Physicochemical, techno-functional and antioxidant characterization of coffee silverskin

Caracterización fisicoquímica, tecno-funcional y antioxidante de la piel plateada del café

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ABSTRACT

Coffee residues have been considered a valuable source of nutritional and functional components, thus are considered as a potential ingredient for foods. The aim of this study was to evaluate the physicochemical, techno-functional, and antioxidant properties of coffee silverskin flakes and powder. The results indicated that coffee silverskin flakes and powder showed pH near to neutrality, and the color was Roman coffee and Deep coffee, respectively, which show that milling process change this parameter. Coffee silverskin flakes showed the highest water and oil-holding capacity, while both coffee residues exert slight swelling and foam capacity, and foam stability, without effect of milling process. However, both residues do not exert emulsion and gelling capacity, as well as emulsion stability. The presence of phenols, flavonoids, caffeoylquinic acid and alkaloids (powder > flakes) were detected in both residues, which exert free- and radical-cation scavenging activity (powder = flakes), reducing power properties, and lipid oxidation inhibition (powder > flakes). In conclusion, coffee silverskin can be proposed as a functional ingredient for food industry.
Keywords: coffee residues, chemical compounds, physicochemical properties, techno-functional properties, antioxidant.

RESUMEN

Los residuos de café se han considerado una fuente valiosa de componentes nutricionales y funcionales, por ello se consideran un ingrediente potencial para la industria alimentaria. El objetivo del estudio fue evaluar las propiedades fisicoquímicas, tecno-funcionales y antioxidantes de hojuelas y harina de la piel plateada de café. Las hojuelas y la harina de piel plateada de café mostraron un pH cercano a la neutralidad, y el color fue café romano y café profundo, respectivamente, lo que indica que el proceso de molienda cambia este parámetro. Los resultados indicaron que las hojuelas de cascarilla de café mostraron la mayor capacidad de retención de agua y aceite, mientras que ambos residuos presentaron ligera capacidad de hinchamiento, formación de espuma y estabilidad de espuma, sin efecto del proceso de molienda. Sin embargo, ambos residuos no presentaron capacidad de emulsión y gelificación, así como estabilidad de la emulsión. La presencia de fenoles, flavonoides, ácido cafeoilquínico y alcaloides (harina > hojuelas) fue detectada en ambos residuos, los cuales ejercieron actividad contra radicales libres y cationes (harina = hojuelas), poder reductor e inhibición de oxidación de lípidos (harina > hojuelas). En conclusión, la cascarilla de café puede proponerse como ingrediente funcional para la industria alimentaria.
Palabras clave: residuos de café, compuestos químicos, propiedades fisicoquímicas, propiedades tecno-funcionales, antioxidante.

INTRODUCTION

In Mexico, processed food production represented 22.5 % of the manufacturing GDP (gross domestic product) and 3.6 % of total GDP in 2018, mainly bakery products followed by the meat sector (CDRSSA, 2019). Regarding meat products, poultry is the most popular meat used in their formulation (51 % of total production), especially destined to produce hams and sausages. Meat products formulated with red meats (22 % of total production) were represented by hams, including cooked, American, Virginia, smoked, baked, and York. Cold meats represented 27 % of total production, including sausages, chorizo, bacon, mortadella, and others. Additionally, the average domestic consumption of meat products was 0.7 kg in the last five years (COMECARNE, 2021).

Moreover, intrinsic and extrinsic factors may adversely affect food quality and shelf life in terms of lipid oxidation, during formulation, transportation, and storage period. Consequently, lipid oxidation results in negative effects on physicochemical and functional properties. Thus, food additives have been widely used in the meat industry to improve nutrimental, sensory, and functional properties (Oswell *et al*., 2018; Domínguez *et al*., 2019).

A food additive is any substance used directly or indirectly in the production, processing, treatment, packaging, transport, or storage, becomes a component, or otherwise affects the characteristics of any food. However, these substances may be given to a testing and approval process to be generally recognized as safe or GRAS (USDA, 2021). Although consumer feelings on synthetic additives have been discus-

sed, meat processors have used natural ingredients to improve technological requirements and increase consumer's expectations (Balestra and Petracci, 2019).

In this context, it has been proved that coffee residues (husk, pulp, silverskin, and spent coffee grounds) are an important source of nutritional and functional components. Thus, spent coffee grounds powder and extracts have been used as functional ingredients for minced pork and chicken meat to reduce the oxidation process (Jully *et al*., 2016; Kim *et al*., 2016). Also, it has been reported that coffee husk powder improves physicochemical (pH and color), techno-functional (cooking loss), and oxidative stability (lipid oxidation) in raw and cooked pork patties (Martuscelli *et al*., 2021a). However, data on coffee residues' physicochemical and functional properties as natural additives are still limited.

Therefore, this work aimed to evaluate coffee silverskin's physicochemical, techno-functional, and antioxidant properties.

MATERIALS AND METHODS
Coffee residues processing
A commercial supplier (CAFFENIO®) in Hermosillo, Mexico, donated coffee silverskin flakes from dark *Coffea arabica* L. To obtain the powder, coffee silverskin flakes were pulverized at 20 mesh of particle size (hammer mill, Pulvex 200, DF, Mexico). Both materials were packed under vacuum (vacuum sealer, Food Saver®, FLA., USA) and stored at room temperature (25 °C) until analysis.

Physicochemical characterization
Measurement of pH
The pH of coffee residues and the commercial standard was measured after homogenization with distilled water at a 1:10 ratio with a potentiometer (pH211, Hanna Instruments Inc., RI, USA) with automatic temperature control (AOAC, 2020).

Color measurement
The color measurement was performed using a spectrophotometer (CM-508d, Konica Minolta Inc., TYO, Japan). The registered values were lightness (L*, ranging from 0-black to 100-white), redness (a*, takes positive values for reddish colors and negative values for greenish colors), yellowness (b*, takes positive for yellowish colors and negative for bluish colors), Chroma (C*), and hue angle (h*). The coffee residues were placed in 3.5 cm diameter Petri dishes, and ten measurements were performed on the samples surface (Robertson *et al*., 1977).

Techno-functional characterization
The techno-functional properties of coffee residues and commercial standard were measured as previously described with slight modifications (Haque *et al*., 2020; López-Marcos *et al*., 2015).

Water-holding capacity (WHC)
Samples (0.1 g) were homogenized with 1.5 mL of distilled water at 10,000 rpm for 1 min, and kept at 25 °C for 30 min. Subsequently, the test tubes were centrifuged at 15,000 x g for 20 min at 4 °C. The supernatant was decanted, and the test tubes with the sediments were weighed. The WHC (%) was calculated as [(Final weigh of the tube with the sample – Initial weigh of the tube with the sample) / (Weigh of the sample)] x 100.

Oil-holding capacity (OHC)
Samples (0.1 g) were homogenized with 1.5 mL of commercial corn oil at 10,000 rpm for 1 min, and kept at 25 °C for 30 min. Subsequently, the test tubes were centrifuged at 15,000 x g for 20 min at 4 °C. The supernatant was decanted, and the test tubes with the sediments were weighed. The OHC (%) was calculated as [(Final weigh of the tube with the sample – Initial weigh of the tube with the sample) / (Weigh of the sample)] x 100.

Swelling capacity (SC)
Samples (0.5 g) were homogenized with 5 mL of distilled water at 10,000 rpm for 1 min, using a graduated tube, and kept at 25 °C for 1 h. The initial and final volume occupied by the samples was measured, and the increase in sample volume after incubation indicates SC.

Foaming capacity (FC)
Samples (0.5 g) were homogenized with 10 mL of distilled water at 5,000 rpm for 5 min at 4 °C (Ultraturrax T25, IKA, Stau, Germany). The foam produced within 30 sec, shows FC.

Foaming stability (FS)
The volume of the foam initially produced was measured within 30 sec, and test tubes were incubated at 25 °C for 30 min. Then, the volume of the foam was measured, and a reduction in the volume showed the absence of FS.

Emulsion capacity (EC)
Samples (0.5 g) were homogenized with 10 mL of distilled water at 8,000 rpm for 1 min at 4 °C. The resultant solution was homogenized with 10 mL of commercial corn oil, under the same conditions. A two-phase suspension formation shows EC.

Emulsion stability (ES)
The previously prepared emulsion was heated for 30 min at 80 °C, cooled at 25 °C, and centrifuged at 12,000 x g for 5 min at 4 °C. If the first emulsion is not broken, it indicates ES.

Gelling capacity (GC)
The coffee residues were homogenized with distilled water to obtain several suspensions at 0, 2.5, 5, 10, 15, and 20 % (w/v) and boiled for 1 h. Subsequently, test tubes were cooled for 1 h at 0 °C. The tubes were inverted to see gel formation.

Antioxidant activity
Phytochemical profile

The qualitative phytochemical analysis of coffee residues was conducted according to standard methods (Griffiths *et al*., 1992; Samejo *et al*., 2011; Samejo *et al*., 2013). Texturized soy protein was used as a commercial standard. A total of 0.5 g of coffee residues and the commercial standard were homogenized with 10 mL of distilled water at 10,000 rpm for 1 min (vortex mixer, Fisher Scientific™, CA, USA) and filtered (Whatman 1 filter paper) to extract phytochemicals (stock solution). In flavonoids and steroids analysis, methanol and $CHCl_3$ were used as solvent extraction, respectively. In addition, phenols, flavonoids and caffeoylquinic acid profile were determined by the ferric chloride, Shinoda and sodium nitrite tests, respectively. While, alkaloids, terpenoids, steroids and saponins were evaluated by the Dragendorff´s, Salkowski, Lieberman-Burchard and foam tests, respectively.

Phytochemical content

The quantitative phytochemical analysis of the coffee residues and the commercial standard was also conducted. In brief, the compounds were extracted using an aqueous solution as solvent (1:10, solid-solvent ratio) by ultrasound-assisted method at 42 KHz for 30 min at 25 °C (Bransonic 3800, Ultrasonics Corp., Jeju, Korea). The resultant solution was filtered (Whatman No. 4 filter paper), concentrated under reduced pressure at 60 °C (rotary evaporator Yamato RE-301BW, Tokyo, Japan) and dried (Freeze dryer Yamato DC401, Tokyo, Japan). The obtained extracts were stored at −20 °C in the dark until analysis.

Total phenolic content (TPC) was determined by the Folin-Ciocalteu method (Ainsworth and Gillespie, 2007). An aliquot of each extract (20 µL, 5 mg/mL) was homogenized with 80 µL of distilled water, 60 µL of Na_2CO_3 (7 %, w/v), and 40 µL of Folin-Ciocalteu's reagent (0.25 N). The resultant solution was mixed with 80 µL of distilled water and incubated for 1 h at 25 °C, in the dark. The absorbance was measured at 750 nm in a spectrophotometer (Multiskan FC UV-Vis, Thermo Scientific, Tokyo, Japan), and results were expressed as mg equivalents of gallic acid per g of dried extract (mg GAE/g).

Total flavonoids content (TFC) was evaluated by the aluminum chloride-complex formation method (Popova *et al*., 2004). An aliquot of each extract (20 µL, 5 mg/mL) was homogenized with 130 µL of methanol and 20 µL of $AlCl_3$ (5 %, w/v). The resultant mixture was incubated for 30 min at 25 °C, in the dark. The absorbance was measured at 415 nm, and results were expressed as mg equivalents of quercetin per g (mg QE/g).

Caffeoylquinic acid content (CAC) was also determined (Griffiths *et al*., 1992). An aliquot of each extract (100 µL, 5 mg/mL) was homogenized with 200 µL of urea (0.17 M), 200 µL of glacial acetic acid (0.1 M) and 500 µL of distilled water. The resultant solution was mixed with 500 µL of $NaNO_2$ (0.14 M) and 500 µL of NaOH (1 M), centrifuged at 2,250 *x* g for 10 min at 4 °C (Sorvall ST18R, Thermo Fisher Scientific, Waltham, USA). The absorbance was measured at 510 nm, and results were expressed as mg equivalents of chlorogenic acid per g (mg CAE/g).

Free-radical scavenging activity

The free-radical scavenging activity (FRSA) was determined by the DPPH test (Molyneux, 2004). An aliquot of each extract (100 µL, 5 mg/mL) were homogenized with 100 µL of DPPH˙ solution (300 µmol), and incubated for 30 min at 25 °C, in the dark. Ascorbic acid (25 µg/mL) was used as a positive control. The absorbance was measured at 520 nm, and results expressed as FRSA (%) = [(Absorbance of DPPH˙ solution at 0 min) − (Absorbance of DPPH˙ solution + extract at 1 h) / [(Absorbance of DPPH˙ solution at 0 min)] × 100.

Radical cation scavenging activity

The radical cation scavenging activity (RCSA) was determined by the ABTS˙+ test (Re *et al*., 1999). Prior to obtain the radical cation, equal parts of ABTS solution (7 mM) and potassium persulfate (2.45 mM) were homogenized and incubated for 16 h at 25 °C, in the dark. Afterward, the formed radical was diluted with an ethanol solution to obtain an absorbance of 0.8, and 20 µL of each extract (5 mg/mL) was mixed with 180 µL of the radical. Ascorbic acid (25 µg/mL) was used as a positive control. The absorbance was measured at 734 nm, and results were expressed as RCSA (%) = [(Absorbance of ABTS˙+ solution at 0 min) − (Absorbance of ABTS˙+ solution + extract at 10 min) / [(Absorbance of ABTS˙+ solution at 0 min)] × 100.

Reducing power ability

The reducing power ability (RPA) was measured by the Prussian-blue test (Berker *et al*., 2010). An aliquot of each extract (100 µL, 5 mg/mL) was homogenized with 300 µL of phosphate buffer (0.2 M, pH 6.6) and 300 µL of potassium ferricyanide (1 %, w/v), and incubated in a water bath for 20 min at 50 °C. The resultant solution was mixed with 300 µL of trichloroacetic acid (10 %, w/v) and centrifuged at 4,200 x g for 10 min at 4 °C. Thereafter, 500 µL of the supernatant was mixed with 100 µL of distilled water and 250 µL of ferric chloride (0.1 %, w/v). Ascorbic acid (25 µg/mL) was used as a positive control. The absorbance was measured at 700 nm, and results expressed as absorbance increase at the same wavelength.

Ferric-reducing antioxidant power

The ferric-reducing antioxidant power (FRAP) test was also determined (Benzie and Strain, 1999). An aliquot of each extract (20 µL, 5 mg/mL) was homogenized with 180 µL of FRAP solution [10:1:1, 300 mM buffer sodium acetate in glacial acetic acid at pH 3.6 and 10 mM 4,4,6-tripyridyl-S-triazine (TPZ) in 40 nM HCl and 20 mM $FeCl_3$] and incubated for 8 min at 25 °C, in the dark. Ascorbic acid (25 µg/mL) was used as a positive control. The absorbance was measured at 595 nm, and results were expressed as mg of Fe^{2+} equivalents per g (mg Fe^{2+}/g).

Lipid oxidation in a meat system

The lipid oxidation (LOX) was measured by the TBARS test (Kim *et al*., 2016). An aliquot of each extract (1 mL, 5 mg/mL) were homogenized with 10 mL of an aqueous pork meat extract (10 %, w/v), and incubated at 37 °C for 8 h in a water bath. After, 0.5 mL of the mixture were mixed with 1 mL of TCA (10 %, w/v) and 1.5 mL TBA solution (0.02 M), placed in a water bath for 20 min at 97 °C, and then cooled. The absorbance was measured at 531 nm, and results were expressed as mg of malondialdehyde per kg of meat (mg MDA/kg).

Statistical analysis

Results obtained from physicochemical, WHO and OHC, antioxidant, phytochemical content, antiradical, reducing power, and lipid oxidation inhibition tests, were expressed as mean ± standard deviation. These data from the three independent trials were subjected to one-way analysis of variance (ANOVA), while Tukey tests were conducted for means comparison at $p < 0.05$. In addition, results of qualitative phytochemical screening, the rest of the test of techno-functional properties and antioxidant activity were expressed as follows: (+), present slight functionality; (++), present moderate functionality; (+++), present high functionality; (-), absent.

RESULTS AND DISCUSSION
Physicochemical properties

Table 1 reports the physicochemical properties of the coffee residues compared to the commercial standard. The results show that coffee silverskin powder and flake showed lower pH values than texturized soy ($p < 0.05$). Also, results of color parameters write down that coffee silverskin powder and flakes showed lower L*, b*, C* and h* values than texturized soy, as well as the highest a* values ($p < 0.05$), while coffee silverskin powder showed the lowest L* values ($p < 0.05$). In addition, the color data also includes information related to the RGB and Hex color of soybeans and the silverskin of coffee in flakes and flour, which according to these the color name is light brown, roman coffee or brown bear, and deep coffee or bole, respectively.

A recent work proposed coffee silverskin powder derived from a mixture of five Arabicas and five Robusta varieties as a potential food-safe ingredient, thus, measuring physicochemical parameters like pH (5.34) and color (L* = 20.8, a* = 4.27, b* = 13.4, C* = 14.2). They concluded that pH values could be associated with phenolic components. At the same time, the color depends on the interaction of constitutive components (polyphenols, melanoidins, among others), protein degradation, and Maillard reactions by the roasting process (Martuscelli *et al*., 2021b). Another study showed that a reduction of particle size in coffee beans increases the sensory acidity in the beverage, which denotes in the extractable compounds (Getaneh *et al*., 2020).

In contrast with our study, a decrease was reported for pH values of coffee parchment residue (*C. arabica*) by effect of the milling procedure, which was associated with the bioavailability of certain phytochemicals such as phenolic acids (Benitez *et al*., 2019). It is important to know pH values of natural ingredients because this allows knowing the type of food matrix into which they could be incorporated without affecting their functional properties (López-Marcos *et al*., 2015; Benitez *et al*., 2019). In addition, color also plays a key role in the perception, acquisition, and consumption of food. Therefore, knowing and measuring this sensory attribute is crucial for chefs, food bloggers, packaging designers, industrial food processors, among others (Spence, 2018). In agreement, it has been proven that a reduction in particle size x time does not affect a* values (Mugabi, 2021). While a reduction in particle size of various powders rich in fiber reduce L* values, which show that samples became darker (Liu *et al*., 2016).

Techno-functional properties

According to the *Codex Alimentarius* (1995), food additives are employed for different purposes, such as sweeteners, flavor enhancers, and colorants, as well as pH regulators and bind food components. In this context, Table 2 reports the techno-functional properties of coffee residues compared to the commercial standard. The results say that coffee silverskin flakes showed the highest WHC and OHC compared to coffee

Table 1. Physicochemical properties of coffee silverskin.
Tabla 1. Propiedades fisicoquímicas de la piel plateada de café.

Item	Soy	Coffee residue	
		Flake	**Powder**
pH values	6.43 ± 0.03[c]	6.09 ± 0.02[a]	6.30 ± 0.01[b]
Color coordinates			
L* (lightness)	72.82 ± 0.03[c]	40.27 ± 1.22[b]	35.94 ± 1.92[a]
a* (redness)	5.47 ± 0.05[a]	7.04 ± 0.41[b]	7.57 ± 0.26[b]
b* (yellowness)	27.43 ± 0.06[b]	18.04 ± 0.70[a]	18.78 ± 0.67[a]
C* (Chroma)	27.92 ± 0.02[b]	19.36 ± 0.79[a]	20.25 ± 0.70[a]
h* (hue angle)	79.13 ± 0.10[c]	60.68 ± 0.63[a]	68.06 ± 0.46[b]
RGB			
Hex color	#CEAE81	#745A42	#6A4F37
Color name	Light brown	Roman coffee or brown bear	Deep coffee or bole

Values expressed as mean ± standard deviation of at least three independent experiments (n = 9). Different superscripts (a-c) between the same row differ significantly ($p < 0.05$).

Table 2. Techno-functional properties of coffee silverskin.
Tabla 2. Propiedades tecno-funcionales de la piel plateada de café.

Item	Soy	Coffee residue	
		Flake	Powder
WHC (%)	49.75 ± 1.05[b]	53.75 ± 1.24[c]	29.09 ± 0.03[a]
OHC (%)	15.79 ± 0.34[a]	52.90 ± 1.67[c]	36.28 ± 1.13[b]
SC	+	+	+
FC	+	+	+
FS	+	+	+
EC	+++	-	-
ES	+++	-	-
GC			
0%	-	-	-
2.5%	-	-	-
5%	++	-	-
10%	+++	-	-
15%	+++	-	-
20%	+++	-	-

Values expressed as mean ± standard deviation of at least three independent experiments (n=9). Different superscripts (a-c) between the same row differ significantly (p < 0.05).

WHC, water-holding capacity; OHC, oil-holding capacity; SC, swelling capacity; FC, foaming capacity; EC, emulsion capacity; ES, emulsion stability; GC, gelling capacity. (+), present slight functionality; (++), present moderate functionality; (+++), present high functionality; (-), absent.

silverskin powder and texturized soy. The WHC of coffee residues depends on the polysaccharides content in coffee residues. A reduction of these components during processing could affect WHC due to a lack of site interactions for water retention. This parameter is desirable in meat products like sausages because these residues can absorb water without dissolving proteins. While OHC of coffee residues depends on the surface availability of hydrophobic non-polar chains, such as dietary components or amino acids, which bind the hydrocarbon side chain of oil. This parameter is related to the physical entrapment of oil and food stabilization, which could function as a flavoring retainer (Benitez *et al*., 2019).

Further, all samples exert slight SC, FC, and FS, without effect of milling process. While no EC, ES, and GC were shown in coffee silverskin powder, they were the highest in texturized soy. In agreement, it has been reported that a mixture of coffee silverskin powder (*C. arabica* and *C. robusta*) exerts WHC and OHC (Martuscelli *et al*., 2021b). Also, previous work revealed that coffee silverskin and spent coffee grounds powders (a mixture of *C. arabica* and *C. robusta*) showed approximately 50 % of WHC and OHC. In disagree with our study, both residues showed EC and ES (Ballesteros *et al*., 2014). Additionally, it has been reported a decrease of WHC values of coffee parchment residue (*C. arabica*) by effect of the milling procedure. In contrast with our study, OHC values were unaffected (Benitez *et al*., 2019).

WHC and OHC are important parameters that express the potential of an ingredient to retain water and oil in a food matrix (López-Marcos *et al*., 2015; Martuscelli *et al*., 2021b). SC is the capacity of an ingredient to increase the surface volume in the presence of excess water (Benitez *et al*., 2019), while FC and FS express the capacity of an ingredient to increase the interfacial area and the effectiveness to maintain the foam stable after the time (Haque *et al*., 2020). EC express the capacity of an ingredient to form a homogeneous dispersion of two immiscible liquids or emulsion, while ES describes the effectiveness of an ingredient in maintaining a stable emulsion after the thermal effect (Ballesteros *et al*., 2014; López-Marcos *et al*., 2015; Martuscelli *et al*., 2021b).

Antioxidant properties

Moreover, phytochemicals (from the Greek word Phyto, meaning plant) are bioactive chemical compounds found in different amounts in plant parts (fruits, seeds, flowers, leaves, stems, and roots), which depends on plant species, growing, and processing conditions. Also, it is well known that phytochemicals improve the protection to plant cells against environmental hazards like pollution, stress, UV-exposure, and pathogenic damage. Although these compounds are not essential nutrients for human body, it has been reported that they exert several biological functions of interest for the food industry (Saxena *et al*., 2013). Table 3 reports the phytochemical content of the coffee residues compared to the commercial standard. The results of the qualitative phytochemical profile showed that phenols and

Table 3. Phytochemical content of coffee silverskin.
Tabla 3. Contenido de fitoquímicos de la piel plateada de café.

Qualitative profile	Soy	Coffee residue	
		Flake	Powder
Phenols	+	++	+++
Flavonoids	+	++	++
Caffeoylquinic acid	-	++	+++
Alkaloids	-	+	++
Terpenoids	-	-	-
Steroids	-	-	-
Saponins	-	-	-
Quantitative profile	**Soy**	**Coffee residue**	
		Flake	Powder
TPC (mg GAE/g)	115.07 ± 3.51[a]	263.31 ± 2.90[b]	268.17 ± 2.39[b]
TFC (mg QE/g)	55.08 ± 2.08[a]	64.42 ± 2.60[b]	64.39 ± 2.36[b]
CAC (mg CAE/g)	25.47 ± 0.51[a]	74.48 ± 1.90[b]	82.59 ± 1.78[c]

(+), slightly present; (++), moderately present; (+++), highly present; (-), absent.

Values expressed as mean ± standard deviation of at least three independent experiments (n = 9). TPC, total phenolic content; TFC, total flavonoid content; CAC, caffeoylquinic acid content. Different superscripts (a-c) between the same row differ significantly (p < 0.05).

caffeoylquinic acid were highly present in coffee silverskin powder, while these compounds were not detected in texturized soy. Flavonoids were moderately present in both coffee residues, and coffee silverskin flakes showed moderately presence of alkaloids. In addition, terpenoids, steroids, and saponins were not detected in all samples. Regarding the quantitative profile, both coffee residues showed high (p < 0.05) TPC and TFC values (>200 mg GAE and 60 mg QE/g, respectively) than texturized soy, while coffee silverskin powder showed high CAC (approx. 80 mg CAE/g) than coffee silverskin flakes and texturized soy (p < 0.05).

It has been evidenced that soy is an important source of nutrients like proteins, essential amino acids, and carbohydrates, although oligosaccharides, stachyose, and raffinose, trypsin inhibitors, lectins, gliadin, phytates, mycotoxins, and saponins have been considered antinutritional substances in soy, which are inactivated by adequate thermal processing (Banaszkiewicz, 2011). In agreement, a preliminary phytochemical screening showed the presence of alkaloids and flavonoids in an ethanol extract obtained from coffee silverskin powder (*C. arabica*). In contrast, saponins and terpenoids were also identified in this extract (Al-Yousef *et al*., 2017). In addition, a quantitative screening demonstrated the presence of phenolic, flavonoids, and caffeoylquinic acid in extracts obtained from coffee residues (*C. arabica*), including coffee silverskin and spent coffee grounds (Zengin *et al*., 2020). Although, phytochemicals are present in diverse types of waste from the coffee processing industry (Ballesteros *et al*., 2014; Zengin *et al*., 2020), it has been also demonstrated that a reduction of the particle size improves chemical compound recovery. For example, an increase in carbohydrates, phenolic, and flavonoid content of coffee parchment residue (*C. arabica*) was reported after the milling procedure (Benitez *et al*., 2019).

Table 4. Antioxidant properties of coffee silverskin.
Tabla 4. Propiedades antioxidantes de la piel plateada de café.

Test	Ascorbic acid	Coffee residue	
		Flake	Powder
FRSA (% DPPH· inhibition)	96.10 ± 0.15[b]	39.42 ± 2.12[a]	38.21 ± 3.39[a]
RCSA (% ABTS·+ inhibition)	90.25 ± 1.52[b]	80.22 ± 0.47[a]	87.89 ± 2.41[a]
RPA (Abs at 700 nm)	1.22 ± 0.11[c]	0.90 ± 0.05[a]	115.07 ± 3.51[b]
FRAP (mg Fe²⁺/g)	2.90 ± 0.15[c]	1.55 ± 0.23[a]	2.65 ± 0.13[b]
TBARS (mg MDA/kg)	0.20 ± 0.01[b]	0.19 ± 0.02[b]	0.09 ± 0.01[a]

Values expressed as mean ± standard deviation of at least three independent experiments n = 9). FRSA, free-radical scavenging activity; RCSA, radical-cation scavenging activity; RPA, reducing power ability; FRAP, ferric-reducing antioxidant power; TBARS, thiobarbituric acid reactive substances. Different superscripts (a-c) between the same row differ significantly (p < 0.05).

The *Codex Alimentarius* (1995) also indicate that food additives are used with preservative purposes, for example, to function as an antimicrobial agent and improve antioxidant effect against the oxidation process. In this regard, Table 4 shows the antioxidant properties of the coffee residues compared with a commercial antioxidant standard (ascorbic acid, Asc), and the results indicate that Asc showed higher FRSA (> 90 % of inhibition) than coffee silverskin powder and flakes (approx. 40 % of inhibition for both), while, Asc and coffee silverskin powder showed higher RCSA activity (approx. 90 % of inhibition for both) than coffee silverskin flakes (< 85 % of inhibition) (p < 0.05), which indicate a positive effect of milling procedure. Concerning reducing power, RPA and FRAP values were presented in the order Asc > coffee silverskin powder > coffee silverskin flakes (p < 0.05). In addition, coffee silverskin powder showed the lowest TBARS values (< 0.1 mg MDA/kg), which indicates a positive effect of the milling procedure.

In agreement, the antiradical (FRSA and RCSA) and the reducing power activity (FRAP) of extracts obtained from coffee residues (*C. arabica*) like silverskin and spent coffee grounds has been demonstrated (Zengin *et al*., 2020). A previous study indicates that coffee silverskin powders and spent coffee grounds (mixture of *C. arabica* and *C. robusta*) exert antiradical FRSA and FRAP potential (Ballesteros *et al*., 2014). Additionally, an increase of RCSA of coffee parchment residue (*C. arabica*) was observed after the milling procedure (Benitez *et al*., 2019). The FRSA (DPPH· assay) are methods that involve the hydrogen atom transfer as reaction mechanisms [free radical (X·) + Antioxidant compound (OH) → Neutralized radical (XH + O·)], while the RCSA (ABTS·+ assay), RPA (Prussian-blue) and FRAP methods involve the electron transfer mechanisms [radical cation (X·+) + Antioxidant compound (OH) → Neutralized radical (XH + O·+)] (Berker *et al*., 2010; Echegaray *et al*., 2021). In addition, it has been reported that TBARS method could involve both mechanisms (Velázquez *et al*., 2021).

CONCLUSIONS

Physicochemical results indicated that coffee silverskin flakes and powder showed pH near to neutrality, and the color was Roman coffee and Deep coffee, respectively, which indicates that the milling process changed this parameter. In addition, techno-functional determinations showed that coffee silverskin flakes showed the highest WHC and OHC, while both coffee residues exert slight SC, FC, and FS, without the effect of the milling process. However, both residues not showed EC, ES, and GC. Furthermore, phytochemical screening revealed the presence of metabolites in coffee silverskin (powder > flakes), like phenols, flavonoids, caffeoylquinic acid, and alkaloids, while terpenoids, steroids, and saponins were not detected. Regarding antioxidant activity, coffee silverskin powder showed high FRSA, RCSA, RPA, and FRAP values, as well as the lowest TBARS values, which indicate that the milling process increases antioxidant properties. In conclusion, coffee silverskin can be proposed as a functional ingredient for the food industry.

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REFERENCES

Al-Yousef, H.M., Sawab, A. and Alruhimi, M. 2017. Pharmacognostic studies on coffee Arabica L. husks: a brilliant source of antioxidant agents. European Journal of Pharmaceutical and Medical Research. 4: 86-92.

Ainsworth, E.A. and Gillespie, K.M. 2007. Estimation of total phenolic content and other oxidation substrates in plant tissues using Folin–Ciocalteu reagent. Nature Protocols. 2(4): 875-877. https://doi.org/10.1038/nprot.2007.102

AOAC. 2020. AOAC 943.02, pH of flour, potentiometric method. Association of Official Analytical Chemists. [Consulted 27 April 2022]. Available in: http://www.aoacofficialmethod.org/index.php?main_page=product_info&products_id=937

Balestra, F. and Petracci, M. 2019. Technofunctional ingredients for meat products: Current challenges. In Sustainable meat production and processing. C.M. Galanakis (ed.), pp 45-68. Academic Press. Elsevier. Inc., New York.

Ballesteros, L.F., Teixeira, J.A. and Mussatto, S.I. 2014. Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. Food and Bioprocess Technology. 7(12): 3493-3503. https://doi.org/10.1007/s11947-014-1349-z

Banaszkiewicz, T. 2011. Nutritional value of soybean Meal. In: Soybean and Nutrition. Hany El-Shemy (Ed.), pp 1-23. IntechOpen, Croatia.

Benitez, V., Rebollo-Hernanz, M., Hernanz, S., Chantres, S., Aguilera, Y. and Martin-Cabrejas, M.A. 2019. Coffee parchment as a new dietary fiber ingredient: Functional and physiological characterization. Food Research International. 122: 105-113. https://doi.org/10.1016/j.foodres.2019.04.002

Benzie, I.F. and Strain, J.J. 1999. Ferric reducing antioxidant power assay: Direct measurement of total antioxidant activity of biological fluids and modified version for simultaneous measurement of total antioxidant power and ascorbic acid concentration. Method Enzymology. 299: 15-27. https://doi.org/10.1016/S0076-6879(99)99005-5

Berker, K.I., Güçlü, K., Demirata, B. and Apak, R. 2010. A novel antioxidant assay of ferric reducing capacity measurement using ferrozine as the colour forming complexation reagent. Analytical Methods. 2: 1770-1778. https://doi.org/10.1039/C0AY00245C

CDRSSA. 2019. Evolución de la producción y consumo de alimentos en México (2000-2018). [Consulted 27 April 2022]. Available in: http://www.cedrssa.gob.mx/files/b/13/13MSMM-F_EvolucionProd-Cons.pdf

Codex Alimentarius. 1995. Norma general para los aditivos alimentarios [Consulted 27 April 2022]. Available in: http://www.fao.org/gsfaonline/docs/CXS_192s.pdf

COMECARNE. 2021. Consejo Mexicano de la Carne, compendio estadístico. [Consulted 27 April 2022]. Available in: https://comecarne.us2.list-manage.com/track/click?u=22650f36f23cf8841c5225d13&id=85af93fc6f&e=834f0eecf8

Domínguez, R., Pateiro, M., Gagaoua, M., Barba, F.J., Zhang, W. and Lorenzo, J.M. 2019. A comprehensive review on lipid oxidation in meat and meat products. Antioxidants. 8: 429. https://doi.org/10.3390/antiox8100429

Echegaray, N., Pateiro, M., Munekata, P.E., Lorenzo, J.M., Chabani, Z., Farag, M.A. and Domínguez, R. 2021. Measurement of Antioxidant Capacity of meat and meat products: methods and applications. Molecules. 26(13): 3880. https://doi.org/10.3390/molecules26133880

Getaneh, E., Fanta, S. W. and Satheesh, N. (2020). Effect of broken coffee beans particle size, roasting temperature, and roasting time on quality of coffee beverage. Journal of Food Quality. Article ID 8871577: 1-15. https://doi.org/10.1155/2020/8871577

Griffiths, D.W., Bain, H. and Dale, M.F.B. 1992. Development of a rapid colorimetric method for the determination of chlorogenic acid in freeze-dried potato tubers. Journal of the Science of Food and Agriculture. 58(1): 41-48. https://doi.org/10.1002/jsfa.2740580108

Haque, M.A., Akter, F., Rahman, H. and Baqui, M.A. 2020. Jackfruit seeds protein isolate by spray drying method: the functional and physicochemical characteristics. Food and Nutrition Sciences. 11: 355-374. https://doi.org/10.4236/fns.2020.115026

Jully, K.M.M., Toto, C.S. and Were, L. 2016. Antioxidant effect of spent, ground, and lyophilized brew from roasted coffee in frozen cooked pork patties. LWT-Food Science and Technology. 66: 244-251. https://doi.org/10.1016/j.lwt.2015.10.046

Kim, J.H., Ahn, D.U., Eun, J.B. and Moon, S.H. 2016. Antioxidant effect of extracts from the coffee residue in raw and cooked meat. Antioxidants. 5: 21. https://dx.doi.org/10.3390%2Fantiox5030021

Liu, T., Hou, G. G., Lee, B., Marquart, L. and Dubat, A. 2016. Effects of particle size on the quality attributes of reconstituted whole-wheat flour and tortillas made from it. Journal of Cereal Science. 71: 145-152. https://doi.org/10.1016/j.jcs.2016.08.013

López-Marcos, M.C., Bailina, C., Viuda-Martos, M., Pérez-Alvarez, J.A. and Fernández-López, J. 2015. Properties of dietary fibers from agroindustrial coproducts as source for fiber-enriched foods. Food and Bioprocess Technology. 8: 2400-2408. https://doi.org/10.1007/s11947-015-1591-z

Martuscelli, M., Esposito, L. and Mastrocola, D. 2021a. The role of coffee silverskin against oxidative phenomena in newly formulated chicken meat burgers after cooking. Foods. 10: 1833. https://doi.org/10.3390/foods10081833

Martuscelli, M., Esposito, L., Di Mattia, C. D., Ricci, A. and Mastrocola, D. 2021b. Characterization of coffee silverskin as potential food-safe ingredient. Foods. 10(6): 1367. https://doi.org/10.3390/foods10061367

Molyneux, P. 2004. The use of the stable free radical diphenyl picrylhydrazyl (DPPH) for estimating antioxidant activity. Songklanakarin Journal of Science and Technology. 26: 211-219.

Mugabi, R. 2021. Effect of particle size on color of ground coffee. Asian Food Science Journal. 20(10): 137-144.

Oswell, N.J., Thippareddi, H. and Pegg, R.B. 2018. Practical use of natural antioxidants in meat products in the US: A review. Meat Science. 145: 469-479. https://doi.org/10.1016/j.meatsci.2018.07.020

Popova, M., Bankova, V., Butovska, D., Petkov, V., Nikolova-Damyanova, B., Sabatini, A. G., Marcazzan, G.L. and Bogdanov, S. 2004. Validated methods for the quantification

of biologically active constituents of poplar type propolis. Phytochemical Analysis: An International Journal of Plant Chemical and Biochemical Techniques. 15(4): 235-240. https://doi.org/10.1002/pca.777

Re, R., Pellegrini, N., Proteggente, A., Pannala, A., Yang, M. and Rice-Evans, C. 1999. Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Radical Biology and Medicine. 26: 1231-1237. https://doi.org/10.1016/S0891-5849(98)00315-3

Robertson, A.R., Lozano, R.D., Alman, D.H., Orchard, S.E., Keitch, J.A., Connely, R., Graham, L.A., Acree, W.L., John, R.S., Hoban, R.F., et al. 1977. CIE Recommendations on uniform color spaces, color-difference equations, and metric color terms. Color Research and Application. 2: 5-6.

Samejo, M.Q., Memon, S., Bhanger, M.I. and Khan, K.M. 2011. Preliminary phytochemicals screening of *Calligonum polygonoides* Linn. Journal of Pharmacy Research. 4: 4402-4403.

Samejo, M.Q., Sumbul, A., Shah, S., Memon, S.B. and Chundrigar, S. 2013. Phytochemical screening of *Tamarix dioica* Roxb. ex Roch. Journal of Pharmacy Research. 7: 181-183. http://dx.doi.org/10.1016/j.jopr.2013.02.017

Saxena, M., Saxena, J., Nema, R., Singh, D. and Gupta, A. 2013. Phytochemistry of medicinal plants. Journal of Pharmacognosy and Phytochemistry. 1: 168-182.

Spence, C. 2018. Background colour & its impact on food perception & behaviour. Food Quality and Preference. 68: 156-166. https://doi.org/10.1016/j.foodqual.2018.02.012

USDA. 2021. US Department of Agriculture, additives in meat and poultry products. [Consulted 27 April 2022]. Available in: https://www.fsis.usda.gov/food-safety/safe-food-handling-and-preparation/food-safety-basics/additives-meat-and-poultry

Velázquez, L., Quiñones, J., Díaz, R., Pateiro, M., Lorenzo, J.M. and Sepúlveda, N. 2021. Natural antioxidants from endemic leaves in the elaboration of processed meat products: current status. Antioxidants. 10: 1396. https://doi.org/10.3390/antiox10091396

Zengin, G., Sinan, K.I., Mahomoodally, M.F., Angeloni, S., Mustafa, A.M., Vittori, S., Maggi, F. and Caprioli, G. 2020. Chemical composition, antioxidant and enzyme inhibitory properties of different extracts obtained from spent coffee ground and coffee silverskin. Foods. 9(6): 713. https://doi.org/10.3390/foods9060713.