in the literature (Ajila *et al.*, 2007). It is also important to take into account the variability due to plant material related to genetic, agronomic, and physiological aspects, which brings different results in the quality of the extract. Besides that, this comparison suggests that the mango peel residue and the technologies applied in the present work provide satisfactory extraction of phenolic components detected by the Folin-Ciocalteu colorimetric method.

Phenolic compounds profile

Phenolic compounds from low pressure extraction methods

The phenolic compounds profile by HPLC of mango peel extracts are shown in Tables 2 and 3 for organic solvent extracts and supercritical extracts, respectively. Low pressure methods (SOX, MAC, and UAE) with ethanol or ethyl acetate provided extracts with the highest flavanol contents, more specifically procyanidin A2 (up to 0.29 mg/g). In contrast, benzoic acid, procyanidin B2, isorhamnetin, and myricetin were hardly detected in all extracts, suggesting they are not typical mango peel substances. Flavonols were the prevailing class of compounds

in mango peel extracts. For the SOX method, the ethyl acetate extracts provided high concentrations of kaempferol 3-glucoside (3.1 mg/g), quercetin piranoside (6.46 mg/g), and quercetin 3-glucoside (3.28 mg/g); and for rutin (6.6 mg/g), the best result was obtained by maceration. The high contents of kaempferol 3-glucoside, quercetin 3-glucoside, quercetin piranoside, and rutin, as compared to TPC results with 1.2 to 63 mg GAE/g (Table 1), suggest that they are the main phenolic compounds in mango peel extracts. The components kaempferol and quercetin are associated with numerous health benefits such as anti-inflammatory, anticancer, and protective properties against neurodegenerative diseases (Carvalho *et al.*, 2017).

Additionally, the flavonol contents in the present work are high when compared to those from Ubá mango peel reported by Ribeiro *et al.* (2008), with values of 35.3 mg/kg for kaempferol 3-O-glucoside of a total of 785.1 mg/kg from seven types of quercetin. According to the literature, phenolic compounds such as mangiferin, isomangiferin and mangiferin gallate were also detected from mango peels (Jahurul *et al.*, 2015; Asif *et al.*, 2016). The presence of gallotannins, which also have antioxidant and other pharmaceutical properties, has also been described in mango peel (Coelho *et al.*, 2019). Therefore, the high flavonols content (Table 2) confirms the good performance of extracts from Tommy Atkins mango peel from the São Francisco River Valley, Brazil.

Phenolic compounds from supercritical fluid extraction

Alternatively, supercritical extracts (Table 3) showed fewer identified phenolic compounds as compared to organic solvent extracts due to the non-polar characteristic of CO₂, providing analogous results as compared to hexane (low pressure methods). The use of ethanol as co-solvent (2.5 to 7.5%) enhances the polarity of the solvent mixture (da Silva *et al.*, 2016b) and considerably increases the content of quercetin 3-glicoside and rutin in the extracts.

Finally, to optimise selectivity processes, additional studies focusing on particular classes of components are needed to better address the functionalities of Tommy Atkins mango peel extracts. These studies should be based on the results previously discussed, which are very compelling about the good performance of this relevant agro-industrial residue.

Table 2. Phenolic compound profile of mango peel extracts obtained by low-pressure extraction methods.

| Extraction techniques | Flavanol (mg/g) ⁽²⁾ | | | | | Phenolic acid (mg/g) ⁽²⁾ | | | | | | | Flavonol (mg/g) ⁽²⁾ | | | |
|-----------------------|--------------------------------|---------------------------|-----------------------------|----------------------------|---------------|-------------------------------------|---------------------------|---------------------------|----------------------------|---------------------------|--------------|-------------|--------------------------------|--|--|--|
| | Catechin | Procyanidin A2 | Procyanidin B1 | Procyanidin B2 | Cinnamic acid | Benzzoic acid | Kaempferol 3-glucoside | Quercetin piranoside | Quercetin 3-glucoside | Rutin | Isorramnetin | Myricetin | | | | |
| SOX | Ethanol | 0.04 ± 0.01 ^{ab} | 0.16 ± 0.01 ^{cde} | 0.06 ± 0.00 ^b | nd | nd | 0.84 ± 0.02 ^{ef} | 2.78 ± 0.04 ^c | 0.24 ± 0.00 ⁱ | 2.85 ± 0.01 ^{fg} | nd | nd | | | | |
| | Hexane | 0.02 ± 0.00 ^c | 0.02 ± 0.00 ^{hi} | nd | nd | nd | 0.15 ± 0.02 ^g | 0.45 ± 0.01 ^g | 0.13 ± 0.01 ^{ijk} | 0.51 ± 0.01 ⁱ | nd | nd | | | | |
| | Ethyl acetate | 0.02 ± 0.00 ^c | 0.25 ± 0.01 ^{ab} | 0.04 ± 0.00 ^{bc} | nd | nd | 3.10 ± 0.30 ^a | 4.32 ± 0.12 ^{cd} | 2.01 ± 0.07 ^b | 4.22 ± 0.06 ^c | 0.07 ± 0.01 | 0.12 ± 0.02 | | | | |
| MAC | Ethanol | 0.02 ± 0.00 ^c | 0.10 ± 0.00 ^{efgh} | 0.06 ± 0.00 ^b | nd | nd | 0.79 ± 0.07 ^f | 3.48 ± 0.22 ^{de} | 0.60 ± 0.01 ^{fg} | 3.50 ± 0.20 ^{de} | nd | nd | | | | |
| | Hexane | nd | nd | nd | 0.06 ± 0.00 | nd | 0.02 ± 0.00 ^g | 0.05 ± 0.01 ^g | 0.02 ± 0.00 ^k | 0.07 ± 0.01 ^j | nd | nd | | | | |
| | Ethyl acetate | 0.03 ± 0.01 ^b | 0.19 ± 0.01 ^{bed} | 0.03 ± 0.01 ^{cd} | nd | nd | 1.50 ± 0.10 ^d | 6.46 ± 0.32 ^a | 3.28 ± 0.04 ^a | 3.90 ± 0.20 ^{cd} | nd | nd | | | | |
| UAF | Ethanol | 0.04 ± 0.01 ^a | 0.26 ± 0.02 ^{ab} | 0.09 ± 0.01 ^a | nd | nd | 1.45 ± 0.07 ^d | 4.50 ± 0.18 ^{bc} | 0.45 ± 0.01 ^h | 4.00 ± 0.20 ^c | nd | nd | | | | |
| | Hexane | 0.02 ± 0.00 ^c | 0.02 ± 0.00 ^{hi} | 0.01 ± 0.01 ^{de} | nd | nd | 0.05 ± 0.01 ^g | 0.16 ± 0.01 ^g | 0.02 ± 0.00 ^k | 0.15 ± 0.01 ^j | nd | nd | | | | |
| | Ethyl acetate | 0.04 ± 0.01 ^a | 0.29 ± 0.01 ^a | 0.06 ± 0.00 ^{cd} | nd | nd | 1.90 ± 0.10 ^b | 5.00 ± 1.00 ^{bc} | 1.20 ± 0.03 ^d | 6.60 ± 0.02 ^a | nd | nd | | | | |
| SOX | Ethanol | 0.02 ± 0.00 ^c | 0.18 ± 0.02 ^{bcde} | 0.06 ± 0.00 ^b | nd | nd | 0.93 ± 0.05 ^{ef} | 2.80 ± 0.20 ^c | 0.19 ± 0.03 ^j | 2.50 ± 0.20 ^g | nd | nd | | | | |
| | Hexane | 0.02 ± 0.00 ^c | nd | nd | nd | nd | 0.03 ± 0.01 ^g | 0.08 ± 0.01 ^g | 0.04 ± 0.00 ^k | 0.06 ± 0.02 ^j | nd | nd | | | | |
| | Ethyl acetate | 0.02 ± 0.01 ^c | 0.11 ± 0.01 ^{defg} | 0.04 ± 0.01 ^{cd} | nd | nd | 1.48 ± 0.03 ^d | 3.01 ± 0.01 ^e | 0.87 ± 0.02 ^c | 3.25 ± 0.01 ^{ef} | nd | nd | | | | |
| MAC | Ethanol | 0.02 ± 0.00 ^c | 0.20 ± 0.10 ^{cdef} | 0.04 ± 0.00 ^{bc} | nd | nd | 1.10 ± 0.10 ^e | 3.49 ± 0.33 ^{de} | 0.76 ± 0.06 ^{ef} | 3.50 ± 0.30 ^e | nd | nd | | | | |
| | Hexane | 0.02 ± 0.00 ^c | nd | nd | nd | nd | 0.02 ± 0.00 ^g | 0.06 ± 0.00 ^g | 0.04 ± 0.00 ^k | 0.06 ± 0.02 ^j | nd | nd | | | | |
| | Ethyl acetate | 0.02 ± 0.00 ^c | 0.05 ± 0.01 ^{efhi} | 0.02 ± 0.00 ^{ade} | nd | nd | 0.80 ± 0.10 ^f | 1.46 ± 0.02 ^f | 0.69 ± 0.12 ^{fg} | 1.20 ± 0.20 ^b | nd | nd | | | | |

⁽¹⁾Air drying; at 23 - 36°C, 30 - 80% relative humidity, at atmospheric pressure for 8 d; forced drying: in an oven with forced air circulation at 40 ± 2°C for 24 h; ⁽²⁾different letters indicate significant difference at $p < 0.05$; nd = not detected.

Table 3. Phenolic compound profile of mango peel extracts obtained by supercritical fluid extraction (SFE) from forced dried samples.

| SFE (P / T) | Solvent/mixture | Flavanol (mg/g) ⁽¹⁾ | | | Phenolic acid (mg/g) ⁽¹⁾ | | | Stilbene (mg/g) ⁽¹⁾ | | | Flavanol (mg/g) ⁽¹⁾ | |
|----------------|--------------------------------|--------------------------------|--------------------------|--------------------------|-------------------------------------|---------------------------|---------------------------|--------------------------------|--|--|--------------------------------|--|
| | | Catechin | Procyanidin A2 | Procyanidin B1 | Cinnamic | trans-Resveratrol | Quercetin 3 | Rutin | | | | |
| 100 bar / 40°C | CO ₂ | nd | nd | nd | nd | nd | 0.02 ± 0.00 ^{cd} | 0.04 ± 0.02 ^c | | | | |
| 100 bar / 50°C | | nd | 0.03 ± 0.01 ^c | nd | nd | 0.02 ± 0.00 ^e | 0.06 ± 0.02 ^{bc} | 0.14 ± 0.02 ^b | | | | |
| 100 bar / 60°C | | nd | 0.02 ± 0.00 ^a | nd | - | 0.02 ± 0.00 ^{bc} | 0.02 ± 0.00 ^{cd} | 0.18 ± 0.02 ^{ab} | | | | |
| 200 bar / 40°C | | 0.02 ± 0.00 ^a | nd | nd | 0.04 ± 0.00 ^a | 0.02 ± 0.00 ^b | 0.02 ± 0.00 ^{cd} | nd | | | | |
| 200 bar / 50°C | | 0.02 ± 0.00 ^a | nd | nd | 0.04 ± 0.00 ^a | 0.02 ± 0.00 ^b | 0.02 ± 0.00 ^{cd} | nd | | | | |
| 200 bar / 60°C | | 0.02 ± 0.00 ^a | nd | nd | 0.04 ± 0.00 ^a | 0.02 ± 0.00 ^b | 0.02 ± 0.00 ^{cd} | nd | | | | |
| 300 bar / 40°C | | 0.02 ± 0.00 ^a | nd | nd | 0.04 ± 0.00 ^a | 0.02 ± 0.00 ^b | 0.02 ± 0.00 ^{cd} | nd | | | | |
| 300 bar / 50°C | | 0.02 ± 0.00 ^a | 0.04 ± 0.00 ^b | nd | nd | 0.02 ± 0.00 ^b | 0.02 ± 0.00 ^{cd} | nd | | | | |
| 300 bar / 60°C | | nd | 0.06 ± 0.00 ^a | nd | nd | 0.02 ± 0.00 ^b | 0.02 ± 0.01 ^d | 0.03 ± 0.01 ^c | | | | |
| | CO ₂ + 2.5% ethanol | 0.02 ± 0.00 ^a | nd | nd | nd | 0.04 ± 0.00 ^a | 0.06 ± 0.00 ^b | nd | | | | |
| 300 bar / 50°C | CO ₂ + 5.0% ethanol | 0.02 ± 0.00 ^a | nd | 0.02 ± 0.00 ^a | nd | 0.04 ± 0.00 ^a | 0.16 ± 0.04 ^a | 0.21 ± 0.09 ^{ab} | | | | |
| | CO ₂ + 7.5% ethanol | nd | nd | nd | nd | 0.02 ± 0.00 ^b | 0.14 ± 0.02 ^a | 0.23 ± 0.01 ^a | | | | |

⁽¹⁾different letters indicate significant difference at $p < 0.05$; nd = not detected.

Table 4. Antioxidant activity *in vitro* (AOX) in % AP by DPPH and by β -carotene bleaching methods for mango peel extracts obtained by low-pressure techniques.

| Extraction method | Drying ⁽¹⁾ | Solvent | DPPH % AP (500 mg/mL) ^(2,3) | %AP_120 min ^(2,4) |
|--------------------------------|-----------------------|--------------------------------|--|------------------------------|
| Soxhlet extraction | Air | Ethanol | 95.7 ± 0.4 ^a | 15.6 ± 5.3 ^{ij} |
| | | Hexane | 30.1 ± 0.6 ^h | 58.5 ± 2.5 ^{cde} |
| | | Ethyl Acetate | 95.2 ± 0.4 ^a | 29.6 ± 4.9 ^{hi} |
| | Forced | Ethanol | 95.5 ± 0.7 ^a | 9.5 ± 1.8 ⁱ |
| | | Hexane | 44.3 ± 0.3 ^e | 85.8 ± 1.3 ^a |
| | | Ethyl Acetate | 96.5 ± 0.5 ^a | 69.1 ± 5.2 ^{bcd} |
| Maceration | Air | Ethanol | 95.6 ± 0.8 ^a | 56.2 ± 1.6 ^{def} |
| | | Hexane | 29.0 ± 2.0 ^h | 70.5 ± 3.4 ^{abc} |
| | | Ethyl Acetate | 95.4 ± 0.4 ^a | 49.3 ± 4.6 ^{efg} |
| | Forced | Ethanol | 94.7 ± 0.1 ^a | 35.3 ± 9.7 ^{gh} |
| | | Hexane | 47.6 ± 0.4 ^f | 79.6 ± 1.9 ^{ab} |
| | | Ethyl Acetate | 84.0 ± 1.0 ^b | 76.5 ± 3.9 ^{ab} |
| Ultrasound assisted extraction | Air | Ethanol | 94.4 ± 0.4 ^a | 14.4 ± 1.7 ^{ij} |
| | | Hexane | 23.3 ± 0.9 ⁱ | 59.7 ± 2.3 ^{cde} |
| | | Ethyl Acetate | 79.7 ± 0.3 ^c | 41.0 ± 7.9 ^{fg} |
| | Forced | Ethanol | 72.4 ± 0.7 ^d | 43.7 ± 10.0 ^{gh} |
| | | Hexane | 21.5 ± 0.8 ⁱ | 70.8 ± 3.8 ^{abcd} |
| | | Ethyl Acetate | 61.0 ± 26.0 ^c | 73.3 ± 2.9 ^{abc} |
| SFE | | | | |
| Pressure (bar) | Temperature (°C) | Solvent / mixture | DPPH - % AP (500 mg/mL) ⁽²⁾ | %AP_120 min ⁽²⁾ |
| 100 | 40 | CO ₂ | 15.0 ± 6.0 ^c | 94.2 ± 1.2 ^a |
| 100 | 50 | CO ₂ | 37.0 ± 2.0 ^{ab} | 95.4 ± 6.3 ^{ab} |
| 100 | 60 | CO ₂ | 17.0 ± 2.0 ^{de} | 84.4 ± 1.1 ^{abcde} |
| 200 | 40 | CO ₂ | 25.0 ± 2.0 ^{cd} | 78.6 ± 2.5 ^{bcd} |
| 200 | 50 | CO ₂ | 18.0 ± 2.0 ^{de} | 77.5 ± 2.6 ^{cdef} |
| 200 | 60 | CO ₂ | 32.0 ± 2.0 ^{bc} | 52.4 ± 2.7 ^{kl} |
| 300 | 40 | CO ₂ | 25.2 ± 0.8 ^{cd} | 82.3 ± 2.6 ^{abc} |
| 300 | 50 | CO ₂ | 34.0 ± 2.0 ^{ab} | 87.3 ± 4.9 ^{abc} |
| 300 | 60 | CO ₂ | 25.0 ± 3.0 ^{cd} | 93.2 ± 2.7 ^a |
| 300 | 50 | CO ₂ + 2.5% ethanol | 33.2 ± 0.4 ^{bc} | 63.1 ± 0.8 ^{ghijk} |
| 300 | 50 | CO ₂ + 5.0% ethanol | 37.0 ± 5.0 ^{ab} | 56.0 ± 2.9 ^{ijkl} |
| 300 | 50 | CO ₂ + 7.5% ethanol | 41.4 ± 0.6 ^a | 63.8 ± 1.1 ^{ghijk} |
| TBHQ (Standard) | | | 91.2 ± 0.8 | 76.0 ± 2.0 |

⁽¹⁾Air drying: at 23 - 36°C, 30 - 80% relative humidity, at atmospheric pressure for 8 d; forced drying: in an oven with forced air circulation at 40 ± 2°C for 24 h; ⁽²⁾different letters indicate significant difference at $p < 0.05$, performed for two groups of assays (low pressure methods and high pressure methods); ⁽³⁾% AP (500 mg/mL) = % antioxidant potential to higher extraction concentration by DPPH method; ⁽⁴⁾AP_120 min = antioxidant potential after 120 min-reaction by β -carotene bleaching method.

In vitro antioxidant activity

The antioxidant potential results of extracts obtained by low pressure methods and by SFE, and evaluated according to DPPH and β -carotene methods are compared in Table 4. The statistical analysis of the data was performed for the values resulting from SOX, MAC, UAE, and SFE.

The antioxidant potential by DPPH, tested with extract concentration of 500 mg/mL, showed

the highest % AP values (Table 4) for Soxhlet and maceration of ethanolic extracts (air- and forced-dried samples), all statistically similar, with values up to 96.54 ± 0.45% AP. Ethyl acetate also gave statistically similar DPPH results (% AP) as compared to ethanolic extracts, for Soxhlet and maceration procedures. DPPH results for ethanolic extracts produced % AP higher than TBHQ, a synthetic antioxidant with recognised antioxidant

potential, reported by Salvador *et al.* (2016) ($91.2 \pm 0.8\%$, at $500 \mu\text{g}/\text{mL}_{\text{extract}}$), indicating good antioxidant potential of these mango peel extracts. The best DPPH values for the air-dried raw material were obtained for ethanolic extracts from SOX, MAC, and UAE (95.7 ± 0.4 , 95.6 ± 0.8 , and $94.4 \pm 0.4 \mu\text{g}/\text{mL}$, respectively), probably due to the use of a high-polar solvent. The extracts obtained using ethanol and ethyl acetate are also considered high antioxidant agents, exhibiting DPPH values above those resulting from TBHQ standard ($91.2 \pm 0.8 \text{ mg}/\text{mL}$) (Salvador *et al.*, 2016), confirming the high antioxidant performance of mango peel extracts. Several authors (Kitzberger *et al.*, 2007; de Campos *et al.*, 2008; Benelli *et al.*, 2010) also achieved a better performance with polar solvents for antioxidants extraction. In contrast, the % AP by DPPH of mango peel extracts obtained by

supercritical CO_2 showed the highest value, 41.4 ± 0.6 (300 bar/ 50°C and 7.5% co-solvent). Co-solvent use showed no significant effect on DPPH values. By observing the results obtained from the DPPH analysis, a better antioxidant performance was detected by using high polarity solvents, particularly organic solvents used in low pressure methods (SOX, MAC, and UAE). In Figure 1, a correlation between antioxidant results with the phenolic content from the various extracts is presented. Figure 1A shows a comparison between the antioxidant values obtained by the DPPH method (Table 4) and the TPC data, expressed in terms of raw material amount (Tables 2 and 3, considering the extraction yield from Table 1). From this, the correlation between the data (DPPH and TPC) was 0.61, and the extracts whose values are close to the TBHQ value (Salvador *et al.*, 2016)

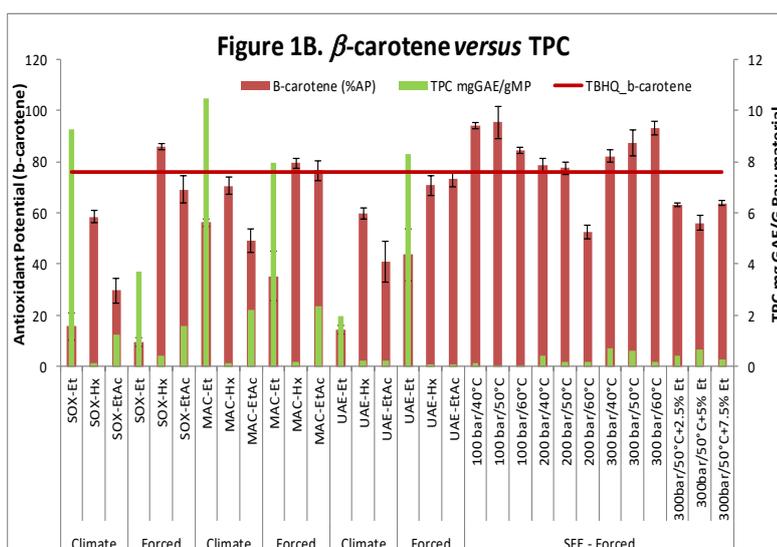
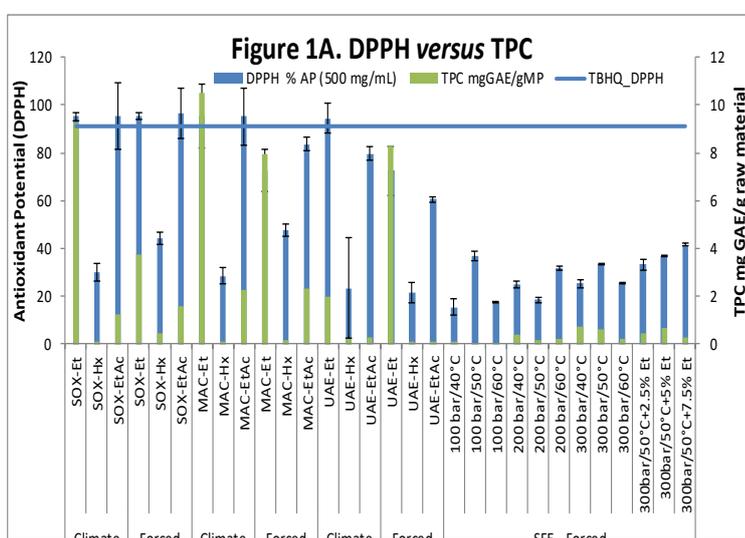


Figure 1. Antioxidant potential and TPC values of mango peel extracts obtained by Soxhlet (SOX), maceration (MAC), and ultrasound assisted extraction (UAE) using ethanol (Et), hexane (Hx), and ethyl acetate (EA) as solvents, for samples submitted to air drying (Ad) or forced drying (Fd). (1A): antioxidant potential by DPPH versus TPC values compared with DPPH values of standard TBHQ obtained by Salvador *et al.* (2016); (1B): antioxidant potential by β-carotene bleaching method versus TPC values compared with β-carotene result for standard TBHQ obtained by Salvador *et al.* (2016).

were those obtained by low pressure methods. The DPPH results from low pressure extracts were better than those from supercritical extracts. The reduced performance of SFE is probably due to the non-polar character CO₂, which limits the extraction of antioxidant compounds detected by the DPPH method. Ajila *et al.* (2007) found good antioxidant potential by DPPH in mango peel extracts from the Badami and Raspuri varieties, extracted with acetone. The best results, compared to the present data, probably due to differences among mango varieties, solvents used, and certain physiological aspects and agronomic procedures, which led to differences in relation to plant quality.

The DPPH method is considered a wide range assay suitable for detecting antioxidant mechanisms performed by polar to medium polar compounds and is therefore recognised as a standard antioxidant activity procedure. Alternatively, the β -carotene bleaching method detects oxidative reactions induced by light, heat, or peroxy radicals, which promotes the bleaching of carotenoids (Prior *et al.*, 2005). Thus, it is important to evaluate the antioxidant potential by combined assays, taking into account the variety of antioxidative mechanisms.

Considering the β -carotene bleaching method, we detected a significant improvement in the performance of non-polar solvents (hexane and CO₂) to obtain antioxidant substances, as compared to the above-mentioned methods. The high antioxidant performance detected by the β -carotene / linoleic acid system is possibly associated to the presence of compounds other than phenolic substances, present in the mango peel extracts, such as carotenoid fractions. The best % AP_{120 min} (β -carotene method) results for low-pressure extracts were obtained by maceration with ethyl acetate from forced-dried raw material, followed by Soxhlet with hexane from air-dried mango peel. Good results of % AP_{120 min} were also observed in extracts from Soxhlet-hexane/forced-drying and maceration-hexane/air-drying, indicating the suitability of low polar solvents for the recovery of antioxidant compounds (from mango peel), detectable by the β -carotene bleaching method.

The % AP_{120 min} values from SFE ranged from $52.4 \pm 2.7\%$ (200 bar / 60°C) to $95.4 \pm 6.3\%$ (100 bar / 50°C). Very good % AP_{120 min} values were also observed at 100 bar and 40°C and at 300 bar and 60°C, with no clear influence of pressure and temperature. SFE at 300 bar and 50°C without co-solvent showed significant difference when compared with the use of co-solvent at the same operating conditions, although various ethanol concentrations

as co-solvent showed no significant effect in β -carotene bleaching method. These behaviours are justified because this method seems more suitable for non-polar extracts (SFE without co-solvent). Most % AP_{120 min} values from SFE (Tables 4) are higher than the TBHQ value ($76 \pm 2\%$), while the values of most extracts recovered by low pressure methods (SOX, MAC, UAE) are close to the TBHQ value and lower. These results suggest that mango peel is a very good source of antioxidants. Therefore, in general, the SFE separation process was more effective than the low pressure extraction methods for recovering components measurable by the β -carotene bleaching method. When observing the β -carotene bleaching analysis result set, we detected a better antioxidant performance in extracts recovered by SFE and low pressure methods (SOX, MAC, and UAE) using non-polar solvents. Figure 1B shows the comparison between the antioxidant values resulting from the β -carotene bleaching method (Table 4) and TPC, expressed in terms of raw material amount (Tables 2 and 3, considering the extraction yield from Table 1). From Figure 1B, no correlation between data (% AP and TPC) was detected, and all supercritical extracts presented TPC values closer (or even higher) than TBHQ standard (by β -carotene bleaching method) values. The results in Figure 1 (A and B) show the good overall performance of the supercritical methods in relation to the selectivity of phenolic compounds with antioxidant potential, suggesting them as a good option to process this agro-industrial residue.

Conclusion

“Tommy Atkins” dried mango peels are promising raw materials due to the high quality substances that remain in this industrial waste. The Soxhlet procedure with ethanol provided the highest extraction yield and the highest *in vitro* antioxidant activity. SFE extracts presented low yields, but a better antioxidant potential by the β -carotene bleaching method. In addition, the use of ethanol as co-solvent changed the SFE selectivity, resulting in flavonol enriched extracts. Several phenolic compounds were quantified from mango peel extracts obtained at low pressure methods, particularly kaempferol 3-glucoside, quercetin piranoside, quercetin 3-glucoside, isorhamnetin, myricetin, and especially rutin, the main compound in all extracts. Finally, the results of the present work show that mango peel is an agro-industrial residue with high nutraceutical value and, for the best possible use of its bioactive content, a suitable separation process should be defined.

Acknowledgement

Authors thank the Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE) for the scholarship (process no.: BCT-0387-5.07/12) and the research grant (project no.: APQ-0962-5.07/10); and the National Council of Technological and Scientific Development (CNPq) (Process no: 473153/2012-2) for the research grant received in the completion of the present work.

References

- Ajila, C. M., Naidu, K. A., Bhat, S. G. and Prasada Rao, U. J. S. 2007. Bioactive compounds and antioxidant potential of mango peel extract. *Food Chemistry* 105(3): 982-988.
- Angus, S., Armstrong, B. and de Reuck, K. M. 1976. *International thermodynamic tables of the fluid state: carbon dioxide*. Oxford: Pergamon Press.
- Asif, A., Farooq, U., Akram, K., Hayat, Z., Shafi, A., Sarfraz, F., ... and Aftab, S. 2016. Therapeutic potentials of bioactive compounds from mango fruit wastes. *Trends in Food Science and Technology* 53: 102-112.
- Association of Official Agricultural Chemists (AOAC). 2012. *Official methods of analysis of AOAC International*. 19th ed. United States: AOAC.
- Barwick, V. J. 1997. Strategies for solvent selection - a literature review. *Trends in Analytical Chemistry* 16(6): 293-309.
- Benelli, P., Riehl, C. A. S., Smânia, A., Smânia, E. F. A. and Ferreira, S. R. S. 2010. Bioactive extracts of orange (*Citrus sinensis* L. Osbeck) pomace obtained by SFE and low pressure techniques: mathematical modeling and extract composition. *The Journal of Supercritical Fluids* 55(1): 132-141.
- Carvalho, C. 2017. *Brazilian Fruit Yearbook (Anuário Brasileiro da Fruticultura)*. Brazil: Editora Gazeta Santa Cruz.
- Carvalho, D., Paulino, M., Polticelli, F., Arredondo, F., Williams, R. J. and Abin-Carriquiry, J. A. 2017. Structural evidence of quercetin multi-target bioactivity: a reverse virtual screening strategy. *European Journal of Pharmaceutical Sciences* 106: 393-403.
- Castro-Vargas, H. I., Ballesteros Vivas, D., Ortega Barbosa, J., Morantes Medina, S. J., Aristizabal Gutiérrez, F. and Parada-Alfonso, F. 2019. Bioactive phenolic compounds from the agroindustrial waste of Colombian mango cultivars 'Sugar Mango' and 'Tommy Atkins' - an alternative for their use and valorization. *Antioxidants* 8(2): article ID 41.
- Coelho, E. M., de Souza, M. E. A. O., Corrêa, L. C., Viana, A. C., de Azevêdo, L. C. and dos Santos Lima, M. 2019. Bioactive compounds and antioxidant activity of mango peel liqueurs (*Mangifera indica* L.) produced by different methods of maceration. *Antioxidants* 8(4): article ID 102.
- da Silva, J. K., Cazarin, C. B., Correa, L. C., Batista, Â. G., Furlan, C. P., Biasoto, A. C., ... and Maróstica Junior, M. R. 2016a. Bioactive compounds of juices from two Brazilian grape cultivars. *Journal of the Science of Food and Agriculture* 96(6): 1990-1996.
- da Silva, R. P. F. F., Rocha-Santos, T. A. P. and Duarte, A. C. 2016b. Supercritical fluid extraction of bioactive compounds. *Trends in Analytical Chemistry* 76: 40-51.
- de Campos, L. M., Leimann, F. V., Pedrosa, R. C. and Ferreira, S. R. 2008. Free radical scavenging of grape pomace extracts from Cabernet sauvignon (*Vitis vinifera*). *Bioresource Technology* 99(17): 8413-8420.
- Dembitsky, V. M., Poovarodom, S., Leontowicz, H., Leontowicz, M., Vearasilp, S., Trakhtenberg, S. and Gorinstein, S. 2011. The multiple nutrition properties of some exotic fruits: biological activity and active metabolites. *Food Research International* 44(7): 1671-1701.
- Dorta, E., González, M., Lobo, M. G., Sánchez-Moreno, C. and De Ancos, B. 2014. Screening of phenolic compounds in by-product extracts from mangoes (*Mangifera indica* L.) by HPLC-ESI-QTOF-MS and multivariate analysis for use as a food ingredient. *Food Research International* 57: 51-60.
- Fernández-Ponce, M. T., Casas, L., Mantell, C., Rodríguez, M. and Martínez de la Ossa, E. J. 2012. Extraction of antioxidant compounds from different varieties of *Mangifera indica* leaves using green technologies. *The Journal of Supercritical Fluids* 72: 168-175.
- Fernández-Ponce, M. T., Parjikolaie, B. R., Lari, H. N., Casas, L., Mantell, C. and Martínez de la Ossa, E. J. 2016. Pilot-plant scale extraction of phenolic compounds from mango leaves using different green techniques: kinetic and scale up study. *Chemical Engineering Journal* 299: 420-430.
- Garcia-Mendoza, M. P., Paula, J. T., Paviani, L. C., Cabral, F. A. and Martinez-Correa, H. A. 2015. Extracts from mango peel by-product obtained by supercritical CO₂ and pressurized solvent processes. *LWT - Food Science and Technology* 62(1): 131-137.
- Gu, Z., Chen, D., Han, Y., Chen, Z. and Gu, F. 2008. Optimization of carotenoids extraction from *Rhodobacter sphaeroides*. *LWT - Food Science and Technology* 41(6): 1082-1088.
- Jahurul, M. H., Zaidul, I. S., Ghafour, K., Al-Juhaimi, F. Y., Nyam, K. L., Norulaini, N. A., ... and Mohd Omar, A. K. 2015. Mango (*Mangifera indica* L.) by-products and their valuable components: a review. *Food Chemistry* 183: 173-180.
- Kang, H. J., Chawla, S. P., Jo, C., Kwon, J. H. and Byun, M. W. 2006. Studies on the development of functional powder from citrus peel. *Bioresource Technology* 97(4): 614-620.
- Khajeh, M., Yamini, Y., Sefidkon, F. and Bahramifar, N. 2004. Comparison of essential oil composition of *Carum copticum* obtained by supercritical carbon dioxide extraction and hydro-distillation methods. *Food Chemistry* 86(4): 587-591.

- Kim, H., Kim, H., Mosaddik, A., Gyawali, R., Ahn, K. S. and Cho, S. K. 2012. Induction of apoptosis by ethanolic extract of mango peel and comparative analysis of the chemical constituents of mango peel and flesh. *Food Chemistry* 133(2): 416-422.
- Kitzberger, C. S. G., Smânia, A., Pedrosa, R. C. and Ferreira, S. R. S. 2007. Antioxidant and antimicrobial activities of shiitake (*Lentinula edodes*) extracts obtained by organic solvents and supercritical fluids. *Journal of Food Engineering* 80(2): 631-638.
- Lerma-Torres, J. M., Navarro-Ocaña, A., Calderón-Santoyo, M., Hernández-Vázquez, L., Ruiz-Montañez, G. and Ragazzo-Sánchez, J. A. 2019. Preparative scale extraction of mangiferin and lupeol from mango (*Mangifera indica* L.) leaves and bark by different extraction methods. *Journal of Food Science and Technology* 56(10): 4625-4631.
- Liu, F.-X., Fu, S.-F., Bi, X.-F., Chen, F., Liao, X.-J., Hu, X.-S. and Wu, J.-H. 2013. Physico-chemical and antioxidant properties of four mango (*Mangifera indica*) cultivars in China. *Food Chemistry* 138(1): 396-405.
- López-Cobo, A., Verardo, V., Diaz-de-Cerio, E., Segura-Carretero, A., Fernández-Gutiérrez, A. and Gómez-Caravaca, A. M. 2017. Use of HPLC- and GC-QTOF to determine hydrophilic and lipophilic phenols in mango fruit (*Mangifera indica* L.) and its by-products. *Food Research International* 100(Part 3): 423-434.
- Martins, N. and Ferreira, I. C. F. R. 2017. Wastes and by-products: upcoming sources of carotenoids for biotechnological purposes and health-related applications. *Trends in Food Science and Technology* 62: 33-48.
- Masibo, M. and He, Q. 2009. Mango bioactive compounds and related nutraceutical properties - a review. *Food Reviews International* 25(4): 346-370.
- Matthäus, B. 2002. Antioxidant activity of extracts obtained from residues of different oilseeds. *Journal of Agricultural and Food Chemistry* 50(12): 3444-3452.
- Mensor, L. L., Menezes, F. S., Leitão, G. G., Reis, A. S., dos Santos, T. C., Coube, C. S. and Leitão, S. G. 2001. Screening of Brazilian plant extracts for antioxidant activity by the use of DPPH free radical method. *Phytotherapy Research* 15(2): 127-130.
- Michelin, D. C., Moreschi, P. E., Lima, A. C., Nascimento, G. G. F., Paganelli, M. O. and Chaud, M. V. 2005. Evaluation of the antimicrobial activity of vegetal extracts. *Revista Brasileira de Farmacognosia* 15(4): 316-320.
- Montgomery, D. C. 2005. Design and analysis of experiments. 6th ed. United States: John Wiley and Sons.
- Pereira, C. G. and Meireles, M. A. A. 2007. Evaluation of global yield, composition, antioxidant activity and cost of manufacturing of extracts from lemon verbena (*Aloysia triphylla* [L'herit.] Britton) and mango (*Mangifera indica* L.) leaves. *Journal of Food Process Engineering* 30(2): 150-173.
- Peschel, W., Sánchez-Rabaneda, F., Diekmann, W., Plescher, A., Gartzia, I., Jiménez, D., ... and Codina, C. 2006. An industrial approach in the search of natural antioxidants from vegetable and fruit wastes. *Food Chemistry* 97(1): 137-150.
- Pourmortazavi, S. M. and Hajimirsadeghi, S. S. 2007. Supercritical fluid extraction in plant essential and volatile oil analysis. *Journal of Chromatography A* 1163(1-2): 2-24.
- Prior, R. L., Wu, X. and Schaich, K. 2005. Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. *Journal of Agricultural and Food Chemistry* 53(10): 4290-4302.
- Reichardt, C. 2003. Solvents and solvent effects in organic chemistry. 3rd ed. Germany: Wiley-VCH.
- Ribeiro da Silva, L. M., Teixeira de Figueiredo, E. A., Silva Ricardo, N. M., Pinto Vieira, I. G., Wilane de Figueiredo, R., Brasil, I. M. and Gomes, C. L. 2014. Quantification of bioactive compounds in pulps and by-products of tropical fruits from Brazil. *Food Chemistry* 143: 398-404.
- Ribeiro, S. M. R., Barbosa, L. C. A., Queiroz, J. H., Knödler, M. and Schieber, A. 2008. Phenolic compounds and antioxidant capacity of Brazilian mango (*Mangifera indica* L.) varieties. *Food Chemistry* 110(3): 620-626.
- Ruiz-Montañez, G., Ragazzo-Sánchez, J. A., Calderón-Santoyo, M., Velázquez-de la Cruz, G., de León, J. A. and Navarro-Ocaña, A. 2014. Evaluation of extraction methods for preparative scale obtention of mangiferin and lupeol from mango peels (*Mangifera indica* L.). *Food Chemistry* 159: 267-272.
- Sachindra, N. M., Bhaskar, N. and Mahendrakar, N. S. 2006. Recovery of carotenoids from shrimp waste in organic solvents. *Waste Management* 26(10): 1092-1098.
- Salvador, A. A., Podestá, R., Block, J. M. and Ferreira S. R. S. 2016. Increasing the value of pecan nut [*Carya illinoensis* (Wangenh) C. Koch] cake by means of oil extraction and antioxidant activity evaluation. *The Journal of Supercritical Fluids* 116: 215-222.
- Sellamuthu, P. S., Denoya, G. I., Sivakumar, D., Polenta, G. A. and Soundy, P. 2013. Comparison of the contents of bioactive compounds and quality parameters in selected mango cultivars. *Journal of Food Quality* 36(6): 394-402.
- Siddiq, M., Brecht, J. K. and Sidhu, J. S. 2017. Handbook of mango fruit: production, postharvest science, processing technology and nutrition. 1st ed. United States: Wiley-Blackwell.
- Sogi, D. S., Siddiq, M., Greiby, I. and Dolan, K. D. 2013. Total phenolics, antioxidant activity, and functional properties of 'Tommy Atkins' mango peel and kernel as affected by drying methods. *Food Chemistry* 141(3): 2649-2655.
- Straccia, M. C., Siano, F., Coppola, R., La Cara, F. and Volpe, M. G. 2012. Extraction and characterization of vegetable oils from cherry seed by different extraction processes. *Chemical Engineering Transactions* 27: 391-396.

Zetzi, C., Brunner, G. and Meireles, M. A. A. 2003. Standardized low-cost batch SFE Units for University education and comparative research. In Proceedings of the 6th International Symposium on Supercritical Fluids, p. 577-581. Versailles, France.