Food Engineering Reviews
https://doi.org/10.1007/s12393-020-09259-4

Iron-Fortified Pineapple Chips Produced Using Microencapsulation, Ethanol, Ultrasound and Convective Drying

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Received: 16 March 2020 / Accepted: 2 October 2020
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Abstract

The present work proposes using microencapsulation, ethanol, ultrasound and convective drying to obtain iron fortified pineapple chips. Iron microparticles were produced by ferrous sulphate encapsulation with maltodextrin by spray drying. As a hydrophilic material, microparticles were dispersed in ethanol to be incorporated into the pineapple tissue, with or without the application of ultrasound. Then, the effect of different pre-treatment times with ethanol and ethanol + ultrasound was evaluated on pineapple drying. Finally, the residue of ethanol was evaluated in the final products. Pre-treatment with ethanol and ethanol + ultrasound allowed to increase significantly the iron content of pineapple chips (up to 1000% in comparison with control). In addition, the drying time decreased from 35.4 to 51.9% with the utilization of ethanol and ultrasound. Pre-treatment for 7.5 min allowed to reduce the drying time and to achieve negligible residual ethanol in the sample. The results demonstrated that the combination of the proposed technologies can be used to obtain pineapple chips enriched in iron, with reduced time of drying and a negligible residue of ethanol.

Keywords Air drying · Nutritional value · Emerging technologies · Dehydration · Dried fruits

Introduction

There is a rising concern about the nutritional aspects of food products, including deficiencies in world population and how to improve the nutritional quality of food during processing. The most prevalent nutritional deficiency in the world is in relation of iron, which is the main cause of anaemia [6]. According to World Health Organization, 24.8% of the world population (~ 1.62 billion people) are affected by anaemia, which is an important percentage [11]. A diet containing foods naturally rich in iron is necessary to supply this deficiency, or, alternatively, iron can be obtained by supplements or enriched foods.

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However, when iron is directly incorporated in food products, it can be oxidized and promote undesirable organoleptic alterations, such as in colour, odour and flavour [6]. Microencapsulation, thus, is an interesting alternative for this purpose. However, the most common products enriched with iron are formulated products, such as cereal flours, breakfast cereals, cooking oils and salt, being difficult the incorporation into structured food matrix—such as vegetable tissues. For instance, [6] [10] obtained high bioavailability by enriching bread and milk with iron microparticles. However, the possibility of expanding the available enriched products is interesting to achieve more consumers and different ways of consuming.

Drying can be an interesting approach to obtain stable, convenient and nutritional food products, such as fruit chips [2, 14, 25, 26]. However, drying is a long and energy consuming process. Therefore, in addition to improve the final product, there is constantly searching for technologies that allows enhanced processes. With this purpose, different pre-treatments have been studied to improve drying. Recently, pre-treatments with ethanol and emerging technologies such ultrasound, pulsed electric fields and/or high-pressure processing were employed as pre-treatments to faster food drying, with positive impact on product quality [12].

Published online: 31 October 2020

Ethanol is an easy-to-apply pre-treatment, which promotes drying intensification caused by structural changes in the product, partial osmotic dehydration and the Marangoni effect. In fact, the pre-treatments with ethanol and ultrasound can be an interesting option to incorporate iron into food products. [25] incorporated iron microparticles into pumpkin by using ethanol and ultrasound. Although good levels of iron content were obtained, some questions were not evaluated, such as the residue of ethanol or the impact on drying kinetics. Further, although pumpkin is a popular vegetable, it would be important to develop different products, prone to be direct consumed as chips. Fruits are perfect for that (and pineapple presents a complex structure in relation to the high homogeneous pumpkin pulp, which in parts justify its selection in the present work, as described as follows).

Finally, notwithstanding the crescent interest in ethanol as a pre-treatment to drying [27] [28] [25] [26] [40] [23] [43], the residue of ethanol in the final product was still not demonstrated—which is an important information in fortified foods. [3] [4] identified qualitatively the volatile compounds of pineapple dried in atmosphere modified with ethanol. In their study, they obtained dried pineapple with high amount of residual ethanol (although they also presented *in natura* samples with huge variability). The condensation of the ethanol present in the air, on the sample surface, was a possible explanation for these results. However, further evaluation is needed, especially considering the pre-treatment by immersion in this compound—as conducted in the present work.

Therefore, the present work studied the obtention of a dried pineapple chip enriched with iron microparticles. For this purpose, the effects of pre-treatments with ethanol and ultrasound were studied regarding to the iron content of pineapple chips, the kinetics of convective drying and the residual ethanol in the final product.

Material and methods

Raw material and sample preparation

The pineapples (*Ananas comosus* cv. Perola) were acquired in a local market of Piracicaba, SP, Brazil. The fruits were chosen by the colour of the peel (green with few yellow points), presenting moisture content about 86.4% (w.b.). The fruits were cut in short cylinders with 1.5 cm of diameter and 1.0 cm of height Fig. 1.

Iron microparticle production and characterization

Iron microparticles were produced by spray drying using ferrous sulphate as active and maltodextrin as wall materials, as described in [25]

Maltodextrin (0.23 g/g dry matter) and ferrous sulphate (Fe_2SO_4, 0.07 g/g dry matter) were dissolved in distilled water with a magnetic stirrer, and the solution was dried in a spray dryer (Mini Spray Dryer Labplant UK Ltd, Model SD 06, UK). The drying was carried with an atomizer nozzle of 1 mm diameter, atomization pressure of 4 bar and 150 ± 3 °C inlet temperature. The feed rate up to 35.3 mL/min was used to obtain an outlet temperature of 80 ± 3 °C.

The particle size distribution (PSD) was measured using a laser analyser equipment (Horiba, Partica LA-950V2 Laser Particle Size Analyser, Japan), using ethanol (99.5%) to disperse the microparticles. The obtained data were evaluated using the software LA-950 for Windows (HORIBA, Japan).

The microparticle morphology was evaluated by scanning electronic microscopy (FEI Company, Model Inspect F50, Japan) operating at an acceleration voltage of 2.0 kV and available at LNNano, Campinas, Brazil. To prepare the samples, a double sticky carbon tape was fixed on a circular aluminium stub, and the microparticles

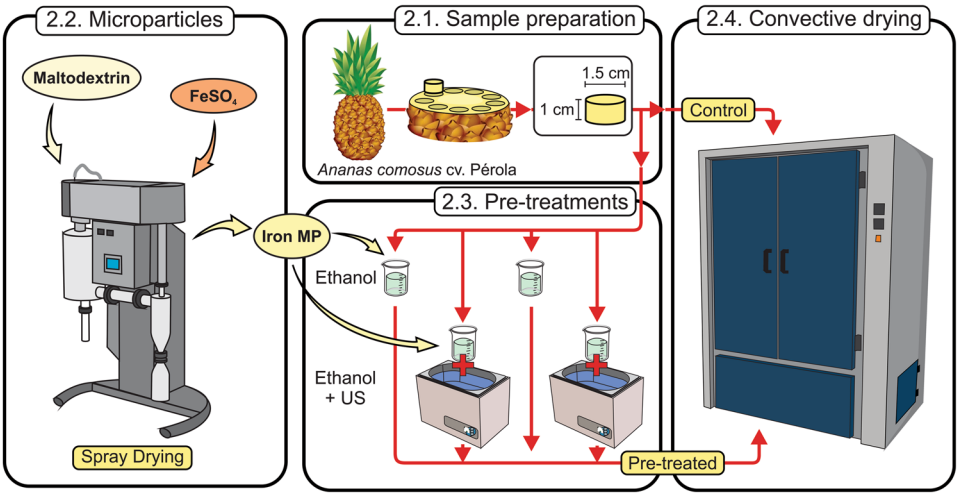

Fig. 1 Experimental setup for treatments with incorporation of microencapsulated iron particles, ethanol, ultrasound and convective drying of pineapple pulp

were sprinkled on the tape. A brush was used to ensure a uniform layer of powder particles. The stubs were then coated with gold (~ 4 nm) and evaluated in the microscope using an Everhart-Thornley Detector (ETD) for secondary electrons.

Powdered microparticles presented an iron content of 4.35 ± 0.20 g/100 g (measured according to methodology described in "Iron Quantification"), ranging from ~ 0.5 to ~ 100 µm, whose distribution is presented in Fig. 2. Their morphology presents full and deflated balls, with smooth and wrinkled surfaces, which is consistent with particles obtained through spray-drying Fig. 2.

Pre-treatments and iron incorporation

Once both maltodextrin and ferrous sulphate are hydrophilic, water cannot be used as the medium to incorporate this nutrient into the food matrix (otherwise, the microparticles would demolish, being solubilized in water). Therefore, ethanol was used to this. In fact, ethanol has been proposed to enhance drying process and product properties [12, 23, 24, 30], being this an extra advantage of the present proposal.

The pre-treatments were carried out by complete immersion of samples in ethanol at 25.0 ± 1.0 °C, with and without the microparticles and with and without the ultrasound technology Table 1,Fig. 1. The control treatment consisted

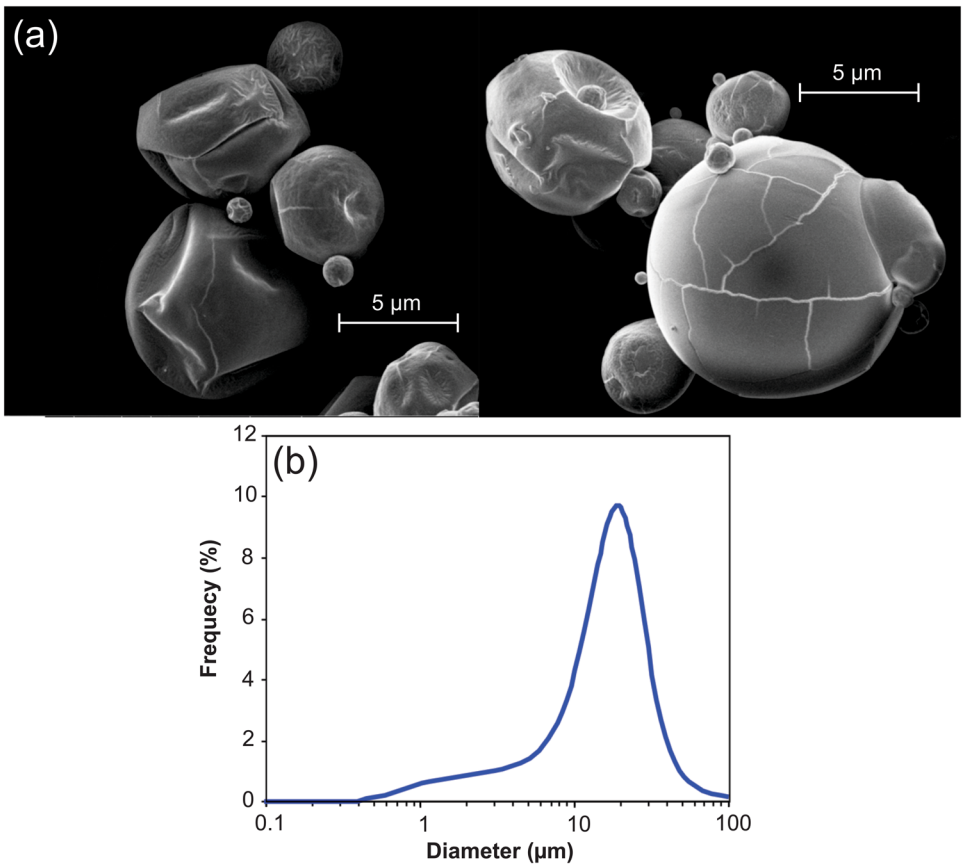

Fig. 2 **(a)** Iron microparticles morphology obtained by scanning electronic microscopy and **(b)** their particle size distribution

Table 1 Codes of pre-treatments applied on pineapple before drying

Treatment length	No treatment (control)	Treatments			
		Ethanol	Ethanol + ultrasound	Ethanol + iron microparticles	Ethanol + iron microparticles + ultrasound
0 min	CT	-	-	-	-
7.5 min	-	Et7.5	EtUS7.5	EtFe7.5	EtFeUS7.5
15 min	-	Et15	EtUS15	EtFe15	EtFeUS15
30 min	-	Et30	EtUS30	EtFe30	EtFeUS30

in the cut pineapple, without further operations, which was directly dried.

Approximately 100 g of pineapple cylinders were immersed in a beaker containing ethanol 99% (v/v), for 7.5, 15 and 30 min. The incorporation of iron was carried out adding 0.25 g of microencapsulated iron microparticles into 500 mL of ethanol. The treatments with ultrasound application were made placing the beaker into an ultrasonic bath (25 kHz, real volumetric power, determined by the calorimetric method, was 14.9 W/L, Unique, USC1450, Brazil).

After the treatments, the samples were removed from the ethanol/suspension, rinsed with 500 mL of ethanol to remove the excess of microparticles on the surface and gently dried using absorbing paper. After removing the pineapple samples from the solution, the electric conductivity of the solution was measured using a conductivimeter (Digimed, DM-3P, Brazil).

Convective drying

Drying experiments were carried out in an oven (Marconi, MA 035, Brazil) with circulation of air (1 ± 0.1 m/s) at 50 °C Fig. 1. The samples were placed in stainless steel grids and dried until reach their equilibrium moisture. Their mass over the time was recorded to evaluate the drying kinetics.

Experimental data were modelled with the Page model (Eq. 1 [20], where MR is the moisture ratio (Eq. 2), t is the time of drying (in minutes), X is the moisture (d.b.) at the time t, X_0 is the initial moisture (d.b.), X_{eq} is the equilibrium moisture (d.b.), k and n are the Page's model parameters.

During ethanol treatments, the samples lose water and solids and gain ethanol. Therefore, according to [24], the sample "moisture" after ethanol treatment includes both the two volatile liquids (i.e. the remaining water and the gained ethanol).

Although the Page model is an empirical model, a phenomenological evaluation was proposed to interpret it [32]. In this interpretation, k represents the drying rate (min^{-n}), while n (dimensionless) represents the mass transfer behaviour—which can be diffusional ($n = 1$), sub-diffusional ($n < 1$) or super-diffusional ($n > 1$).

$$MR = \exp(-kt^n) \tag{1}$$

$$MR = \frac{X - X_{eq}}{X_o - X_{eq}} \tag{2}$$

The parameters of Page model were obtained by nonlinear regression with the software OriginPro 8.1 (OriginLab Corporation, USA) using the Levenberg-Marquardt algorithm. The interactions were made considering the reduced chi-square as target to be minimized, with tolerance of 1×10^{-9}. For this purpose, the model was adjusted once for all replicates, in order to minimize adjustment errors from each replicate. From the drying curves and the Page model parameters, the required time to pineapple reach 20% moisture (w.b.) was calculated as the "drying time" (as it was described by [42] as the upper limit for guarantee stability of dried fruits).

During the pineapple drying, thermal images were recorded for each sample using an infrared camera (Testo, Testo 865, Germany) with 0.95 of emissivity. The thermal images were analysed using the software IRSoft 4.5 (Testo SE & Co, Germany).

Iron quantification

After drying, the pineapple chips were powdered using a stainless-steel analytical mill (IKA, A11 Basic Analytical Mill, Germany) and sieved (0.5 mm of screen) to obtain a homogenous powder. The iron content was determined by an energy dispersive X-ray fluorescence spectrometer (Shimadzu, EDX-720, Japan), according to the methodology of [21] as in our previous works.

Residue of ethanol in the final product

The residue of ethanol in pineapple chips was measured by headspace-gas chromatography coupled to mass spectrometry (GC-MS) (Shimadzu, GCMS-QP 2010 Plus, Japan).

The dried samples were frozen and milled using a stainless-steel analytical mill (IKA, A11 Basic Analytical Mill, Germany) in the presence of liquid nitrogen to avoid sample heating. An aliquot of 1 g was weighted in a 20-mL vial. Then, 5 mL of NaCl saturated solution (30%, w/v) was added to promote the salting out, and the vial was incubated under agitation at 60 °C for 10 min for the formation of gas phase. GC-MS method conditions are shown in Table 2.

A calibration curve was made measuring ethanol present in the nontreated (CT) dried sample added by known aliquots (1, 2, 3 and 4% v/w) of high purity ethanol (HPLC

Table 2 GC-MS experimental conditions for residual ethanol determination in dried pineapple chips

Gas chromatography		Mass spectrometry	
Column name	RTX-5MS	Ion source temp	250 °C
Column length	30 m	Interface temp	250 °C
Column diameter	0.25 µm	Threshold	1000
Carrier gas	He	Scan time	1.82 min
Column flow	0.99 mL/min	End time	5.0 min
Column oven temp	40 °C	Event time	0.5 min
Injection temp	270 °C	Scan speed	476
Injected volume	250 µL		
Split ratio	50		

analytic standard degree, J.T. Baker Chemical Co.) before incubation.

Experimental design and statistical analysis

All experimental conditions and analysis were conducted at least 3 times. The analysis of variance (ANOVA) was carried out with a significance level of 5%, and Tukey's test was used to determine differences among experimental conditions. Statistical analyses were made using the Minitab 16.1.1 (Minitab Inc., USA).

Results and discussion

Iron incorporation

Figure 3 shows the iron content in the dried pineapple after different pre-treatments using ethanol and ultrasound. Both compounds of iron microparticles (ferrous sulphate and maltodextrin) are water soluble materials, and, therefore, they cannot be placed in water (otherwise, they would solubilize). Consequently, the microparticles were dispersed in ethanol, and this dispersion was incorporated into the pineapple matrix.

The control dried pineapple (CT) presented an iron content of 28.3 ± 10.4 mg/kg (d.b.), which is in accordance with the work of [13], which reported iron content for fresh pineapple of 21.32 mg/kg (d.b.).

Both Et (ethanol) and EtUS (ethanol + ultrasound) pre-treatments were efficient to incorporate iron microparticles into pineapple. Longer pre-treatments resulted in higher iron content ($p < 0.05$), but the ultrasound did not affect significantly the incorporation of Fe. The iron content in pineapple increased 423.5, 771.8 and 1046.4% for the pre-treatment for 7.5, 15 and 30 min in ethanol, respectively, and 572.6, 763.3 and 1157.5% for the pre-treatment for 7.5, 15 and 30 min in ethanol and ultrasound, respectively Fig. 3.

[25] Obtained similar results during the incorporation of iron microparticles in pumpkin during the pre-treatment with ethanol and ethanol + ultrasound for 30 min: ultrasound did not affect the iron incorporation but improved the homogeneity of the added iron microparticles. This behaviour can also be observed in the present work: in pineapple, the pre-treatments applying ultrasound for 15 and 30 min presented smaller errors bars, showing higher homogeneity between the samples Fig. 3. While it was possible to observe particle agglomeration in the ethanol suspension, ultrasound can promote better dispersion of the microparticles in ethanol and also in the sample. Therefore, even if ultrasound did not increase significantly the amount of incorporated iron, from an industrial point of view, this technology would be interesting by improving process and product homogeneity.

Considering the same final moisture content of 20% (w.b.), which represents the product to be eaten, the obtained enriched pineapple chips presented iron content of 11.29, 17.4 and 24.98 mg/100 g for 7.5, 15 and 30 min of pre-treatment, respectively. These values are similar or superior than other food products considered sources of iron, such as chicken liver (34.23 mg/100 g), raw stripped beans (17.69 mg/100 g), spinach (5.3 mg/100 g) and collards greens (4.4 mg/100 g) (TACO, 2011). Additionally, it is important to stand out that these products are usually consumed after some process and with higher moisture contents, which reduce the amount of iron ingestion.

Moreover, some works evaluated iron incorporation in food products[25] evaluated the iron incorporation in dried pumpkin using the same iron microparticles and concentration in solution. They increased the iron content in dried pumpkin to 2186 and 1562%, using pre-treatments for

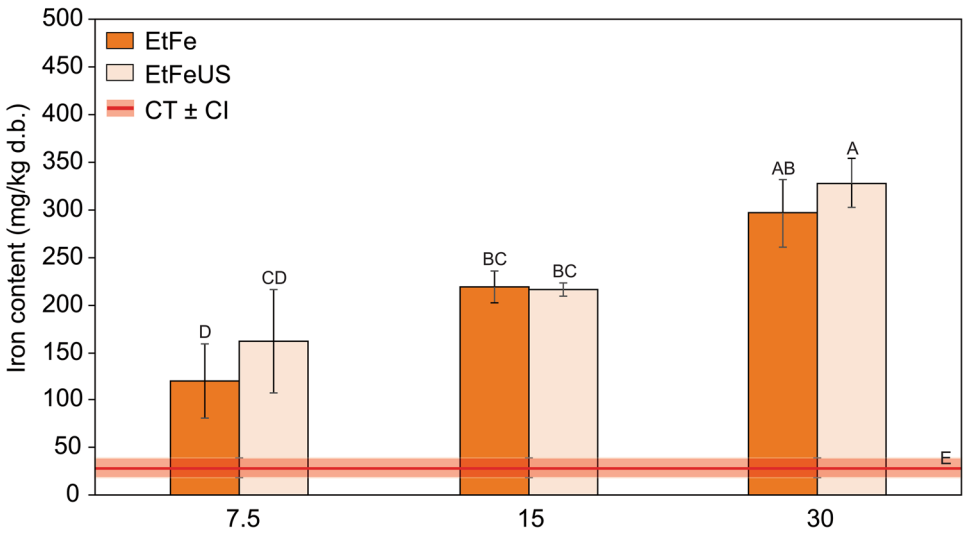

Fig. 3 Iron content of dried pineapple: control and pre-treated samples for 7.5, 15 and 30 min in ethanol or ethanol and ultrasound. *Different letters represent significant difference ($p < 0.05$) among the samples. Columns represent the means and bars represent the standard deviations. The control treatment and its confidence interval (CT ± CI 95%) is represented by the red line and shaded area, respectively

30 min with ethanol and ethanol + ultrasound, which corresponds to iron contents of ~ 490 and 350 mg/kg (d.b.), respectively—similar values of the present work. Miano and Augusto [17] studied the ultrasound assisted hydration as an opportunity of incorporation of iron in beans. In their approach, iron was solubilized directly in water ($FeSO_4$ solution 0.1 g_{iron}/100 $g_{solution}$), and the solution was used to hydrate the grains. The samples treated with ultrasound presented iron content 74 and 2659% higher than the samples treated without ultrasound and control samples, respectively. However, the hydrated beans are high moisture products, with low stability, being their nutritional enrichment an approach interesting for direct consumption or thermal processing—an approach different from the present proposal, where stable chips were produced. [15] also incorporated solubilized iron into potato using ultrasound and vacuum. The application of ultrasound increased 72% the iron content when compared with only vacuum impregnation.

It is difficult to determine the iron requirements because it depends on several factors inherent to populational groups and the intestinal absorption (Blanco-Rojo et al., 2019). Even so, according to World Health Organization (WHO 2014), the total absolute iron requirements range from 0.58 to 3.27 mg/day, depending on gender, age and mean body weight. Additionally, Brazilian National Agency of Sanitary Vigilance [5] considers an iron bioavailability of 10% and then recommends a consumption of 14 mg/day. To fulfil this requirement using the control dried pineapple here presented, it would be necessary to consume proximately 617 g of control chips (with moisture content of 20% (w.b.)), which is an excessive amount to be consumed. This amount can be considerably reduced by incorporating iron microparticles (124.0, 80.5 and 56.10 g, for the treatments for 7.5, 15 and 30 min, respectively), making the enriched pineapple a viable alternative to increase iron intake.

Moreover, more important than the quantity of iron consumed is its bioaccessibility and bioavailability. [36] [34] [6] attributed the ascorbic acid as a component that improves the absorption of iron. Although the ascorbic acid content of pineapple depends on several factors like variety and cultivation conditions, this fruit is considered rich in this compound [13], which can improve the absorption of the incorporated iron. Furthermore, the iron microparticles were produced using maltodextrin as wall material, which are expected to be easily digested in human body and to facilitate the iron absorption. However, it is worth to mention that future evaluations considering the iron bioaccessibility and bioavailability are needed.

Therefore, ethanol and ultrasound treatments were effective to produce chips with enhanced iron content due to its incorporation as microparticles. This reinforces the possibility of obtaining enriched fruit chips by combining four technologies (microencapsulation, ethanol, ultrasound and convective drying). However, it is also necessary to evaluate the drying processes and the residue of ethanol in the obtained chips, as described as follows.

Ethanol and ultrasound improving the drying process

The drying curves of pineapple pulp *in natura* and pretreated with ethanol and ultrasound are shown in Fig. 4. The addition of iron microparticles did not alter the drying curve, and, to simplify visualization, they are not represented in Fig. 4 (although the kinetic parameters are described on Table 3. In all cases, the adjustments of Page model (Eq. 1)

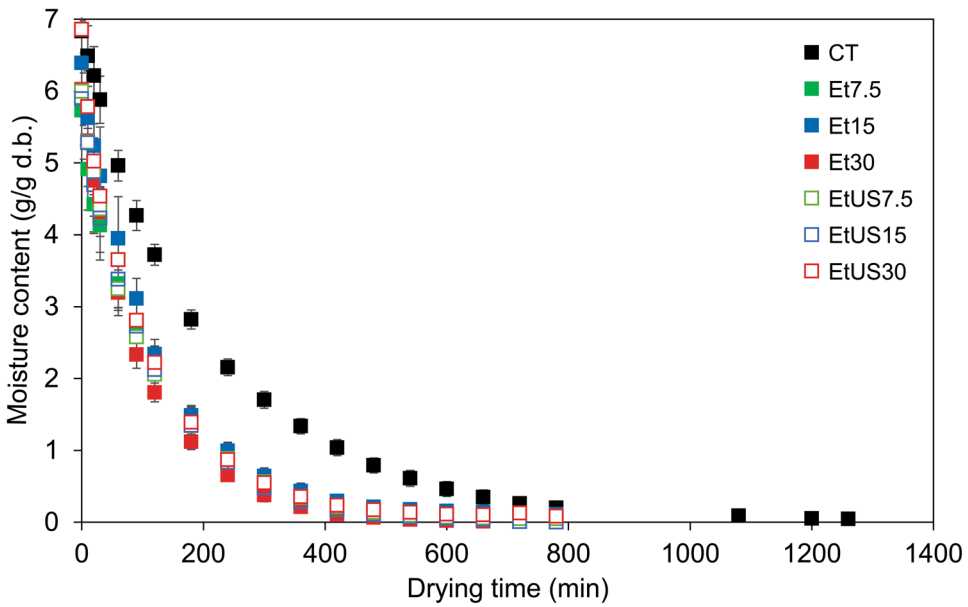

Fig. 4 Drying kinetics of pineapple (mean ± SD) *in natura* and pre-treated samples with ethanol and ultrasound. Dots are the averages values, and vertical bars are the standard deviation

Table 3 Kinetic parameters of adjustment of the Page model to the experimental data of drying of pineapple

Pre-treatment		Page model parameters		Time (min) to reach 20% (w.b.)
		k (min^{-n})	n (-)	
CT		0.0064 ± 0.0009^{D}	0.950 ± 0.025^{A}	723.3 ± 61.4^{A}
Et	7.5 min	0.0182 ± 0.0035^{ABC}	0.847 ± 0.020^{AB}	441.5 ± 39.2^{BC}
	15 min	0.0121 ± 0.0066^{CD}	0.954 ± 0.120^{A}	398.5 ± 31.0^{BC}
	30 min	0.0152 ± 0.0019^{BCD}	0.914 ± 0.030^{AB}	347.7 ± 16.4^{C}
EtUS	7.5 min	0.0156 ± 0.0021^{BCD}	0.890 ± 0.028^{AB}	395.9 ± 53.1^{BC}
	15 min	0.0141 ± 0.0025^{BCD}	0.907 ± 0.027^{AB}	395.1 ± 25.0^{BC}
	30 min	0.0257 ± 0.0074^{ABC}	0.810 ± 0.048^{B}	413.9 ± 23.8^{BC}
EtFe	7.5 min	0.0173 ± 0.0039^{BCD}	0.856 ± 0.039^{AB}	467.5 ± 15.2^{B}
	15 min	0.0175 ± 0.0011^{BCD}	0.879 ± 0.015^{AB}	388.8 ± 32.2^{BC}
	30 min	0.0195 ± 0.0052^{AB}	0.866 ± 0.061^{AB}	373.7 ± 34.4^{BC}
EtFeUS	7.5 min	0.0136 ± 0.0008^{BCD}	0.896 ± 0.011^{AB}	451.5 ± 23.5^{BC}
	15 min	0.0165 ± 0.0010^{ABCD}	0.888 ± 0.021^{AB}	376.9 ± 26.7^{BC}
	30 min	0.0271 ± 0.0020^{A}	0.800 ± 0.015^{B}	401.7 ± 27.0^{BC}

to the experimental data (Table 3) presented good fitness, with R^2 higher than 0.99.

Control (CT) pineapple samples took about 12 h to reach moisture content of 0.2 g/g (wet basis, which is equivalent to 0.25 g/g in dry basis), while, in the treated samples, this time was reduced to 5.8–7.8 h, which represents a reduction from 35.4 to 51.9% of the drying time Fig. 5. [9] dried pineapple *in natura* at 40 °C and took also about 12 h to reach 0.25 g/g (d.b.). When compared with other vegetable products, pineapple proved to be difficult to dry. At the same drying conditions (50 °C and air velocity of 1.0 ± 0.1 m/s), pumpkin needed about 7 h to dry and, when pre-treated with ethanol, drying time reduced 49.5% [24] obtained reduction of 4.9 to 13.4% on time to reach MR of 0.02 during drying of apple slices pre-treated with ethanol and ultrasound for 5, 15, 60 and 180 s.

The reduction in the drying time is important not only to accelerate a long process and save energy, but it is also desired to avoid excessive shrinkage, degradation of sensorial properties and functional compounds [19]. For instance, [28] avoid carotenoid degradation in pumpkin drying by using pre-treatments with ethanol and ultrasound for 15 and 30 min. In their cases, the utilization of pre-treatments allowed to reduce the drying time of 48 to 59%.

The major and significant effect ($p < 0.05$) in pineapple drying was attributed to ethanol, responsible for 88.4% of contribution on the drying time reduction. The application of high-intensity ultrasound also differs significantly ($p < 0.07$)

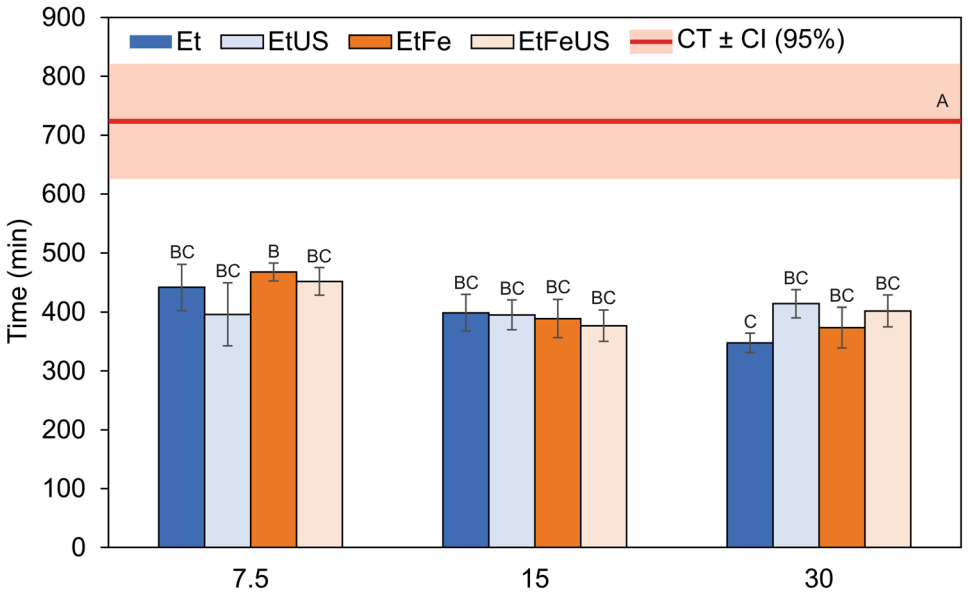

Fig. 5 Drying time required to pineapple pulp (*in natura* and pre-treated for 7.5, 15 and 30 min) reach moisture of 0.2 g/g (w.b.). *Different letters represent significant difference ($p < 0.05$) among the samples. Columns represent the means, and bars represent the standard deviations. The control treatment and its confidence interval (CT ± CI 95%) are represented by the red line and shaded area, respectively

in this parameter, but contributing only with 2.2% on the drying time reduction.

Therefore, similarly to other works, the effect of ethanol was higher than the ultrasound application [28] and/or the presence of microparticles. The only exception is the treatment using ultrasound by 30 min, which presented a slightly increase in drying rate, when compared with other treatments.

Once microparticles are hydrophilic, it could be expected that their presence would hinder the water vaporization during pineapple drying. However, they did not. Once their presence did not affect the drying kinetics, what can be considered an interesting result?

Figure 6 shows the parameters of adjustment of Page model (k and n). Pre-treatments increased the drying rate parameter of Page model (k) Fig. 6a, when compared with control treatment. The constant rate was 0.0064 ± 0.0009 min^{-n} for the control treatment and, for the pre-treated samples, it ranged from 0.0121 ± 0.0066 to 0.0271 ± 0.002 min^{-n}.

The parameter n, according to Simpson et al. [32], is correlated with the pattern of mass transport phenomena. For $n = 1$, the mass transport is given by diffusion. In case of $n > 1$, mass transport is considered super-diffusional and, $n < 1$, sub-diffusional. In previous works [24], [18], the drying kinetics was described by $n > 1$, whose value increased after ultrasound processing—results discussed in relation to the importance of capillarity.

However, the n parameter of pineapple drying was always lower than 1 Fig. 6b. The control treatment presented 0.950 ± 0.025. The pre-treatments with ethanol and ultrasound reduced the n value, ranging from 0.950 ± 0.102 to 0.800 ± 0.015.

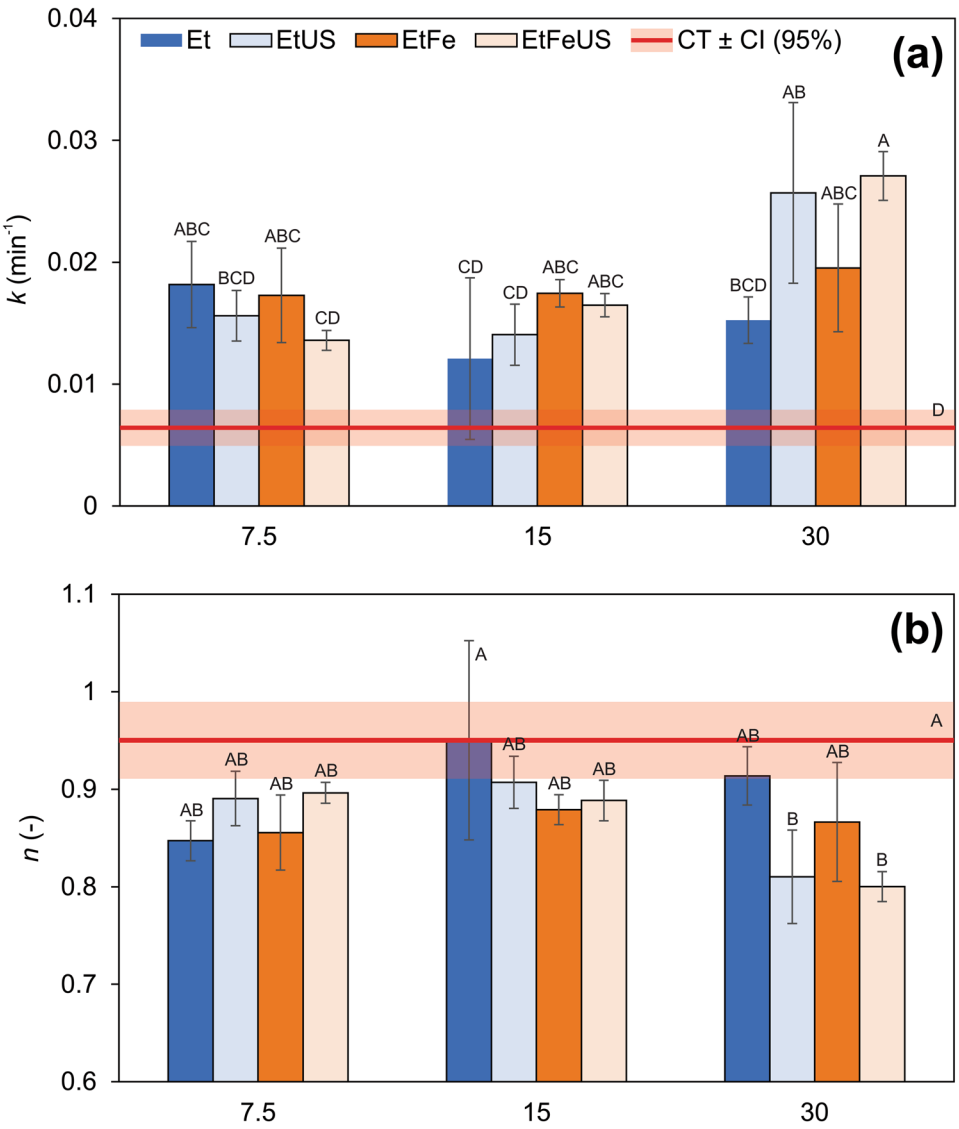

Fig. 6 Parameters of Page model, **a** k and **b** n, to pineapple drying (*in natura* and pre-treated for 7.5, 15 and 30 min). *Different letters represent significant difference ($p < 0.05$) among the samples. The control treatment and its confidence interval (CT ± CI 95%) are represented by the red line and shaded area, respectively

The *n* parameter decreased for all pre-treatments, but only the treatments using ethanol and ultrasound for 30 min differed significantly ($p < 0.05$) from the control Fig. 6b. [28], in previous work, also related an unexpected decrease in *n* value when using ethanol and ultrasound as pre-treatment to pumpkin drying. Ultrasound application results in microchannel formation in the product structure, and, consequently, it could be expected an increase in *n* value, due to mass transport by capillarity. However, this was not observed in this work.

[18] Demonstrated that ultrasound processing in food can generate different types of cavities, including tortuous, isolated, without connectivity and with external medium connectivity. These different types of cavities and microchannels with different tortuosities, permeabilities and diffusivities can improve or impair the mass transport in several ways [27]

In the case of pineapple drying, the *n* value lower than 1 represents a process slower than Fickian diffusion [16]. This behaviour can be attributed to the structure and composition of pineapple pulp, which difficult the drying process. For instance, although thin channels promote liquid flow through capillarity, larger channels may not be able to do it and, as the isolated cavities, they can reduce the rate of liquid outflow from the sample by damming it—thus representing a possible sub-diffusion system [27]. Moreover, the pineapple high sugars content and hygroscopicity can difficult water release.

When the samples are immersed in ethanol, different mechanisms take place, which enhance the further water/ethanol vaporization during drying.

Due to the difference between the surface tension of ethanol and water, the ethanol enters the sample (due to the Marangoni effect [31]. Moreover, part of the sample water flows to the outside due to the difference in osmotic pressure. These mass transfer can be enhanced by the direct effects of applying ultrasound—the so-called sponge effect [7, 33, 18]. Consequently, a faster vaporization of the sample moisture is achieved during drying, due to reductions in the surface tension [30] and in the boiling point [38].

Furthermore, ethanol promotes structural changes, like solubilization of cellular components and thinning of the cell wall. These structural changes can facilitate the mass transport during the drying process, and they can also be related to the reduction of drying time. Moreover, the mass transfer can be enhanced by the indirect effects of applying ultrasound, due to structural modifications [25] [12].

The electric conductivity in the resultant solutions of pineapple pre-treatments is shown in Fig. 7. The pure ethanol presented an electrical conductivity of 0.558 ± 0.023 µS/cm, which increases with the addition of water and electrolytes from the cells. Therefore, the electric conductivity can be used as an indirect method to evaluate the ultrasound effect and action in the sample structure. After the pre-treatments, the conductivity was increased from 5.58 to 13.81 µS/cm ($p < 0.05$), while the pre-treatments with ultrasound resulted in higher electric conductivity and lower standard deviation. These results demonstrate that ethanol pre-treatment absorbs part of the product water, which can facilitate the following drying process. Moreover, it demonstrates that, as expected, the ultrasound technology was able to partially disrupt pineapple tissues and/or cells, which can facilitate the water outflux during drying.

The incorporated ethanol has also impact in the sample thermal history during drying—which was evaluated by

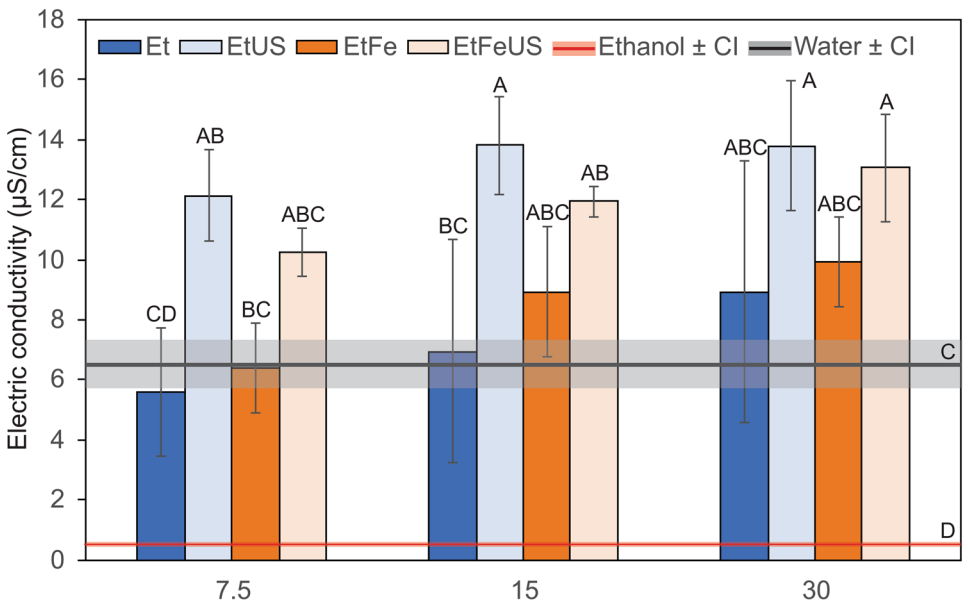

Fig. 7 Electric conductivity of solutions after pre-treatments for 7.5, 15 and 30 min with ethanol, iron microparticles and ultrasound. *Different letters represent significant difference ($p < 0.05$) among the samples. Columns represent the means, and bars represent the standard deviations. The electric conductivity of ethanol and water and their confidence interval (CT ± CI 95%) are represented by the red and black line and shaded areas, respectively

thermal images right after the treatment and during the drying process using an infrared camera.

Figure 8 a, b show the increase in the sample surface temperature and the sample average surface temperatures during drying, respectively. At the initial time ($t = 0$), i.e. shortly after the pre-treatment, the ethanol presence resulted in lower temperatures, which were decreasing with the time of the pre-treatment and with the ultrasound application. Further, longer pre-treatments and the application of ultrasound resulted in higher inlet of ethanol in the sample. Due to ethanol volatility, as higher the amount of incorporated ethanol, lower becomes the temperature, because it absorbs energy from the environment to evaporate. It was also observed by [8], during the study of drying of banana, and [28], during the drying of pumpkin.

It is also possible to observe that the control treatment started the drying process with higher surface temperature, due to the effects of ethanol already discussed previously. However, during the drying process, the treatments with ethanol reached higher temperatures faster than the control treatment, due to the faster moisture evaporation. From four hours of drying, the treatments with ethanol reached constant temperature (~ 45 °C), while the control treatment temperature was lower. This fact occurred as the control treatment still have water, and the evaporation of this moisture maintains the temperature below 45 °C—in fact, this treatment will need ~ 12 h to reach the moisture of 20% (w.b.).

Figure 9 shows the relation between the sample surface average temperatures after the pre-treatment and the residual ethanol (through the chromatographic areas) present into the dried pineapple.

Summarizing both ethanol and ultrasound accelerated pineapple drying, being the effect of ethanol more important. However, not only the process improvement must be evaluated but also, in this context, the amount of incorporated iron and the residual ethanol in the obtained chips, once this information is highly relevant for the consumption. Consequently, the residue of ethanol was evaluated in the obtained chips.

Residue of ethanol in the obtained chips

Although the interest in ethanol pre-treatment to drying is growing [12], the determination of residual ethanol is rare, mainly due to experimental difficulties. In fact, only the work of [3] has initiated this evaluation, using ethanolic atmosphere to dry pineapple. However, in their work, ethanol was extracted by manual headspace solid-phase microextraction (SPME), separated and identified by gas chromatography-mass spectrometer (GC-MS), but its content was expressed only as "chromatographic peak area". Even so, by using this approach, [3] reported that the residue of ethanol in the dried pineapple using atmosphere modified with ethanol was higher than the content of this compound in fresh fruit and in the sample dried in normal atmosphere.

In the present work, the pre-treatments with ethanol and ethanol + ultrasound were carried out by immersion, and the residue of ethanol in the obtained pineapple chips was measured by headspace-gas chromatography coupled with mass spectrometry (GC-MS).

Figure 10 presents the ethanol peak in the chromatogram of the control treatment (i.e. the *in natura* pineapple submitted to drying), the different pre-treatments using ethanol and ultrasound and samples used to estimate the final ethanol content. To obtain these samples, different quantities of ethanol (HPLC grade) were added to the dried control pineapple in order to obtain chips with the final concentration of control + 1, 2, 3 and 4% (v/m), corresponding to additions of 0.01, 0.02, 0.03 and 0.04 mL/g of pineapple control sample, respectively.

As observed, even the control sample presents a residue of ethanol. Moreover, the ethanol residual present in dried samples was treated with ethanol and ethanol + ultrasound for 7.5 min, and ethanol for 15 min did not differ significantly ($p < 0.05$) from the control.

By comparing the chromatographic areas of control and samples with added ethanol (1–4%), the ethanol content in the control sample could be estimated of about 0.1095% or 1.095 μL/g (d.b.), which is consistent with the literature. This amount depends of several factors, such as variety, degree of maturity and storage conditions, among others. [29] related, in their work, an ethanol content in a range from 0.1 to 0.4 μL/g for fresh pineapple (moisture content about ~ 81%) or stored at 10 °C up to 12 days. [22] reported a natural ethanol content of 0.026–3.07 μL/g for fresh pineapple variety *Ninh Binh* (moisture content of ~ 81%) or stored up to 25 days.

Longer pre-treatment times resulted in higher residual ethanol in dried samples.

Pineapple samples pre-treated for 30 min only with ethanol and with ethanol and ultrasound resulted in residual ethanol from 2.1 to 5.5% (v/m d.b.), which corresponds to 20.9 and 55.45 μL/g (d.b.), respectively. Therefore, although these treatments reduced the drying processing time, they also resulted in chips with ethanol content similar to some alcoholic beverages, such as beer. In general, this alcoholic claim is not interesting for nutrient enriched fruit chips, thus limiting the application of the cited technology. However, a new product may be obtained in this way (with or without the iron incorporation), with particular interest of specific consumers and a possible market niche. The discussion of this reliability, however, is outside of this work scope.

The chips, obtained by using the ethanol pre-treatment for 15 min, resulted in residual ethanol from 0.211 to 0.597% (d.b.) without and with the ultrasound application, respectively. Although these values are below those found in

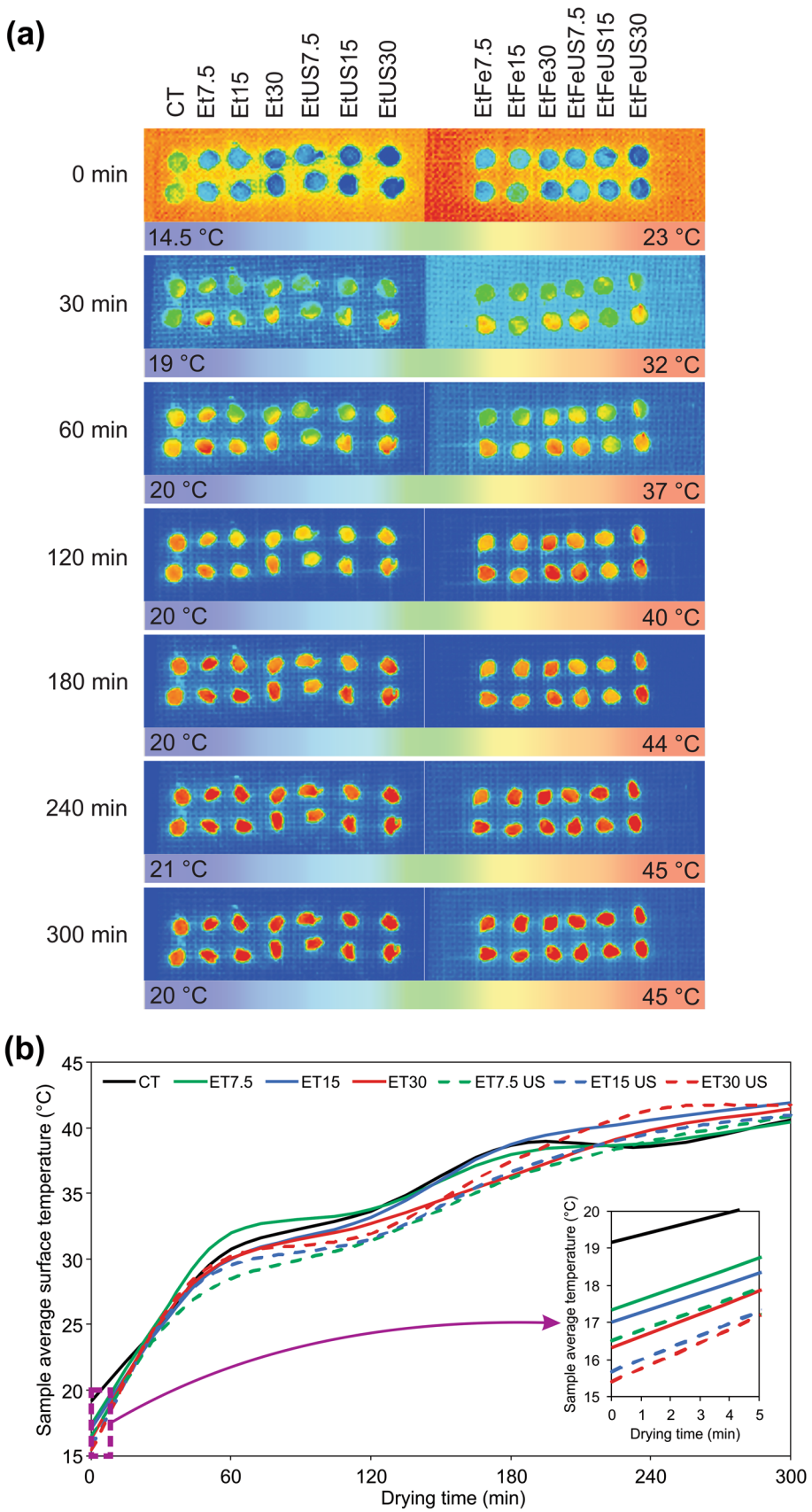

Fig. 8 **a** Surface temperature of pineapple samples during convective drying. Lower colour bars above each image represent the temperature scale at each processing time. **b** Average surface temperature of the samples during convective drying

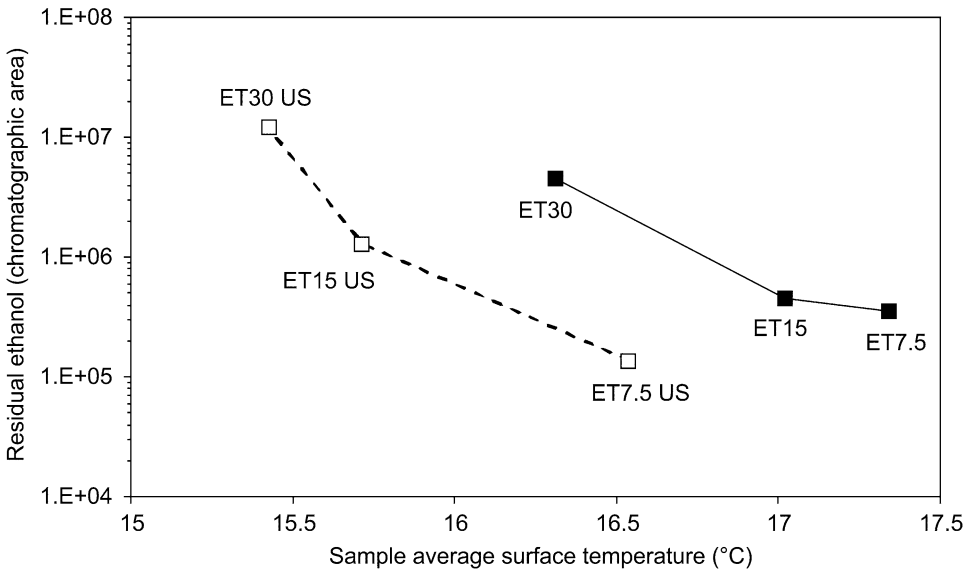

Fig. 9 Correlation between the sample average surface temperature after pre-treatments and the residual ethanol present in the dried samples

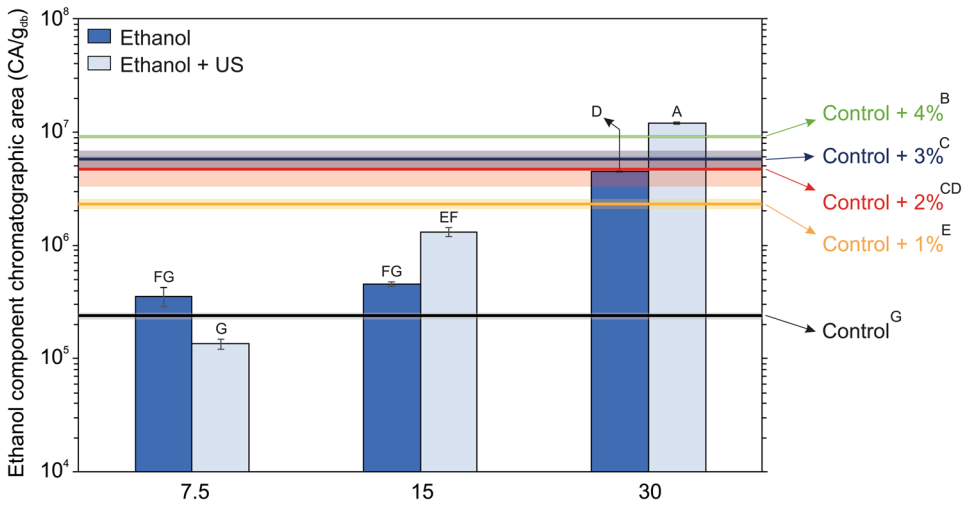

Fig. 10 Ethanol content of dried pineapple: control, pre-treated samples for 7.5, 15 and 30 min in ethanol or ethanol and ultrasound and standard curve (control + 1, 2, 3 and 4% (v/m) of ethanol). *Different letters represent significant difference ($p < 0.05$) among treatments. Columns represent the means, and bars represent the standard deviations. The control treatment, standard curve and their confidence interval (CT ± CI 95%) are represented by the lines and shaded area, respectively

alcoholic beverages, they are still high if the product claim is observed. Therefore, a small amount of residual ethanol is desired.

Only the chips obtained after 7.5 min of treatment reached residual ethanol values close to the control sample, being the only treatment also using ultrasound that resulted in a residual ethanol lower than the control. This effect may be attributed to the ultrasound action, which may have promoted structural changes such as breaking tissues and cells and, consequently, favouring the release of ethanol during drying. This result is of high interest; once by combining ethanol and ultrasound as a treatment during 7.5 min, it is possible to reduce from 35.4 to 51.9% the drying time Fig. 5, achieving iron-rich chips with negligible final ethanol content.

With the amount of ethanol estimated for all treatments, it is possible to correlate this concentration with the average superficial temperature of the pineapple right after the pre-treatments and before drying process. Figure 9 shows this correlation. As observed, higher residual ethanol contents in dried pineapple are correlated with lower average surface temperatures right after the pre-treatments. With the exception of treatment for 7.5 min, ultrasound application resulted in higher residual ethanol and lower average surface temperature after pre-treatment.

The correlation of ethanol amount and the temperature of the sample treated, if well established, can be a useful way to estimate the ethanol entering in the sample during pre-treatments to improve the drying process, because it is easier to measure the temperature of the sample than the amount of ethanol by chromatography, for example.

Final consideration

This work demonstrated the possibility of using four technologies (microencapsulation, ethanol, ultrasound and convective drying) to obtain iron-enriched fruit chips in a faster process and with a negligible ethanol content.

However, it should be mention that despite the objective was fulfilled, this work does not intend to be a reference from the nutritional point of view. Consequently, this work does not propose that the ferrous sulphate is the best source of iron for humans, that maltodextrin is the best choice from a nutritional point of view, nor recommend the incorporation of nutrients in this way as a nutritional politic. Moreover, this work does not intend to discuss safe/desired/accepted ethanol ingestion quantities.

Even so, we highlight the relevance of this work as a prospective study of using the cited technologies to obtain products with better quality and through better processes.

Future studies must be performed to determine if the incorporated iron is bioaccessible and bioavailable, also considering different conditions of storage. Further, the incorporation of nutrients in this way must be evaluated through possible nutritional politics. In all the cases, the Food Process Engineering can be applied in a clever way to fulfil the nutritional requirements.

Conclusion

The combination of technologies (microencapsulation, ethanol, ultrasound and convective drying) presented in this work can successfully be used to produce pineapple chips enriched with iron. The pre-treatments with ethanol and ultrasound were efficient to reduce the drying time of pineapple and to increase significantly the iron content of the product—when compared with natural levels of this component. The analysis with GC-MS was employed for the first time to demonstrate and quantify the residue of ethanol present in dried products pre-treated with ethanol. It was possible to show that longer pre-treatment times resulted in higher residual ethanol in pineapple chips. However, the reduction of pre-treatment time to 7.5 min was sufficient to decrease the ethanol amount to natural levels of the pineapple. The utilization of thermal images made it possible to correlate the surface temperature of the sample with residual ethanol present in the dried sample. It can be a useful tool to evaluate and describe drying process with pre-treatment with ethanol and other compounds.

Acknowledgments The authors are grateful to the valuable help and discussion by/with Eng. Karoline Costa dos Santos and Prof. Dr. Severino Matias de Alencar.

Funding The present work was funded by the São Paulo Research Foundation (FAPESP, Brazil) for funding the project n° 2019/05043-6 and the GR Carvalho postdoctoral fellowship (2018/17844-0), the National Council for Scientific and Technological Development (CNPq, Brazil) for funding the productivity grant of P.E.D. Augusto (306557/2017-7) and the LNNano (CNPEM, Brazil) for technical support and facilities during electron microscopy work (Project SEM-24192).

Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflicts of interest.

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