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The potential of the pecan nut cake as an ingredient for the food industry

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ABSTRACT

Pecan nut [*Carya illinoinensis* (Wangenh.) K. Koch] cake (PNC) is a co-product from the oil extraction industry and its potential as an ingredient for the food industry are not well known. In this work, the nutritional composition and the functional properties of PNC were studied. Additionally, the influence of different solvents (ethanol, water, and acetic acid) on the phytochemical composition and antioxidant capacity (reducing potential of the hydrophilic compounds – RPHC, 2,2-diphenyl-1-picrylhydrazyl - DPPH, and total reducing capacity – TRC) of PNC extracts were established using a simplex-centroid design. PNC is a source of carbohydrates, protein, and dietary fiber (40.5; 21.87 and 13.01 g 100 g^{-1}, respectively). The PNC exhibited a low energy value when compared to the raw nut (398.8 kcal 100 g^{-1} and 645.54 kcal 100 g^{-1}, respectively). Mg, Mn and Co (416.74; 23.21 mg 100 g^{-1} and 59.00 µg 100 g^{-1}, respectively) were the main minerals identified in PNC. The PNC also presented functional properties such as emulsifying and oil absorption capacities and a great ability to absorb water. Using the proposed solvent mixture system, the content of total phenolic compounds and condensed tannins recovered from PNC ranged between 172.43 and 2744.24 mg GAE 100 g^{-1}, and 253.42 to 1376.44 mg CE 100 g^{-1}, respectively. The antioxidant capacity of the PNC extract was showed through its ability to reduce hydrophilic (172.06–1714.96 mg GAE 100 g^{-1}) to transfer hydrogen atoms (12.55–74.11% scavenging activity) and lipophilic compounds (509.87–2070.80 mg QE 100 g^{-1}) using RPHC, DPPH, and TRC methods, respectively. Combining ethanol, water, and acetic acid at 30 °C for 15 min, positively affects the extraction of bioactive compounds from PNC, as well as the antioxidant activity of the extracts. The physicochemical, functional, phytochemical, and antioxidant properties demonstrate that pecan nut cake may represent a potential ingredient or additive for the food, pharmaceutical, and cosmetic industries.

1. Introduction

Diets based on the consumption of a wide variety of vegetables (e.g., fruits, unprocessed cereals, and nuts), a moderate amount of animal protein (preferably fish) and low saturated and trans-fat, such as the Mediterranean diet, have been widely studied in the recent years. The nuts, an important component of these diets, are rich in mono-unsaturated fatty acids, polyphenols, and other phytochemicals involved in many biological functions (Chang, Alasalvar, Bolling, & Shahidi, 2016; Ros, 2010; USDA, 2019). Almond, pistachio, pine nut, macadamia, hazelnut, European walnut, Brazil nut, pecan, and cashew nut are the main nuts sold worldwide (Alasalvar & Shahidi, 2009; INC, 2018).

Globally popular and known for its sensory and nutritional attributes, as well as, for its commercial value, the pecan nut (*Carya illinoinensis* (Wangenh.) K. Koch) is among the main nuts sold worldwide (Alasalvar & Shahidi, 2009; INC, 2018). Originally from the southern United States and northern Mexico, pecan nut belongs to the Juglandaceae family. American immigrants introduced the culture of pecan nut in Brazil in the mid-18th century. This nut has been present in the Brazilian agricultural scenario in the last 50 years, and it is currently grown in the states of Minas Gerais, São Paulo, Santa Catarina, and Rio Grande do Sul (Poletto, Muniz, Poletto, & Baggiotto, 2015). In the 2017/18 harvest, the Brazilian production of native (Brazil nut, cashew and baru nuts) and exotic nuts (pecan and macadamia nuts) accounted for 38,850 tons, which represented 0.92% of the total production worldwide. Pecan nut covers more than 6000 ha planted, with a production of 900 tons per year. The production and consumption of nuts have a high potential for growth. As reported by the São Paulo State Federation of Industries, the production of nuts in

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Brazil is estimated to achieve a revenue equivalent to US$ 1 billion from exports until 2027. In the same period, Brazilian domestic consumption is expected to increase by 8% (FIESP, 2017).

Pecan nuts are rich in mono and polyunsaturated fatty acids, tocopherols, sterols, and phenolic compounds. These compounds are related to its antioxidant activity (Alasalvar & Shahidi, 2009; Atanasov et al., 2018; Ros, 2010). It has been reported that the consumption of nuts is associated with beneficial effects on health, especially against chronic non-communicable diseases (Atanasov et al., 2018; Chang et al., 2016; de la Rosa et al., 2014).

The pecan nut co-products, such as the oil and the cake resulting from the press, are rich in nutrients and phytochemical compounds (Atanasov et al., 2018; USDA, 2019; Wakeling, Mason, D'Arcy, & Caffin, 2001). Despite its nutritional properties and pleasant sensory characteristics, pecan nut cake (PNC) has low commercial value, and it has usually intended for animal feed. Due to its characteristics, PNC has a high potential for utilization by the food industry. Thus, the knowledge of the morphological characteristics and its functional properties such as water and oil retention capacities, and emulsifying properties, binding, swelling, viscosity, and foaming capacity, are important for possible applications of PNC in baked products, snacks, spreads, and yogurts (Chandra, Singh, & Kumari, 2015; Ling, Zhang, Li, & Wang, 2016; Santos et al., 2013).

The efficiency of different solvents in the recovery of phytochemical compounds, as well as the evaluation of the antioxidant profile of pecan nut cake, has been not well established in the literature. In addition, the proper extraction of these compounds depends on many variables such as particle size, proportion and type of solvent, temperature and time besides the extraction methods, that include those using organic solvents, supercritical fluids, subcritical water, microwave, high hydrostatic pressure, pulsed electric fields, and ultrasound (Maciel et al., 2018; Oroian & Escriche, 2015; Yuan, Lu, Eskridge, Isom, & Hanna, 2018). The Response Surface Methodology (RSM) is reported to provide broad and reliable information with a small number of experiments. On the other hand, the simplex-centroid, a mixing design often used in analytical chemistry, allows the investigation of the interaction effects of independent parameters, synergistic or antagonistic effects of the components of the mixture on the dependent variables (responses) (Ferreira et al., 2018).

Based on the commercial and technological potential presented by pecan nut co-products, the present study aimed to determine the nutritional and functional properties of pecan nut cake, as well as to establish the influence of the use of different solvents on its phytochemical composition and antioxidant activity. These results obtained should encourage the use of this raw material as an ingredient in the food industry, adding value to this co-product.

2. Materials and methods

2.1. Chemicals

The standards Ca, Co, Zn, Mn, Mg, Cu, Fe, Na and K, and stock solutions were purchased from Sigma-Aldrich Co. (St. Louis, USA). Gallic acid, Folin-Ciocalteu reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), methanol, quercetin, and catechin were purchased from Sigma-Aldrich (São Paulo, Brazil). All other chemical reagents and solvents used in the experiments were of analytical grade. Ultrapure water was used in the experiments.

2.2. Materials and preparation of the sample

Pecan nut [*Carya illinoinensis* (Wangenh.) K. Koch] sample of the Barton variety (5.0 kg) from Cachoeira do Sul (RS, Brazil) were supplied by Divinut Indústria de Nozes Ltda. The oil was extracted after a triple sequential pressing using a TE-098 Tecnal hydraulic press (São Paulo, Brazil) at 25 °C. The resulting pecan nut cake (PNC) was ground in an analytical mill (model Q298A, Quimis®, Diadema, Brazil) and standardized at 60 Tyler mesh. Subsequently, PNC was stored in low-density polyethylene containers at 4 °C ± 2 until the analysis. The extraction yield (EY) was calculated according to the Eq. (1):

$$EY\,\% = [(\text{weight of extracted oil})/(\text{weight of crushed pecan nut})] \times 100 \quad (1)$$

2.3. Nutritional, mineral composition and color parameters

Determination of moisture (925.09), ashes (923.03), total lipids (920.85), crude protein (920.87) and dietary fiber (991.43) was performed according to the Association of Official Agricultural Chemists (AOAC, 2005). The lipids were obtained by Soxhlet using hexane. For crude protein, a correction factor = N × 5.30 was used. Carbohydrates and total energy were estimated according to Eqs. (2) and (3).

$$\text{Total carbohydrates}(\text{g}\,100\,\text{g}^{-1}) = 100 - (\text{g lipids} + \text{g protein} + \text{g ash} + \text{g fiber}) \quad (2)$$

$$\text{Energy (kcal)} = 4 \times (\text{g protein} + \text{g carbohydrates}) + 9 \times (\text{g lipids}) \quad (3)$$

The content of minerals (Ca, Co, Zn, Mn, Mg, Cu, and Fe) were evaluated by the method proposed by Mologni, de Sá Ploêncio, Machado, and Daguer (2017) and determined by flame atomic absorption spectrometry (F-AAS) in an Analyst 200 equipment (PerkinElmer Inc (Waltham, EUA). Acetylene (purity 99.7%) was used as fuel gas to heat the atomization system, while the air was the compressed gas. All samples were calcined at 520 °C and the ashes treated using 8 mol L^{-1} hydrochloric acid. The cathode lamps of the surveyed elements were of the brand Lumina (PerkinElmer, Inc., Waltham, MA, USA). The results were interpolated in analytical curves constructed for each element. Na and K (mg kg^{-1}) were determined by the atomic emission spectrometry (F-AES). The samples were calcined at 520 °C and treated with 4 mol L^{-1} nitric acid. A 910M flame photometer (Analyser Comércio e Indústria Ltda., São Paulo, Brazil) was used for the readings.

The color of PNC samples was measured using a Chroma Meter CR400 (Konica Minolta, Japan) colorimeter and expressed as the CIE Lab color system, according to the International Commission on Illumination.

2.4. Microstructure and functional properties of pecan nut cake (PNC)

2.4.1. Scanning electron microscopy

The microstructure of the samples was evaluated by scanning electron microscopy (JEOL JSM 6390, Jeol Company, Tokyo, Japan). The ground PNC sample was fixed on an aluminum stub with a double-sided adhesive tape which was later covered with gold (Au). The evaluation was performed under vacuum (10 kV), and the micrographs were captured at 500, 1000, and 2000×.

2.4.2. Functional properties of PNC

The water retention capacity (WRC), the oil retention capacity (ORC), swelling power, and the foaming ability were performed as described by Ling et al. (2016). The WRC and/or ORC was expressed as the amount of oil/water retained per gram of PNC sample. The foam portion was evaluated for foaming capacity (FC) and foam stability (FS).

Emulsion activity index (EAI) and emulsion stability index (ESI) of PNC were determined according to the method as described by Zhang et al. (2015). The absorbances at times 0 (A0), and 10 min (A10) after homogenization was recorded at λ = 500 nm, and the values were used to calculate the EAI and the ESI according to the following Eqs. (4) and (5):

$$IAE(m^2/g) = \frac{2 \times 2.303 \times A_0}{F \times C} \quad (4)$$

$$EEI(\%) = \frac{A_{10} \times \Delta t}{\Delta A} \quad (5)$$

where *F* is the volumetric fraction of oil (0.25); *A0* is the absorbance at time 0, and *A10* at time 10 min after homogenization; $\Delta t = 10$ min; $\Delta A = A0 - A10$.

2.5. Experimental design and ultrasound assisted extraction (UAE)

A simplex-centroid mixture design (cubic model), composed of 10 trials, was used to evaluate the effect of three independent variables (ethanol, water, and acetic acid) on different responses: total phenolics, condensed tannins, reducing potential of hydrophilic compounds (RPHC), DPPH, total reducing ability of hydrophilic and lipophilic compounds (TRC).

For the preparation of the extracts, 0.5 g of PNC was used. The extractions were performed at 40 kHz and 300 W on an EGS-5HD ultrasonic system (Enge Solutions, São Paulo, Brazil) for 15 min at 30 °C (conditions determined in preliminary studies, data not shown). The concentrations of the different solvents varied according to the experimental design, making up the volume of 25 mL. The extracts were centrifuged at 4000 rpm for 10 min and vacuum filtered on quantitative filter paper. Finally, the resulting extract was packed in polyethylene containers, protected from light at 4 °C ± 2 until further analysis.

2.6. Determinations of total phenolic content, condensed tannins and antioxidant activity for PNC extracts

The total phenolic compounds (TPC) were estimated using 96-well microplates (Granato, Santos, Maciel, & Nunes, 2016). In the microplates, 25 μL of Folin-Ciocalteu (2.0 N), followed by 200 μL of ultrapure water was added to 25 μL of PNC extract (1:10 in ultrapure water). After 5 min, 25 μL of Na_2CO_3 (0.943 mol L^{-1}) was added to the mixture. The plate remained in the dark at 25 °C for 60 min, and the absorbance was recorded on a microplate reader (Spectramax Paradigm, Molecular Devices, San Jose-CA, USA) at a wavelength of $\lambda = 725$ nm against a blank (ultrapure water). The content of TPC was determined from a standard curve of gallic acid (0–160 mg L^{-1}, $y = 169.7x - 1.7809$, $R^2 = 0.9977$) and the results were expressed as mg of gallic acid equivalent per 100 g (mg GAE 100 g^{-1}).

The content of condensed tannins (CT) was evaluated according to the vanillin assay (Granato et al., 2016). In a 96-well microplate, 25 μL of the PNC extract (1:5 in methanol) was added to 150 μL of a 4% (w/v) vanillin solution in methanol and 75 μL of a 32% sulfuric acid solution in methanol. The plate remained in the dark at 25 °C for 15 min; then the absorbance was recorded at $\lambda = 500$ nm. The content of condensed tannins was determined from a standard curve of catechin (36–240 mg L^{-1}, y 540.56x + 8.3801, $R^2 = 0.99$) and the results were expressed as mg of catechin equivalent per 100 g (mg CE 100 g^{-1}).

The reducing potential of the hydrophilic compounds (RPHC) was estimated by the Prussian Blue method, as described (Karnopp, Margraf, Maciel, Santos, & Granato, 2017). In microplates, 100 μL of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 0.5 mmol L^{-1}) together with 100 μL of PNC (1:20 in ultrapure water) were added and allowed to react for 2 min. Then, 100 μL of the potassium ferricyanide solution ($K_3[Fe(CN)_6]$ 0.5 mmol L^{-1}) was added, followed by stirring for 20 s, and kept in for 15 min at 25 °C in the dark. The absorbance was recorded at $\lambda = 725$ nm. The reducing potential of the hydrophilic compounds was determined from a standard curve of quercetin (5–20 mg L^{-1}, $y = 34.558x - 0.0917$ $R^2 = 0.997$) and results were expressed as mg of quercetin equivalent per 100 g (mg QE 100 g^{-1}).

The determination of the antioxidant activity by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method was performed according to Brand-Williams, Cuvelier, and Berset (1995). An aliquot of 40 μL of PNC (1:10 in ultrapure water) and 260 μL of a 0.10 mM ethanolic solution of DPPH was added to a 96-well microplate. The mixture remained in the dark at 25 °C for 30 min, and the absorbance was recorded at $\lambda = 517$ nm. The scavenging of the DPPH radical was expressed as percent inhibition, according to Eq. (6):

$$\%\ \text{Scavenging Activity} = \left[1 - \left(\frac{\text{Absorbance (final)}_{517}\ \text{sample}}{\text{Absorbance (initial)}_{517}\ \text{sample}}\right)\right] \times 100 \quad (6)$$

The evaluation of the total reducing capacity (TRC) of hydrophilic and lipophilic compounds was performed in microplates, according to Karnopp et al. (2017). For this, 75 μL of the Folin-Ciocalteu reagent, diluted in 1:2 (v/v) isobutanol together with 50 μL PNC (pure extract) was added in a test tube. After 2 min, 875 μL of 0.1 mol L^{-1} NaOH solution and ultrapure water (1.50 mL) were added to the tube which was stirred for 10 s. After 20 min of reaction, 250 μL of the solution was transferred to 96-well microplates and the absorbance recorded at $\lambda = 665$ nm. The total reducing potential was determined from a standard curve of quercetin (25.2–360 mg L^{-1}, $y = 1186.7x - 42.005$ $R^2 = 0.9924$) and the results were expressed as mg of quercetin equivalent per 100 g (mg QE 100 g^{-1}).

2.7. Statistical analysis

Data were analyzed using Microsoft Office Excel® v. 2016 (Microsoft Inc., USA), Action v.2.9, and Statistica v. 10.0 (StatSoft Inc., USA). Firstly, the data were checked for normality (Shapiro-Wilk test) and homoscedasticity (Brown-Forsythe test). The results were submitted to analysis of variance (ANOVA), followed by the Fisher LSD test ($p \leqslant 0.05$) to detect the differences between the results. The effects of the different solvents on the phytochemicals and the antioxidant profile of the PNC were modeled (Eq. (7)), and the results were presented by response surface methodology (RSM).

$$Y_n(X) = \sum_{i=1}^{3} \beta_i X_i + \sum_{i\hat{a}\copyright \frac{1}{2} j}^{3} \sum_{j}^{3} \beta_{ij} x_i x_j + \beta_{ijk} x_i x_j x_k \quad (7)$$

where Y n is the expected response; b_i are the linear effect coefficients, b_{ij} coefficient of the quadratic effect and $_{ijk}$ coefficient of cubic effect; X_i, X_j e X_k represent the independent coded variables (types of solvents).

The normality of the residues was evaluated according to the Kolmogorov-Smirnov test. Linear correlation between the solvents was calculated. P-values below 5% were considered significant for RSM modeling. The goodness-of-fit for the model was evaluated by the regression coefficient (R^2) and the adjusted R^2 (Maciel et al., 2018).

3. Results and discussion

3.1. Nutritional and mineral composition of PNC

Table 1 shows that pecan nut is a rich source of lipids (62.17 g 100 g^{-1}) and proteins (8.61 g 100 g^{-1}), which contributes to a high energy value (645.74 kcal 100 g^{-1}). These results were similar to that reported in the literature for the same nut (USDA, , 2019; Wakeling et al., 2001). The results between raw pecan nut and the PNC were significantly different ($P < 0.05$). An increase of proteins, minerals, fibers, and carbohydrates and a decrease of 38.2% in the energy value for PNC where observed when compared to the pecan nut.

The mechanical extraction (hydraulic press) of oilseed oils is influenced mainly by the moisture content of the sample, the temperature and applied pressure, and the particle size (Ezeh, Gordon, & Niranjan, 2016). The mechanical pressing produces oil and cake of high quality since the use of solvent and high temperatures can lead to the darkening of the oil, as well as the degradation of thermosensitive minor components (Uitterhaegen & Evon, 2017).

The mechanical pressing, which is reported to produce high-quality

Table 1
Nutritional composition of pecan nut cake (PNC).

Parameters (dry basis)	Pecan Nut	PNC
Moisture (g 100 g^{-1})	3.37 ± 0.01^{b}	5.03 ± 0.11 ^{a}
Ashes (g 100 g^{-1})	1.86 ± 0.06^{b}	2.97 ± 0.07 ^{a}
Lipids (g 100 g^{-1})	62.17 ± 0.006 ^{a}	16.64 ± 0.06^{b}
Protein (F = 5.30) (g 100 g^{-1})	8.61 ± 0.12^{b}	21.87 ± 0.6 ^{a}
Fiber (g 100 g^{-1})	11.1 ± 0.22^{b}	13.01 ± 0.19 ^{a}
Carbohydrates (g 100 g^{-1})	12.87 ± 0.09^{b}	40.5 ± 0.33 ^{a}
Energy value (kcal)	645.54 ^{a}	398.81^{b}
Color		
L*	52.55 ± 0.94^{b}	65.31 ± 0.98 ^{a}
a*	7.19 ± 0.17 ^{a}	4.61 ± 0.24^{b}
B*	21.46 ± 0.62 ^{a}	18.05 ± 0.19^{b}
Hue ° (h*)	71.5^{b}	75.7 ^{a}
Chroma (C*)	22.63 ^{a}	18.62^{b}

* Different letters on the same line indicate significant difference by Student's *t*-test ($P < 0.05$).

oil, provided 73.23% of oil yield in the extraction. Oro, Ogliari, de Amboni, Barrera-Arellano, and Block (2008) and do Prado et al. (2013) using the same process reported an oil yield of 45% and 51% oil, respectively. The mechanical pressing, depending on the design of the equipment, may result in yields of oil extraction between 70 and 80% (for hydraulic press) and 80–90% (screw pressing) (Gong & Pegg, 2015).

The color intensity in the cake was reduced with the extraction of the oil, which carried liposoluble pigments as reported by Ling et al. (2016). Therefore, the cake showed less intense staining, which was significantly different ($P > 0.05$) when compared to the pecan nuts (Table 1). The parameter L* shows that PNC presents coloration with lighter tones in comparison to the pecan nut. The cake also showed a reduction of 35.88% in parameter a* (reddish tones) and 15.89% in the parameter b* (yellowish tones) when compared to the pecan nut. These results were also in agreement with the observed values of C* (chroma), and h (hue angle) which confirm that both samples are closer to yellowish and reddish tones, respectively.

Table 2 shows the profile of minerals of PNC and daily mineral intake index. Macroelements (Ca, Mg, Na and K) and trace elements (Zn, Mn, Cu, Fe, and Co) in PNC and the recommended daily intake (DRI) for these compounds according to the European Food Safety Authority (EFSA, European Food Safety Authority, 2017) and world health organization (WHO, 2012)

Table 2
Profile of minerals of PNC and its Dietary Reference Intakes (DRI).

Elements	PNC*	DRI (mg day^{-1}) **	
		Males	Females
Ca	475.08 ± 76.42	950	950
Mg	416.74 ± 10.8	350	300
Zn	8.50 ± 0.53	16.3	12.7
Mn	23.21 ± 0.50	3	3
Cu	0.75 ± 0.06	1.6	1.3
Fe	2.13 ± 0.08	11	11
K	413.74 ± 14.28	3500	3500
Na	14.54 ± 0.50	< 2300	
Co***	59.00 ± 0.001	5–60	

DRI: Dietary Reference Intakes recommended for adults (males and females, 19–50 years) according to the European Food Safety Authority and World Health Organization; * Analyzes performed in triplicate; **All the elements are expressed in mg 100 g^{-1}, except Co which is expressed in μg 100 g^{-1} and its DRI in μg day^{-1}.
Source: (Cámara-Martos & Moreno-Rojas, 2016; EFSA, European Food Safety Authority, 2017; WHO, 2012).

PNC is also a rich source of Mg (416.74 mg 100 g^{-1}), Mn (23.21 100 g^{-1}) and Co (59.00 μg 100 g^{-1}), followed by Ca, Zn and Cu (475.08, 8.50 and 0.75 mg 100 g^{-1} respectively). The results indicate that 100 mg PNC may be sufficient to reach the recommended adult daily intake of Mg, Mn, and Co (Cámara-Martos & Moreno-Rojas, 2016; EFSA, European Food Safety Authority, 2017; WHO, 2012). Wakeling et al. (2001) reported for two pecan nut cultivars (Wichita and Western Schley) lower values of Mn, Mg, Ca, Zn and Cu (7.2 and 8.3 mg 100 g^{-1}, 120 and 126 mg 100 g^{-1}, 48 and 61 mg 100 g^{-1}, 6.2 and 6.9 mg 100 g^{-1}, and 0.3 and 0.9 mg 100 g^{-1}, respectively). The USDA (2019) also reported lower values for Ca, Mg, Zn, and Mn (70, 121, 4.53, and 4.5 mg 100 g^{-1}, respectively) in pecan nut. Cobalt (Co) values for pecan nut were first reported by Senter (1976) in trace levels. However, substantial results for PNC are reported in the present study. The values obtained indicate that 100 g of PNC are sufficient to meet the daily requirement for Co.

The variation in the obtained and the values reported in the literature indicate that the mineral content in the PNC depends on multiple factors, such as the variety of the cultivar, stage of maturity, age, crop management, and geographical origin. Wakeling et al. (2001) found that the concentrations of Ca, Mn, Na, Mg, and Zn may change depending on the cultivar, maturity, and harvest year. In addition, environmental factors such as climate, soil type, amount of rainfall, the season of the year, storage time, and preservation are also relevant for these variations in the data.

3.2. Microstructure and functional properties of PNC

Fig. 1 shows the morphology of the PNC recorded by scanning electron microscopy (SEM). It was observed that the microstructure of the PNC is composed of different irregular and opalescent bodies with oval, scale, globular, and granular shapes. These characteristics have also been reported for pecan nut (Wakeling, Mason, D'Arcy, Caffin, & Gowanlock, 2003), Brazil nut (*Bertholletia excelsa*) flour (Santos et al., 2013), and sapucaia nut (*Lecythis pisonis* Cambess) defatted flour (Teixeira, Ávila, Hornung, Barbi, & Ribani, 2018). The structures observed are mostly attributed to the entanglement of fibers, carbohydrates, and proteins that are concentrated in the PNC and also possibly to starchy bodies. Santos et al. (2013) reported that surface modifications might be attributed to the raw material processing steps. The extraction of lipids and lipoproteins from its structure lead to deformation of the matrix by altering its original globular shape. Ling et al. (2016) and Wakeling et al. (2003) observed that, in partial degreasing, the lipid-protein and lipid-starch interaction cause deformations, which may explain the presence of a large number of cavities on the surface of the PNC with spongy-looking structures after oil extraction. Ling et al. (2016) also emphasized that the microstructures observed by SEM can provide a better understanding of the functional properties when observing the presence or absence of lipids, protein concentrations and the presence of carbohydrates which affect those properties.

PNC exhibited low emulsifying capacity and stability (3.676 ± 0.2 m^2 g^{-1} of PNC and 1.704 ± 0.14%, respectively) and high oil and water absorption capacity (1.65 ± 0.1 and 6.65 ± 0.3 g g^{-1} of PNC, respectively). Ling et al. (2016) reported that the protein content and their characteristics, such as hydrophilic to hydrophobic amino acid ratio, directly influence the emulsifying properties of vegetable flours. The high content of fiber may be a limiting factor for the production of emulsions using PNC. However, PNC has an excellent ability to retain and absorb water, and it achieved higher WRC values than those reported by Ling et al. (2016) for pistachio kernel flour (2.14–3.65 g/g) and by Teixeira et al. (2018) for sapucaia nut (0.35–1.38 g/g). The WRC and ORC play an essential role in improving the texture, stability, and taste of food products. Chandra et al. (2015) reported that flours with high WRC could be used in the formulation of some foods such as sausage, pasta, processed cheese, and

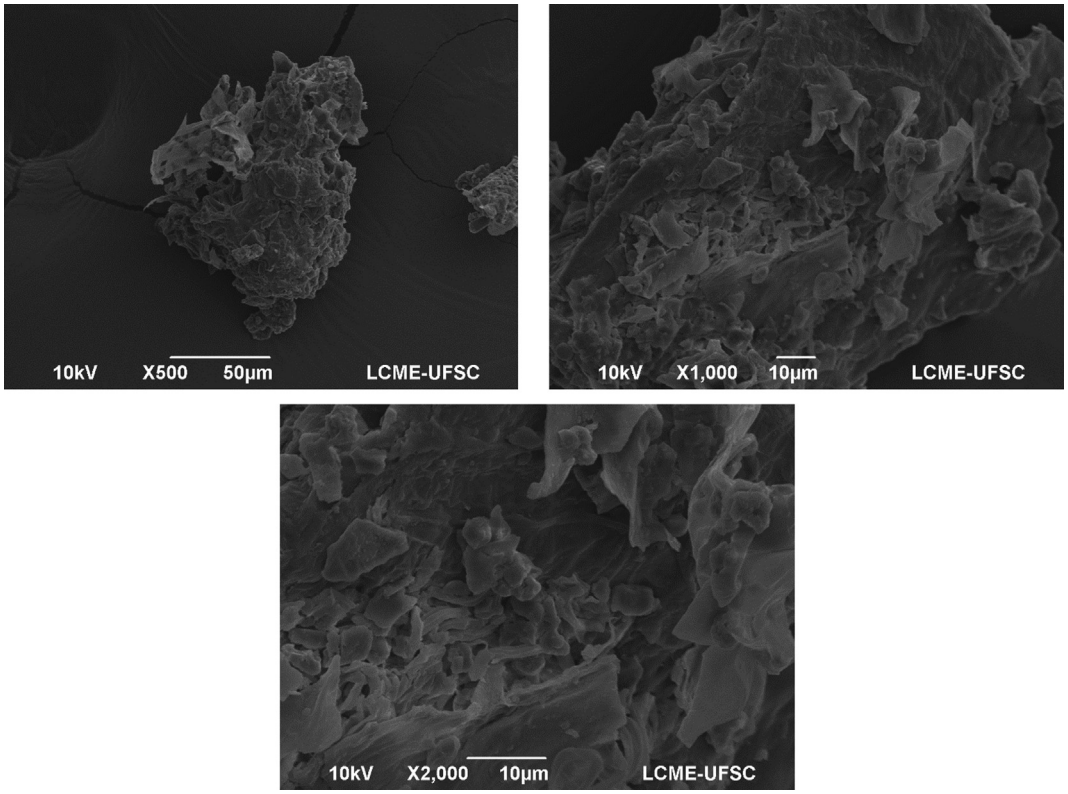

Fig. 1. Scanning electron micrography of pecan nut cake corresponding to 500, 1000 and 2000× magnifications.

bakery products. PNC has a low protein-protein interaction, thus making foaming difficult, resulting in a very thin, low viscosity foam with many scattered and unstable air cells. McWatters and Cherry (1977) reported poor foaming properties for pecan flour suspension (8% w/v). The authors concluded that this raw material is pH-dependent, and emulsifying properties can be dramatically improved in pHs higher than 8. Additionally, this behavior may also be attributed to the composition of PNC proteins which present low solubility. The PNC showed a low swelling power at 60 °C (8.609 ± 0.01 g g^{-1} of PNC) and 80 °C (7.11 ± 0.01 g g^{-1} of PNC), and it is lower at higher temperatures, probably due to the damage caused to the wall cell which may not be strong enough to retain the water.

3.3. Total phenolic content, condensed tannins and antioxidant activity for PNC extracts

Table 3 shows the results obtained for the phenolic content, condensed tannins, and antioxidant activity in PNC. Based on the Shapiro-Wilk test, the normality of the data was verified, and the ANOVA one-factor test ($P < 0.001$) showed significant differences for all response variables.

The contents of TPC and CT obtained in the UAE using the mixtures of ethanol, acetic acid, and water varied statistically ($P < 0.001$) and ranged from 172.43 to 2744.24 mg AGE 100 g^{-1} and 253.42 to 1376.44 mg CE 100 g^{-1}, respectively. The linear regression analysis showed that the models were significant ($P < 0.05$; $R^2_{TPC} = 0.929$ and $R^2_{CT} = 0.938$) being able to explain 92.9% and 93.8% of the variability of the values observed in the results for TPC and CT respectively. The residues found using the Kolmogorov-Smirnov test were suitable, presenting no lack-of-fit to the experimental data ($P_{TPC} = 0.36$ and $P_{CT} = 0.19$). The residuals provide important information on the adequacy of the assumptions underlying the statistical models and, therefore, play an essential role in verifying discrepancies between models and data and in the adequacy of the model (Lemonte & Moreno-Arenas, 2019).

The phenolic content of pecan nut has been reported by different authors (de la Rosa et al., 2014; Jia et al., 2018; Robbins, Gong, Wells, Greenspan, & Pegg, 2015; Sarkis et al., 2014; Villarreal-Lozoya, Lombardini, & Cisneros-Zevallos, 2007). The extraction of the bioactive compounds of the PNC has been reported in the literature after its degreasing using hexane followed by solid-liquid extraction with the use of solvents, with the most frequent being acetone, water, ethanol and methanol and/or combinations with different proportions.

Wu et al. (2004) determined the TPC of a great diversity of foods, including pecan nut using acetone:water:acetic acid (70:29.5:0.5, v/v/v). The authors reported levels of TPC of 20.16 mg GAE g^{-1}. Kornsteiner, Wagner, and Elmadfa (2006) evaluating the TPC content of ten types of nuts obtained values of 1284 mg GAE g^{-1} using 75% acetone and 25% sodium metabisulphite for the extraction. In a study with different pecan nut cultivars (Kanza, Kiowa, Nacono, Pawnee and Shawnee), Villarreal-Lozoya et al. (2007) reported levels of TPC varying from 62 to 106 mg of chlorogenic acid equivalent per g and a CT content of 23 to 47 mg CE g^{-1} for the extraction with acetone:water (70:30, v/v). Malik et al. (2009) used 80% (v/v) aqueous methanol in the extraction of phenolics from pecan kernel. de la Rosa et al. (2014) in a study with pecan nut cultivars from Mexico, reported values between 8.29 and 9.59 mg GAE g^{-1} for TPC, and 28.28 to 39.50 g CE 100 g^{-1} for CT using ultrasonic bath and 80% (v/v) acetone as the solvent. Robbins et al. (2015) evaluated eighteen pecan nut cultivars from different regions of the USA using a mixture composed of 70% acetone, 29.5% water, and 0.5% acetic acid as the extraction solution. The authors observed TPC levels from 1.82 to 2.62 g ellagic acid equivalents (EAE) 100 g^{-1}. Sarkis et al. (2014) in a study using different seed and nut cakes reported 690 mg GAE 100^{-1} TPC for pecan nut using 80% (v/v) ethanol as the extracting solvent. Jia et al. (2018) reported for five different pecan nut cultivars (Pawnee, Stuart, Wichita, Jinhua, and Shaoxing) at different maturation stages from China a TPC content varying from 0.23 to 181.28 mg EAE g^{-1} and CT content in a range of 0.3 to 379.85 CE g^{-1}.

The TPC and CT contents of the PNC using the Folin-Ciocalteu assay

Table 3
Real and coded values, total phenolic content, condensed tannins, and antioxidant activity for PNC extracts.

Independent variables (Real and coded values)				Responses				
Assays	Ethanol (mL)	Water (mL)	Acetic Acid (mL)	TPC (mg GAE 100 g^{-1})	CT (mg CE 100 g^{-1})	RPHC (mg GAE 100 g^{-1}	DPPH (% ScavengingActivity)	TRC (mg QE 100 g^{-1})
A	25(1)	0 (0)	0 (0)	1464.42 ± 38 ^{d}	901.42 ± 23$^{b.c}$	683.80 ± 29.57^{f}	61.13 ± 1.51^{c}	1672.63 ± 19.11^{b}
B	0 (0)	25(1)	0 (0)	501.09 ± 120^{f}	553.88 ± 53 ^{e}	195.79 ± 21.45 ^{g}	35.33 ± 0.18^{f}	127.63 ± 13.36 ^{h}
C	0 (0)	0 (0)	25 (1)	172.43 ± 8 ^{g}	883.18 ± 55$^{c.d}$	172.06 ± 34.70 ^{g}	12.55 ± 1.54 ^{g}	509.87 ± 67.19 ^{g}
D	12.5 (0.5)	12.5 (0.5)	0 (0)	1863.78 ± 26^{c}	1376.44 ± 45 ^{a}	1036.01 ± 11.41^{e}	74.11 ± 0.55^{a}	2070.80 ± 34.85^{a}
E	12.5 (0.5)	0 (0)	12.5 (0.5)	860.57 ± 10 ^{e}	604.11 ± 35 ^{e}	677.64 ± 13.47^{f}	40.93 ± 3.85^{e}	766.21 ± 48.34^{e}
F	0 (0)	12.5 (0.5)	12.5 (0.5)	2464.80 ± 38^{b}	741.73 ± 51 ^{d}	1537.79 ± 34.93^{b}	66.48 ± 0.72b^{c}	1153.01 ± 15.06^{c}
G	8.33 (0.33)	8.33 (0.33)	8.33 (0.33)	2744.24 ± 12 ^{a}	411.54 ± 2^{f}	1714.96 ± 46.12^{a}	67.00 ± 0.11^{b}	1636.11 ± 18.06^{b}
H	16.66 (0.667)	4.17 (0.167)	4.17 (0.167)	1737.63 ± 15^{c}	1072.82 ± 71^{b}	1144.64 ± 27.16^{d}	54.53 ± 0.55^{d}	946.05 ± 53.33^{d}
I	4.17 (0.167)	16.66 (0.667)	4.17 (0.167)	1454.52 ± 29 ^{d}	198.69 ± 18 ^{g}	915.17 ± 22.41^{e}	68.66 ± 0.65^{ab}	611.02 ± 9.01^{f}
J	4.17 (0.167)	4.17 (0.167)	16.66 (0.667)	1769.59 ± 25^{c}	253.42 ± 48 ^{g}	1370.87 ± 12.38^{c}	62.82 ± 0.74^{c}	1121.24 ± 20.58^{c}
Brown-Forsythe test				0.785	0.311	0.691	0.440	0.919
P-value ANOVA				< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

*Different letters in the same column indicate significant difference by Fisher's test. TPC: Total phenolics; CT: Condensed tannins; RPHC: Reducing potential of the hydrophilic compounds; TRC: Total reducing capacity.

and the vanillin assay reported in the literature are very controversial and challenging to compare. Different cultivars from different geographical locations and different harvest periods are natural factors to be considered in the variations between the studies. In addition, there are differences in the preparation of the extracts, and the analytical curves, besides the reaction time before the analyzes. These factors may cause a possible under- or overestimation on the content of bioactive compounds.

The PNC extract obtained in this study showed both the ability to transfer hydrogen atoms and to reduce hydrophilic and lipophilic compounds. The reducing potential of the hydrophilic phenolic compounds ranged from 172.06 to 1714.96 mg GAE 100 g^{-1}. On the other hand, the antioxidant activity determined by the DPPH method ranged from 12.55 to 74.11% of inhibition, and the total reducing capacity varied from 127.63 to 2070.80 mg QE 100 g^{-1}. The linear regression analysis showed that the models were significant ($P < 0.05$) for all the antioxidant trials and no adjustment was made to the experimental data according to residue distribution analysis $P_{RPHC} = 0.403$, $P_{DPPH} = 0.431$ and $P_{TRC} = 0.129$. The coefficients of determinations were $R^2_{RPHC} = 0.987$, $R^2_{DPPH} = 0.989$ and $R^2_{TRC} = 0.823$. These coefficients of determinations were able to explain 98.7%, 98.9%, and 82.3% of the variability of the values observed in the tests, respectively. Overall, our results are in agreement with those observed in the literature.

Pecan nut is a rich source of phenolics, such as catechin, epigallocatechin, epicatechin, gallocatechin 3-O-gallate and epigallocatechin 3-gallate (USDA, 2019) and gallic and ellagic acids (de la Rosa et al., 2014). These compounds are associated with a high antioxidant potential *in vitro* as observed in analysis as the oxygen radical absorbance capacity ORAC (de la Rosa et al., 2014; Robbins et al., 2015; Villarreal-Lozoya et al., 2007; Wu et al., 2004), the scavenging activity of reactive species against 1,1-diphenyl-2-picrylhydrazyl, DPPH, and 2,2′-azinobis (3-ethylbenzthiazoline-6-sulfonic acid), ABTS (de la Rosa et al., 2014; Jia et al., 2018; Sarkis et al., 2014; Villarreal-Lozoya et al., 2007), the ferric reducing antioxidant power, FRAP (Robbins et al., 2015), the hydroxyl radical (OH) scavenging activity, hydrogen peroxide removal ability and evaluation of cell lines (de la Rosa et al., 2014).

Table 4 shows the adjusted regression coefficients of the polynomial models for extracting the chemical constituents and antioxidant activity of the PNC.

The level of recovery of TPC and CT, as well as the antioxidant profile of PNC, are dependent on the interactions between the solvents. The efficiency of the extraction system has been correlated mainly with the reaction medium used. The type and proportion of the solvent were factors related to the efficiency of the extraction (Oroian & Escriche, 2015). The solvents ethanol, water, and acetic acid were selected, considering not only the desired extraction abilities but also the potential applications of the extract generated. Since the selected components are easily accessible, cheap, and widely used in the food industry, they may be alternative to the conventional organic toxic solvents.

The complex nature of plant matrices, which present phenolic compounds with different structures and can be conjugated to proteins through methylation, acylation, hydroxylation or, glycosylation, interferes with the extraction process. Aires (2017) showed that a good system of solvents is one that allows the maximization of phenolic extraction without any modification of its chemical nature. The author also emphasizes that several factors must be considered for choosing a specific solvent, such as the solvent power (selectivity); polarity; boiling temperature (should be low to facilitate removal of the solvent from the product); reactivity (the solvent should not react chemically with the extract and should not be decomposed rapidly); viscosity (low); stability (must be stable to heat, oxygen, and light); safety (non-toxic to consumers and the environment); suitable for re-use (if possible) and compatible with current legislation for food applications.

The effects of the different extraction solvents reported in Table 4, resulted in second-order polynomial models, which were used in the creation of response surfaces. Fig. 2 shows the response surfaces for the extraction conditions.

The two-dimensional display of the response surface graph shows the relationship between the response and the independent variables. When evaluated alone in the linear mode, ethanol is significant ($P < 0.05$) for all response variables. The combined use of the different solvents (ethanol, water, and acetic acid) enables a higher recovery of the compounds in general. In general, evaluating the quadratic and cubic effects, it is observed that acetic acid tends to act negatively in the system when associated only with ethanol. However, when combined in a ternary system to the other solvents, it acts positively. It can be observed mainly for TPC extraction and in the antioxidant profile by RPHC.

The polarity of the solvents plays a fundamental role in increasing the phenolic solubility and its sequential extraction. Ethanol acts on the recovery of both hydrophilic and lipophilic compounds, acting in synergy mainly with water. Depending on the degree of acidity or alkalinity the phenolics exhibit structural equilibrium displacements, being generally more stable at acidic pH. Acidification of the reaction

Table 4
Adjusted regression coefficients to model solvent effects on the PNC extraction.

Parameters	Regression coefficient	Standard error	t-value	p-value	−95% Confidence	95% Confidence
TPC (mg GAE 100 g^{-1})						
(A) Ethanol	58.31664	8.47334	6.88237	0.000043	39.43686	77.19643
(B) Water	16.69983	7.36900	2.26623	0.046870	0.28068	33.11898
(C) Acetic Acid	10.10759	8.47346	1.19285	0.260461	−8.77244	28.98763
AB	4.67053	1.91443	2.43964	0.034870	0.40491	8.93615
BC	13.37207	1.52818	8.75030	0.000005	9.96706	16.77708
ABC	0.92416	0.39081	2.36476	0.039630	0.05339	1.79493
R^2	0.929					
Adjusted R^2	0.893					
P value (model)	< 0.001					
P value (normality of residuals)	0.363					
CT (mg CE 100 g^{-1})						
(A) Ethanol	37.05412	4.058730	9.12949	0.000008	27.87263	46.23560
(B) Water	23.49459	2.666325	8.81160	0.000010	17.46294	29.52623
(C) Acetic acid	31.03540	3.218316	9.64337	0.000005	23.75506	38.31573
AB	3.86044	0.755506	5.10974	0.000637	2.15137	5.56951
AC	−1.81330	0.634826	−2.85637	0.018892	−3.24938	−0.37723
ABC	−1.02071	0.152003	−6.71502	0.000087	−1.36456	−0.67685
AB (A-B)	0.41978	0.076824	5.46417	0.000398	0.24599	0.59357
R^2	0.938					
Adjusted R^2	0.897					
P value (model)	< 0.001					
P value (normality of residuals)	0.198					
RPHC (mg GAE 100 g^{-1})						
(A) Ethanol	25.70958	3.567216	7.20718	0.000176	17.27446	34.14471
(B) Water	7.68640	2.527538	3.04106	0.018819	1.70972	13.66308
(C) Acetic acid	5.69262	3.567181	1.59583	0.154557	−2.74242	14.12766
AB	3.61904	0.668873	5.41066	0.000997	2.03741	5.20068
AC	1.66092	0.573076	2.89825	0.023043	0.30581	3.01603
BC	8.75149	0.535908	16.33019	0.000001	7.48426	10.01871
ABC	0.56877	0.142861	3.98131	0.005315	0.23096	0.90659
AB (A-B)	0.31297	0.080966	3.86542	0.006168	0.12151	0.50442
AC (A-C)	−0.28784	0.073504	−3.91598	0.005779	−0.46165	−0.11403
R^2	0.987					
Adjusted R^2	0.972					
P value (model)	< 0.001					
P value (normality of residuals)	0.403					
DPPH (% scavenging activity)						
(A) Ethanol	2.499061	0.070801	35.2969	0.000000	2.338897	2.659224
(B) Water	1.427139	0.049898	28.6010	0.000000	1.314261	1.540016
(C) Acetic acid	0.469581	0.070800	6.6325	0.000096	0.309421	0.629740
AB	0.156628	0.011532	13.5817	0.000000	0.130540	0.182715
AC	0.033941	0.010770	3.1515	0.011710	0.009578	0.058305
BC	0.273967	0.010078	27.1839	0.000000	0.251168	0.296766
AC (A-C)	−0.016041	0.001223	−13.1198	0.000000	−0.018806	−0.013275
R^2	0.993					
Adjusted R^2	0.989					
P value (model)	< 0.001					
P value (normality of residuals)	0.431					
TRC (mg QE 100 g^{-1})						
(A) Ethanol	57.76929	9.426455	6.12842	0.000111	36.7658	78.77274
(B) Water	3.34436	7.761215	0.43091	0.675677	−13.9487	20.63742
(C) Acetic acid	10.21143	9.426452	1.08327	0.304115	−10.7920	31.21487
AB	6.43942	1.793697	3.59003	0.004929	2.4428	10.43603
BC	5.37751	1.548601	3.47250	0.005996	1.9270	8.82801
AC (A-C)	−0.47520	0.190210	−2.49829	0.031539	−0.8990	−0.05139
R^2	0.823					
Adjusted R^2	0.735					
P value (model)	< 0.001					
P value (normality of residuals)	0.129					

medium with weak and non-toxic organic acids such as acetic acid helps in the breakdown of cell membranes, thus providing the extraction of more complex compounds such as condensed tannins and hydrolysates among others that are associated with macromolecules, mainly polysaccharides, constituents of dietary fiber and proteins (Aires, 2017; Naczk & Shahidi, 2004).

The maximization of TPC, CT, and antioxidant activity of the PNC was predicted by the desirability function. A total of 80 interactions were run to provide the best condition for optimization (higher desirability index, d-value). The d-value calculated from the mathematical interactions between factors was 0.817, indicating a satisfactory result for the optimization procedure. The results for the extraction of PNC with a mixture of solvents predicted an optimized system containing 14.58 mL ethanol, 9.36 mL water, and 1.06 mL acetic acid. Using the proposed solvent system, it was obtained an extract with maximized content of phenolics (1920.91 mg GAE 100 g^{-1}), condensed tannins (1195.19 mg CE 100 g^{-1}), and high antioxidant activity (1200.94 mg GAE 100 g^{-1} of RPHC, 69.58% of inhibition of DPPH·,

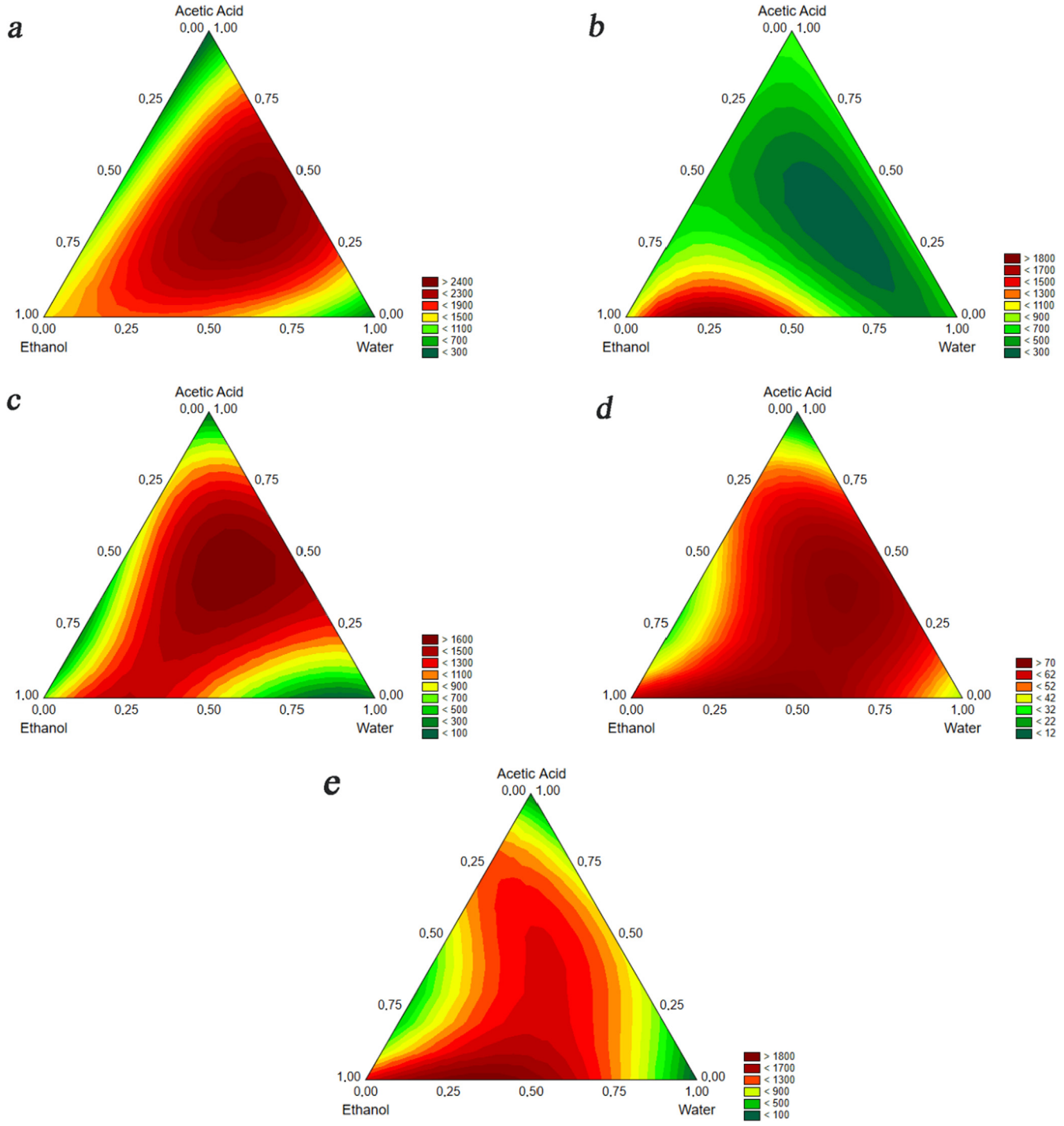

Fig. 2. Effect of the combination of the solvents ethanol, water, and acetic acid on the chemical constituents and the antioxidant profile of the PNC. * a = Total phenolics (TPC); b = Condensed tannins (CT); c = Reducing potential of the hydrophilic compounds (RPHC); d = DPPH; e = Total reducing capacity (TRC).

and 1700.57 mg QE 100 g^{-1} of TRC). The data reported herein showed that the RSM models were significant, robust, and can be considered predictive under the range studied.

4. Conclusions

The cold pressing of pecan nuts resulted in a PNC rich in proteins, fibers, and carbohydrates with a low energy value. The PNC is also a source of Co, Mg, and Mn, which are essential elements for the functioning of the human organism. The morphology evaluation provided a better understanding of the microstructure of PNC, which can affect its functional properties, such as the ability to retain and absorb water, which is the main property of PNC. The report also revealed that PNC is a high source of phenolic compounds and tannins, whose recovery is dependent on the solvent used for the extraction, that also caused an impact on the antioxidant properties. The proposed system presents an adequate prediction level with an R^2 of more than 82% of the data. A multiresponse optimization using the simplex-centroid design was used for obtaining the best solvent system (14.58 mL ethanol, 9.36 mL water, and 1.06 mL acetic acid) for recovering bioactive compounds from PNC. The physicochemical, functional, phytochemical and antioxidant properties demonstrate that pecan nut cake may be a potential

ingredient for the production of foods such as desserts, jelly, yogurts, sausage, pasta, processed cheese and bakery, and confectionery products. Bioactive compounds extracted from this co-product can also be used as ingredients or additives by the food, pharmaceutical, and cosmetic industries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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