



New valorization approach of Algerian dates (*Phoenix dactylifera* L.) by ultrasound pectin extraction: Physicochemical, techno-functional, antioxidant and antidiabetic properties

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ABSTRACT

To exploit the great fortune of date fruits, the current study aimed to valorize an Algerian common variety by extracting pectins. Response surface methodology (RSM) was applied as process optimization tool to achieve the highest yield using ultrasound-assisted extraction (UAE) as compared to conventional acid extraction (CAE). The experimental yield value (6.7%) was well matched with the predicted one (6.6%) at the optimum conditions (60 °C, 90 min, pH 1.5), confirming the validity of the model. The evaluation of the monomeric composition showed higher content of galacturonic acid and lower of neutral sugars in UAE pectin, as compared to CAE pectin. Conventional treatments decreased the molecular weight (Mw) of the extracted pectins (539 kDa) in a higher extent than ultrasound treatment (800 kDa). Fourier-Transform Infrared Spectroscopy (FT-IR) spectral analysis showed that both samples were low-methoxyl pectins. CAE gave rise to pectins with slightly upper technological samples in terms of water and oil holding capacity (5.2 and 3.8 g/g, respectively), and emulsifying activity (38.5 m²/g). Moreover, date pectins obtained by UAE presented enhanced antioxidant activity (24.3 and 61.0 mg/g DW for DPPH and FRAP assays, respectively), and *in vitro* antidiabetic properties, showing higher glucose adsorption capacity (4 mmol g⁻¹ at 200 min), as well as α -amylase inhibition (73.7%) and potential capacity to decrease glucose diffusion (1.4 mmol mM g⁻¹ at 150 min), which could improve the ability to retard starch digestion (0.1 mmol mM g⁻¹ at 150 min), providing potential health-promoting properties.

1. Introduction

Date palm fruit (*Phoenix dactylifera* L.) has been consumed since millennia as a staple food in Berber/Amazigh and Arabic cultures and, nowadays, it is receiving an increasing interest in the international market ascribed to its low-cost and high nutritious value. This fruit is considered an ideal energy source to overcome the current unpredictability of food availability and the anticipated food demand for the future [1]. Owing to that, in 2020, the annual worldwide production of date fruits increased reaching the 9.1 Mt., placing Algeria in the 4th place of date producing countries with 1.1 Mt., after Egypt (1.6 Mt),

Saudi Arabia (1.5 Mt) and Iran (1.3 Mt) [2].

Despite the differences found in dates according to ripening stages, generally, the fruit flesh is rich in simple carbohydrates (~70%), mainly sucrose, glucose and fructose, which provide not only a nice taste but also a good source of rapid energy as they can be readily absorbed. Additionally, their dense and tacky texture facilitate the binding and mixing with complementary ingredients as cereals. This behavior converts this fruit into an ideal substrate for being used directly for dietary intake and included into different value-added products such as sweets, confectionary, syrups, cola, juices, dairy desserts and candies [1,3]. Dates also contain pectin that begin to accumulate during the growing of

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the date fruit and reach the maximum content at the beginning of its maturation stage. In addition, dates have appreciable quantities of polyphenols and are rich in some minerals and vitamins [4,5].

Pectin is a polysaccharide naturally present in the cell walls of all higher plants, whose structure commonly is formed by three domains: (i) homogalacturonan (HG) consisting of 1,4-linked- α -D-galacturonic acid (GalA); (ii) rhamnogalacturonan-I (RG-I) consisting of the repeating disaccharide [-4]- α -D-GalA-(1 $\rightarrow$ 2)- α -L-Rha(-) that bears different side chains composed by arabinose and galactose, and (iii) rhamnogalacturonan-II (RG-II) having a backbone of HG with complex side chains attached to the GalA residues of up to 17 monosaccharides [6,7]. This complex polysaccharide is widely used as stabilizer, emulsifier, and gelling agent in the food industry and as a versatile delivery agent to encapsulate drugs in the pharmaceutical industries. In fact, during the last years, interest of public and health professionals has been drawn towards the potential of pectin in the treatment and prevention of diabetes, one of the most common and chronic diseases worldwide, given that artificial antidiabetic compounds can involve important undesirable effects [8–10].

Because the sales of pectin surpassed the USD 2.4 billion in 2020, there is a necessity to find new sources for its extraction [7]. Due to the emerging interest towards pectin, alternative sources like date by-products or fruits (without extended consumption) are interesting to be explored in order to provide new structural and functional characteristics. Pectin is usually obtained at the industry using mineral acids ($1.5 < \text{pH} < 3.0$), elevated temperatures (60 – 100 °C) during long times (0.5 to 6 h). This entails negative consequences, such as the production of the large effluent volumes, high environmental pollution, time-consuming process, low extraction yield, and insufficient quality and functionality [11–13]. Therefore, environmentally friendly and innovative technologies such as enzymes, microwave and ultrasound-assisted extraction methods (UAE) are being studied to enhance the pectin yield with better rheological and biological properties [11]. Remarkably, the extraction method strongly influences the structural characteristics, and consequently the functional properties of pectins. In this sense, UAE has been proved to be an efficient, fast, and reliable way to preserve the food components bioavailability, improving their functional properties and increase the recovery yields [14]. It is a technology that allows favoring the extraction of compounds from organic materials. A high shear force is generated due to the implosion of cavitation bubbles formed by the propagation of acoustic waves. The collapse of the bubbles gives rise to the rupture of the biological membranes facilitating the release of extractable compounds and improving the penetration of the solvent in cellular materials, thus enhancing the mass transfer, reducing the processing time, and increasing the yield [15].

To the best of our knowledge, limited information is available on the obtainment of pectin from dates (*Phoenix dactylifera* L.). The aim of the present work was the optimization of pectin extraction from “Degla-Beida” date variety using ultrasonic assisted extraction through the response surface methodology, and the comparison with a conventional method. Moreover, the evaluation of pectin structure, physicochemical, techno-functional, antioxidant and antidiabetic properties has been carried out to elucidate the potential benefits of these extracted pectins.

2. Material and methods

2.1. Raw material and chemicals

The common date palm fruit (*Phoenix dactylifera* L.) used in this study was from “Degla-Beida”, an Algerian local dry variety not highly used for direct consumption (a common variety of low marketable value, little appreciated by consumers because of its poor sensory quality, usually transferred for cattle feeding), collected from the Sahara region ($34^{\circ}51'N$ $5^{\circ}44'E/34.850^{\circ}N$ $5.733^{\circ}E/34.850$; 5.733 , Biskra, Algeria). The fruits were cleaned, pitted, dried, ground, sieved (<250 μm) and stored in an airtight container as described previously [16]. All

chemicals and solvents were of analytical grade. Standard monosaccharides (arabinose, xylose, galactose, rhamnose, glucose and GalA, β -phenylglucoside, hexamethyldisilazane, trifluoroacetic acid, citric acid monohydrate, sodium citrate tribasic dihydrate and Pullulan Standard (0.34–805 kDa), a glucan polymer based on $\alpha(1,6)$ linked maltotriose units, α -amylase, glucose and starch were obtained from Sigma (St. Louis, MO, USA).

2.2. Pectin extraction

The obtainment and isolation of pectins from date cell walls was approached in two ways using ultrasound-assisted extraction (UAE) and conventional acid extraction (CAE) technologies, the latter for comparative purposes.

2.2.1. Conventional acid method without and with assistance of ultrasound

Briefly, 10 g of date powder was suspended in 100 mL of distilled water, which was acidified by using nitric acid (53%) to obtain the established pH. Date pectins were extracted without (CAE) and with the assistance of ultrasound (UAE). The CAE conditions were 95 °C, pH of 1.5 for 90 min following the method described by Nesrine et al. [17], in a heating plate with constant shaking (1000 rpm), whereas the ones employed in UAE were the optimal conditions obtained by the response surface methodology (RSM). In this case, an ultrasonic bath with internal dimensions of 24.0 cm $\times$ 14.0 cm $\times$ 10.0 cm, a capacity of 3 L and a frequency of 45 kHz and 350 W power (Sonica Sweep System EP 2200, Soltec, Milan, Italy) was used for the assistance of the extraction method. Once the extraction time elapsed the mixture was centrifuged, and the supernatant was separated from insoluble residue. The mixture was precipitated with an equal volume of ethanol (96%). After centrifugation, the insoluble pectin was washed twice with ethanol (70%) to remove impurity. The recovered pectin was lyophilized and stored at -20 °C. The pectin yield was calculated using the following formula:

$$\text{Pectin yield (\%)} = \frac{\text{Weight of dried pectins (g)}}{\text{Weight of dried date powder (g)}} \times 100 \quad (1)$$

2.2.2. Optimization of ultrasound-assisted extraction

Fifteen assays with three center points were designed using Design Expert software package JMP (10.0.0 version, SAS Institute, USA). Three factors, three levels ($-1, 0, 1$), Box-Behnken design was employed to optimize the process variables and to examine their effect on the response. The upper and lower limits were used in the optimization approach by RSM, to determine the optimum values of each process variable, namely: X_1 -Temperature (40 – 60 °C), X_2 -Sonication time (30 – 90 min) and X_3 -pH (1.5 – 3.5). The assays were performed in a randomized order to avoid systematic errors.

The data collected were subjected to regression analysis to determine the existing relationship between independent and dependent variables. Each response was represented by a mathematical equation that correlates the response surfaces. The response was then expressed as second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{ij}^k \beta_{ij} X_i X_j + E \quad (2)$$

where Y is the measured response variable, which is in our case the pectins yield, β_0 is a constant, β_i is the linear coefficient (main effect), β_{ii} is the quadratic coefficient, β_{ij} is the two factor interaction coefficients, and X_i , X_j are the independent variables.

2.3. Physicochemical properties of pectins

1 g of crude pectins was dried to constant weight at 110 °C for 3 h. Loss of weight upon drying was calculated as the moisture content [18]. Minerals content was determined in the Interdepartmental Research

Service (Sidi-UAM) (Madrid, Spain), by inductively coupled plasma mass spectrometry (ICP-MS) in an Elan 6000 Perkin-Elmer Sciex instrument (Concord, Canada).

2.4. Structural characterization of pectins

2.4.1. Determination of monomeric composition

The monomeric composition of date pectins was determined as described by Muñoz-Almagro et al. [19]. The samples were hydrolyzed with trifluoroacetic acid (TFA) 2 M at 110 °C during 4 h. Then, 500 µL of hydrolysate were placed in a flask and evaporated under vacuum at 43 °C. 400 µL of phenyl-β-D-glucoside (0.5 mg·mL⁻¹) (internal standard, I.S.) were added, and the flask was evaporated again. For the oximes formation, 250 µL of hydroxylamine chloride in pyridine (2.5%) were added and the mixture was vortexed and heated at 70 °C during 30 min with stirring. Samples were persilylated with 250 µL of hexamethyldisylazane (HMDS) and 25 µL of TFA at 50 °C for 30 min, shaken, and centrifuged at 10000 g for 2 min. Regarding the monosaccharide composition, the initial temperature, 150 °C, was held for 17 min, and then was rose to 165 °C at 1 °C/min, then increased at a rate of 10 °C/min to 200 °C and up to 380 °C at 50 °C/min. The released monomers were analysed by gas chromatography with flame-ionization detection (GC-FID) (Agilent Technologies 7890A gas chromatograph, Agilent Technologies, Wilmington, DE, USA) and the data acquisition was done using a HPChem Station software (Hewlett-Packard, Palo Alto, CA, USA).

2.4.2. Estimation of molecular weight distribution

The estimation of date pectins molecular weight (Mw) by high performance size exclusion chromatography (HPSEC-ELSD) was determined following the method described by Muñoz-Almagro et al. [20]. A TSK-Gel guard column (6.0 mm × 400 mm) connected in series with two TSKGel columns G5000 PWXL (7.8 mm × 300 mm, 10 µm) and G2500 PWXL (7.8 mm × 300 mm, 6 µm) (Tosoh Bioscience, Stuttgart, Germany) were used in the samples separation (0.1% w/v, 50 µL). The pectin elution was carried out using 0.01 MNH₄Ac as mobile phase at 0.5 mL/min for 50 min.

2.4.3. Determination of the degree of methylesterification (DM)

For the FT-IR (Fourier-Transform Infrared Spectroscopy) measurements, date pectins were mixed with KBr powder (1:100), ground and then pressed into 1 mm pellets before the analysis. FT-IR spectra were collected at absorbance mode in the frequency range of 400–4000 cm⁻¹ (Bruker Optics, Ettlingen, 76,275 Germany). The DM of pectin was determined as the average of the ratio of the peak area at 1748 cm⁻¹ (COO-R) over the sum of the peak areas of 1744 cm⁻¹ (COO-R) and 1638 cm⁻¹ (COO⁻).

2.5. Techno-functional properties

2.5.1. Water/oil-holding capacity

Fifteen milliliters of water were added to 250 mg of each sample in a 50 mL centrifuge tube. The samples were stirred and left at room temperature for 1 h. After centrifugation at 3000 g for 20 min, the supernatant was discarded, the residue was weighed and the water-holding capacity (WHC) was expressed as g water retained per g of dry sample. The oil-holding capacity (OHC) was determined under the same conditions as WHC using commercial vegetal oil, and was expressed as g oil retained per g of dry sample [21].

2.5.2. Emulsifying activity

Emulsifying activity was calculated by turbidity according to the method described by Pacheco et al. [22]. A volume of 100 mL of pectin solution in water (20%, w/v), were mixed with 5 g of corn oil using an Ultraturrax at 24000 rpm for 1 min to obtain an emulsion. The emulsion was diluted 30, 500 and 900-folds with sodium dodecyl sulphate (SDS)

(1 g·L⁻¹). Turbidity of emulsions was measured in a UV spectrophotometer plate reader, at 500 nm, using the SDS solution as the blank sample.

2.6. In vitro antioxidant activity

In this work, two assays, namely, the (2,2'-diphenyl-1-picrylhydrazyl) DPPH radical scavenging activity and the ferric reducing antioxidant power (FRAP) assay, were employed to evaluate the *in vitro* antioxidant activity of ultrasound-assisted and conventional acid extraction pectins (UAE and CAE). Details of the operation conditions and methods were reported by Chen et al. [23].

2.7. In vitro anti-diabetic activity

To evaluate the *in vitro* antidiabetic activity of date pectins obtained by UAE and CAE, glucose-adsorption capacity, residual α-amylase activity, glucose dialysis retardation capacity and starch digestibility were determined according to the methods described by Benitez et al. [24].

2.7.1. Glucose-adsorption capacity

Approximately, 1 g of date pectins was mixed with 100 mL of glucose solution of increasing concentration (10, 50, 100 and 200 mmol·L⁻¹). Each of these mixtures was mixed well, stirred, and incubated at 37 °C for 6 h, respectively. After incubation, the mixture was centrifuged 3500 g for 15 min and finally the glucose content was determined in the supernatant by using glucose assay kit (Megazyme KGLUC, Wicklow, Ireland).

2.7.2. In vitro α-amylase inhibition

The α-amylase assay was performed by mixing date pectins with α-amylase (Sigma-Aldrich, MO, USA) (4 mg·mL⁻¹) and potato starch solution (40 mg·mL⁻¹). After 60 min of incubation at 37 °C, the reaction was stopped by adding 80 mL of NaOH (0.1 mol·L⁻¹). To determine the glucose production, the content was quantified in the supernatant, obtained after centrifugation at 3500 g for 15 min, using the assay kit KGLUC (Megazyme, Wicklow, Ireland) in a 96-well plate. The absorbance was measured at 580 nm and the percentage inhibitory activity was calculated by using the following equation:

$$\text{Inhibition (\%)} = \left(1 - \frac{\text{Absorbance of the control}}{\text{Absorbance of the test well}} \right) \times 100 \quad (3)$$

2.7.3. In vitro glucose dialysis retardation capacity

The glucose dialysis retardation index (GDRI) was determined to evaluate the capacity to retard *in vitro* the glucose diffusion. The mixture of 25 mL of glucose solution (50 mmol·L⁻¹) and 0.5 g of samples was dialyzed in dialysis bags against 80 mL of distilled water at 37 °C. Further, glucose concentration in the dialysate was determined at time intervals, i.e., 15, 30, 60, 120, and 150 min, using a KGLUC kit (Megazyme, Wicklow, Ireland). A control test without date pectins was also performed. The GDRI was calculated according to the formula below:

$$\text{GDRI} = 100 - \left[\left(\frac{\text{Glucose content in the dialysate with fiber addition}}{\text{Glucose content in the dialysate of control test}} \right) \times 100 \right] \quad (4)$$

2.7.4. In vitro starch digestibility

The effect of date pectins on starch digestibility as a function of time was determined using a pectin-enzyme-starch mixture system. The mixture of 0.2 g of date pectins and 4 mg of α-amylase (Sigma Aldrich, MO, USA) with 10 mL of potato starch solution (4% p/v) was dialyzed against 200 mL of distilled water at 37 °C. Glucose concentration in the dialysate was determined at 15, 30, 60, 120, and 150 min after incubation, using a KGLUC kit (Megazyme, Wicklow, Ireland). A control experiment without date pectins was carried out. GDRI starch was

calculated as explained in Section 2.7.3.

2.8. Statistical analysis

Extractions and analysis were carried out at least in triplicate and means were compared by Tukey's test ($p < 0.05$), using XLSTAT Release 10 (Addinsoft, Paris, France). All statements of significance were based on probability of $p < 0.05$.

3. Results and discussion

3.1. Optimization of ultrasound-assisted extraction

Table 1 lists the extraction parameters used for each run according to the experimental design with their experimental and predicted respective pectin's yield (Y) from date fruit. The independent and dependent variables were then fitted to the following second-order model equation.

$$Y = 2.09 + 0.40X_1 + 0.14X_2 - 0.60X_3 + 0.11X_1X_2 - 0.37X_1X_3 - 0.28X_2X_3 - 0.25X_1^2 + 0.22X_2^2 \quad (5)$$

In this equation, Y represents the yield of pectins calculated by the regression model, and X_1 , X_2 , X_3 are the coded variables.

The analysis of variance (ANOVA) was performed to determine the significance of the linear, quadratic and interaction effects of the independent variables on the dependent variable (Table 2). The significance of each term in the model can be determined according to their p -values, the term with $p < 0.05$ will have a notable effect on date pectin yield. Therefore, the linear terms (X_1 and X_2) and interaction term (X_1X_2) significantly affected the yield. All quadratic terms of sonication time (X_1^2) and pH (X_3^2) were significant, excepting the term corresponding to the temperature (X_2^2). Remarkably, temperature was the most significant variable affecting pectin yield, followed by sonication time and pH. The high F -value (27.4) and low p -value (< 0.0001) implies that the model was highly significant. Taking into account the lack of fit test of the model the developed model was good. Moreover, it is important to highlight that the coefficient of determination (R^2) which indicates the proportion of the variation in the response attributed to the model rather than to random error, also suggested that for good fit model. The ANOVA of the regression model demonstrated that R^2 is 0.9884, which means 99% variability in the response could be explained by this model. The high values of R^2 , adjusted R^2 , and predicted R^2 confirmed the accuracy of the model in showing the relationship between the yield and the variables [25].

For better understanding, the effect of processing parameters (X_1 -

Table 1

Box–Behnken design with experimental and predicted values for pectin yield from date fruit obtained by ultrasound-assisted extraction.

Assays	Temperature (°C)	Time (min)	pH	Pectin yield (%)	
				Experimental	Predicted
1	50	60	2.5	4.0	4.1
2	60	90	2.5	4.7	4.7
3	40	60	1.5	4.4	4.3
4	60	60	3.5	3.8	3.9
5	50	30	1.5	5.0	5.1
6	50	60	2.5	4.1	4.1
7	50	90	1.5	5.9	6.0
8	50	60	2.5	4.1	4.1
9	50	30	3.5	4.5	4.5
10	40	60	3.5	3.8	3.8
11	40	30	2.5	3.7	3.6
12	40	90	2.5	3.6	3.7
13	50	90	3.5	4.3	4.2
14	60	30	2.5	4.3	4.2
15	60	60	1.5	5.9	5.8

Table 2

Analysis of variance (ANOVA) for the fitted quadratic polynomial model.

Source	Sum of squares	DOF	Standard error	F-value	p-Value
Model	7.1	9	0.1	46.1	<0.0001
Temperature	0.4		0.1	8.5	0.0004
Time	0.1		0.1	3.0	0.0292
pH	−0.6		0.1	−12.8	<0.0001
Temperature × Time	0.1		0.1	1.6	0.1612
Temperature × pH	−0.4		0.1	−5.5	0.0026
Time × pH	−0.3		0.1	−4.2	0.0081
Temperature ²	−0.2		0.1	−3.5	0.0181
Time ²	0.2		0.1	3.5	0.0169
pH ²	0.6		0.1	9.5	0.0002
Residual	0.1	5			
Lack of Fit	0.1	3		10.6	0.0875
Pure Error	0.0	2			
Total error	0.1	5			
R ²	0.9881				
R _{adj} ²	0.9666				
RMSE	0.1				
Cor total	7.2	14			

temperature, X_2 -sonication time, and X_3 -pH) on the pectin yield was evaluated and illustrated by three-dimensional (3D) plots. The 3D plots were generated by maintaining one factor at its constant level (in turn its central level), whereas the other two factors were varied in their range. The results are depicted in Fig. 1. According to Hernoux-Villiere et al. [26], the maximum mechanical effect of US is obtained at temperatures near 60 °C, since this value is considered as the maximum temperature for cavitation bubbles to coalesce with vapor bubbles, suggesting values above this temperature might interfere with US effect on pectin extraction. The pH of the solution was another variable that clearly affected the pectin recovery. As can be seen from Fig. 1(B) and (C), the highest yield was found at pH 1.5. Acidic solvent has the ability to hydrolyze polysaccharides and converts them into insoluble to soluble form susceptible of depolymerisation, reducing their molecular weight and modifying their structure [27]. Based on the RSM, the highest yield of date pectins using the UAE can be optimally obtained by applying the following conditions: temperature of 60 °C, sonication time of 90 min and pH 1.5.

Additional experiments (triplicates) were carried at these optimal conditions in order to compare the predicted results with experimental values. Under these conditions, the experimental yield of pectin ($6.7 \pm 0.4\%$) was close to the predicted value ($6.6 \pm 0.6\%$). Thus, for predicting the maximum extraction yield of pectin using UAE, Box–Behnken design was considered an accurate tool.

For comparative purposes, a conventional treatment was carried out following the conditions (90 min, pH 1.5, 95 °C) previously reported by Nesrine et al. [17]. As indicated in Table 3, no significant differences were found in the date pectin recovery (~ 7) between both methods. After CAE the obtained yield was very similar to that found by Nesrine et al. [17]. In the case of US, it is noteworthy that, although the temperature was much lower (60 °C) than in the conventional extraction (90 °C) the yield was very similar, indicating the effectiveness of US application [28].

3.2. Overall characterization of date pectins extracted

Once extraction conditions of date pectins were selected to have the highest yields, the obtained samples were characterized. In a first approach, the compositional characteristics of samples were studied, results are included in Table 3. The moisture content of both pectins was around 14%. Similarly, no significant differences were found in the mineral profiles, being sodium followed by potassium, calcium and magnesium the most abundant elements in both samples. In general, these results might indicate the potential use of the extracted pectins

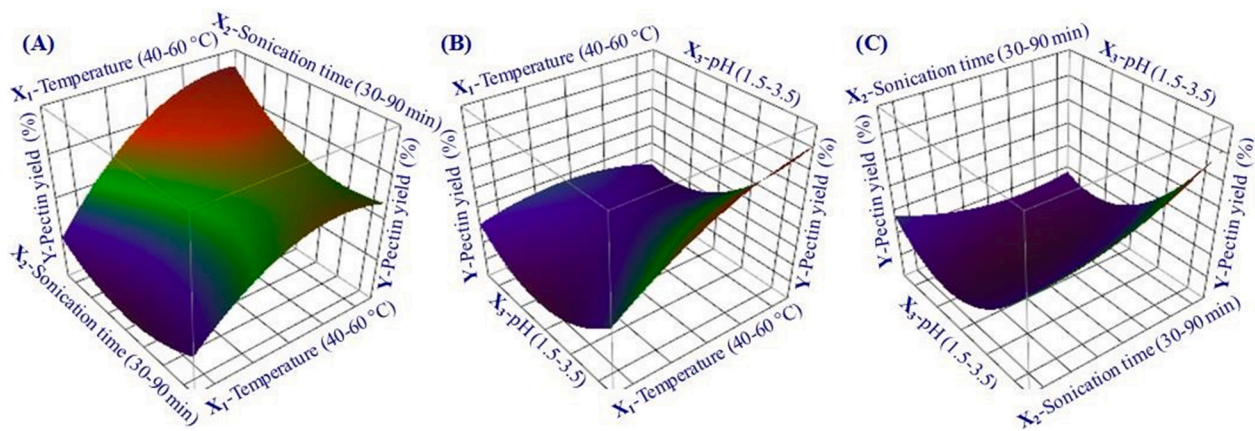


Fig. 1. Response surface analysis for pectin yield from date fruit using ultrasound-assisted extraction (UAE) with respect to temperature and sonication time (A); temperature and pH (B); sonication time and pH (C).

Table 3

Yield, overall characterization, sugar composition, molecular parameters, techno-functional properties and antioxidant activity of date pectins obtained by conventional acid extraction (CAE) and ultrasound-assisted extraction (UAE).

Parameter	CAE	UAE
Yield (%)	6.7 ± 0.4 ^a	7.6 ± 0.6 ^a
Moisture content (%)	13.5 ± 0.5 ^a	15.1 ± 0.7 ^a
Mineral content (mg/100 g DW)		
Na	1430.2 ±	1108.8 ± 12.2 ^b
Mg	10.1 ^a	102.1 ± 0.0 ^a 4.4 ± 0.5 ^a 3.7 ± 0.3 ^a
Al	102.8 ± 3.1 ^a	38.3 ± 0.0 ^a
Si	4.1 ± 0.1 ^a	
P	4.1 ± 0.4 ^a	
S	31.2 ± 2.4 ^b	
Cl	24.8 ± 5.5 ^b	41.2 ± 8.7 ^a
K	25.8 ± 1.7 ^a	1.6 ± 1.2 ^b
Ca	919.7 ±	839.4 ± 6.7 ^b
	12.2 ^a	282.9 ± 14.1 ^a
	229.5 ±	
	12.4 ^b	
Mn	1.3 ± 0.0 ^b	1.7 ± 0.1 ^a
Fe	13.9 ± 0.8 ^a	16.2 ± 1.2 ^a
Zn	3.8 ± 0.0 ^a	3.9 ± 0.6 ^a
Sr	1.6 ± 0.1 ^b	2.5 ± 0.2 ^a
GalA (%)	41.9 ± 3.4 ^b	54.6 ± 2.3 ^a
Rha (%)	6.5 ± 0.1 ^a	4.9 ± 0.2 ^b
Ara (%)	13.7 ± 0.2 ^a	10.3 ± 0.4 ^b
Gal (%)	14.7 ± 0.5 ^a	9.9 ± 0.1 ^b
Xyl (%)	0.2 ± 0.0 ^a	0.1 ± 0.01 ^b
Man (%)	2.8 ± 0.1 ^b	7.0 ± 0.1 ^a
Glc (%)	20.2 ± 0.6 ^a	13.3 ± 0.3 ^b
GalA/Rha	6.5 ± 0.2 ^b	11.2 ± 0.3 ^a
(Ara + Gal)/Rha	4.4 ± 0.0 ^a	4.1 ± 0.1 ^b
Mw (kDa)	539.0/21.0	800.0
Mn (kDa)	341.0/2.7	328.0
Mw/Mn	1.6/7.9	2.3
DM (%)	4.0	25.0
Water holding capacity (g/g)	5.2 ± 0.4 ^a	4.6 ± 0.4 ^a
Oil holding capacity (g/g)	3.8 ± 0.2 ^a	3.3 ± 0.1 ^b
Emulsifying activity (m ² /g)	38.5 ± 0.6 ^a	26.0 ± 0.5 ^b
DPPH (IC50, mg/g DW)	24.3 ± 0.2 ^a	19.1 ± 0.1 ^b
FRAP (mg TE/g DW)	61.0 ± 0.5 ^b	89.1 ± 0.7 ^a

Data are mean values ± standard deviation values with letters (a-b) were Significantly different (Tukey, $p < 0.05$). UAE: ultrasound-assisted extraction; CAE: conventional acid extraction.

from date fruits as a source of health supplements [29,30].

3.3. Structural characterization of date pectins

It is well known the method of extraction can show strong influence on the structure of pectin and consequently, on their technological properties and biological activities [31]. In the present work, pectins extracted from date fruits with and without the assistance of ultrasound in acidic media, were structurally evaluated and compared. Initially, neutral sugars, GalA content, degree of methyl esterification number (DM) and average estimated molecular weight (Mw) for the pectins obtained, are included in Table 3. Regarding the monomeric composition, in all cases, GalA was the most predominant carbohydrate, being significantly upper in the date pectin extracted by US (54.6% vs 41.9%). Remarkably, Nesrine et al. [17] reported a content of GalA of 51% after a conventional extraction of pectin under the same conditions (95 °C, 90 min, pH 1.5) from *P. dactylifera* (Arecaceae). These dissimilarities could be attributed to the different variety of date fruits and method of analysis (colorimetric vs GC), among other factors.

Comparing the data of Table 3, the ratio GalA/Rha shows the number of GalA residues per Rha residue and gives an indication of the RG-I presence in relation to HG content. The structure of pectin obtained by UAE presented more predominance of HG than that obtained by CAE (11.2 vs 6.5%), indicating that the stronger conditions of the conventional treatment could have provoked a major depolymerisation starting from the linkages between the GalA units. In addition, the date pectin obtained conventionally exhibited high amounts of galactose and arabinose surpassing rhamnose content, which could show the substitution of the RG I branching along the HG with numerous galactans, arabinogalactans and arabinans side chains [32,33]. Although, regardless extraction method, the relatively high glucose content derived from cellulose and hemicellulose could suggest that these non-pectin polysaccharides would not have been completely removed during extraction, it is important to highlight that the assistance by ultrasound can improve the purity of pectin, reducing the presence of glucose (13.3 vs 20.2%) [34,35].

The molecular weight also plays an important role in the thickening, gelling and stabilizing of pectins [36]. The modifications monitored by HPSEC-ELSD regarding the estimation of Mw, Mn and polydispersity index of the different fragments are also included in Table 3 and shown in Fig. 2. Unlike UAE sample, it is noteworthy that date pectins extracted conventionally with nitric acid exhibited a bimodal Mw distribution. The first fragment consisted of Mw around 539 kDa, which could correspond to pectin, whereas the second one, with 21 kDa, could be related to modified pectins. In the case of pectin from US treatment, only one peak was detected with an estimated value of Mw of around 800

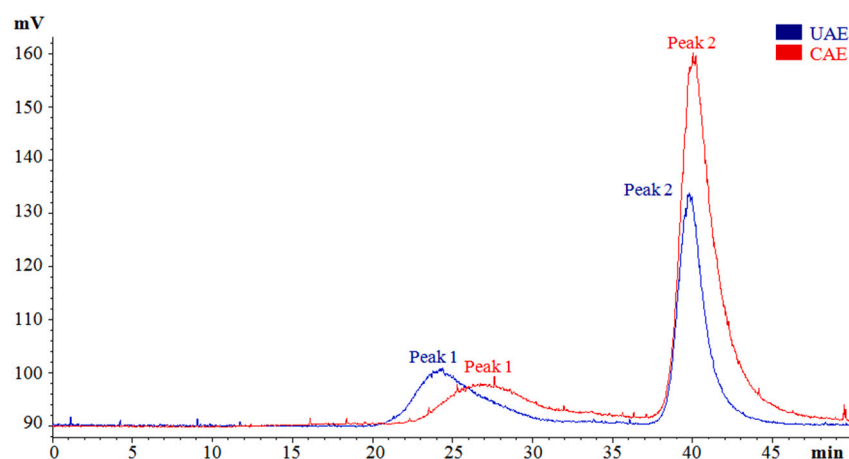


Fig. 2. Chromatographic HPSEC-ELSD profiles of date fruit pectins obtained by ultrasound-assisted extraction (UAE) and conventional acid extraction (CAE).

kDa. These results could indicate that the use of nitric acid as extracting agent without the assistance of US had a depth effect on the reduction of Mw as result of a depolymerisation, in agreement with the above-mentioned results on the content of GalA. However, taking into account the first fragment found in CAE pectin, the Mn was similar in both

samples. In other words, the fragment found in UAE consisted of a wider distribution of the Mw in comparison with the first one exhibited in pectin extracted conventionally (2.3 vs 1.6). Remarkably, the second fragment of pectin extracted at the highest temperature (90 °C) showed the greatest polydispersity (7.9), indicating the hydrolysis was occurred

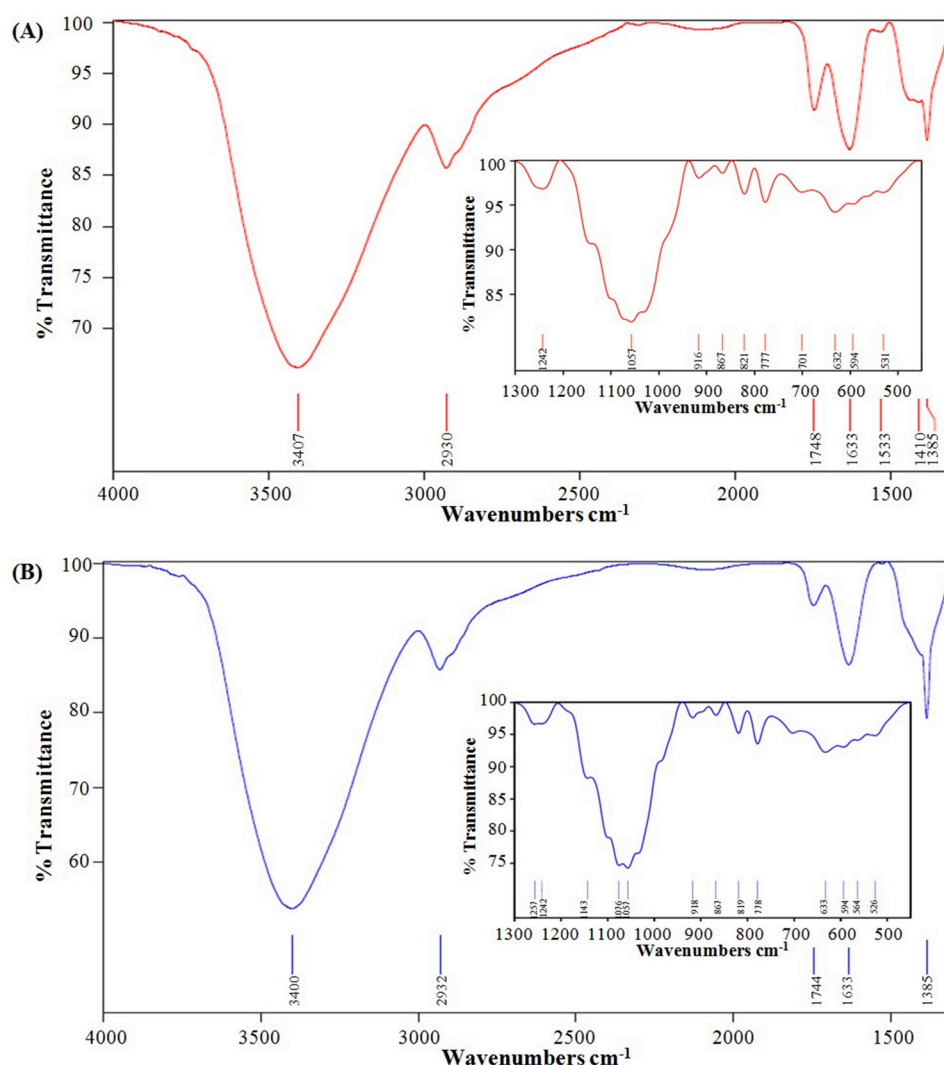


Fig. 3. FT-IR spectrum of date fruit pectins obtained by ultrasound-assisted extraction (A) and conventional acid extraction (B).

in different degree [37]. In general, these results can underline that conventional treatment had a stronger effect on homogalacturonan structure of pectins than the ultrasonic treatment.

The FT-IR spectra shows the functional groups provides structural information about the extracted date fruit pectins (Fig. 3). No major structural differences among FT-IR spectra of both date pectins were observed, except in the absorption bands 1533 , 1410 and 701 cm^{-1} in those obtained by the UAE method, and 1257 , 1143 , 1076 and 564 cm^{-1} absorption bands in pectins obtained by the CAE method. The characteristic functional groups in the wavelengths which extends from 500 to 4000 cm^{-1} revealed that a broad and strong peak near to 3400 cm^{-1} caused by O–H stretching vibration (hydroxyl groups) due to intra- and intermolecular hydrogen bonds of the galacturonic acid polymer was observed in UAE and CAE pectins. A low intensity peak at around 2930 cm^{-1} corresponds to C–H vibration including CH , CH_2 , and CH_3 stretching and bending vibrations occurred. The peak around 1748 cm^{-1} was related to the absorptions of esterified carboxyl ($-\text{COOR}$), whereas the peak at 1633 cm^{-1} was assigned to asymmetric and symmetric stretching of the carboxylate group, respectively [38]. The O– CH_3 stretching bands were not useful for qualitative pectin analysis. However, the ester carbonyl and carboxylate stretching bands could be used for classification [39]. The esterified CH_3 group presented bands in the region 1350 – 1450 cm^{-1} , with symmetric stretching of CH_3 at around 1380 cm^{-1} and asymmetric stretching of CH_3 at around 1440 cm^{-1} . Stretching vibrations of C–O, C–C, and ring structures, as well as deformation of CH_2 groups (characteristic of polysaccharides), produced bands in the region 1250 – 850 cm^{-1} . Bands characteristic of polysaccharides are located close to each other, which can cause identification problems due to band overlapping [40]. The major functional groups in pectins usually showed characteristic peaks in the region between 1000 and 2000 cm^{-1} [41] with intense peaks due to the high homogalacturonan content in pectin. A less intense peak at around 1149 cm^{-1} was characteristic of C–O–C vibrations of glycosidic linkages. Bands at 1045 and 1076 cm^{-1} were associated with sugars such as arabinose, xylose, and galactose, while a band at around 910 cm^{-1} indicated the degree of methyl esterification [42].

In the samples analysed, these qualitative changes were also quantified and expressed as DM (Table 3). All samples analysed were low-methoxyl pectins with values of DM ranging from four to 25% for pectin extracted conventionally and using ultrasonic bath, respectively. These results corroborated that the former could have suffered a higher degradation by removing the methyl ester groups due to the use of nitric acid as extracting agent.

3.4. Techno-functional properties of date pectins

The techno-functional potential of date pectins was evaluated based on three characteristics. The WHC/OHC are the abilities of a material to retain water/oil after centrifugation, respectively [43]. As illustrated in Table 3, the two types of pectin presented good techno-functional properties. No significant differences were observed between the WHC of both pectins, although the value of this property in CAE sample was higher than in UAE pectin. Conversely, the OHC of conventional pectin was significantly upper to the extracted using ultrasound, although the difference was very low. The same tendency was observed in the emulsifying capacity, with higher value in CAE sample. This could be mainly attributed to the different structure of CAE pectin [44].

The proteinaceous component of pectins acts as an anchor at the oil/water interface, while the attached polysaccharide chains provide the thick protective layer that confers steric stabilization during extended storage [45–48]. Leroux et al. [47] postulated that pectins are able to reduce the interfacial tension between oil and water and can be useful in the preparation of emulsions. These results revealed that the new pectic materials isolated from Degla-Beida date fruits may have important applications as emulsifiers in different sectors of the food industry, and that the pectin obtained by conventional extraction has slightly better

techno-functional properties than that obtained by US.

3.5. In vitro antioxidant activity

It is known that date fruits exhibit a high antioxidant capacity due to its composition [49–52]. Numerous studies have demonstrated that pectins can show excellent free radical scavenging ability and antioxidant activity [53–55]. In the current work, the effect of UAE and CAE on the antioxidant activity of date fruit pectins was investigated by the measurement of DPPH radical scavenging activity and ferric reducing antioxidant power (FRAP). The DPPH radical is usually used as one of the effective means for evaluating the free radical scavenging activity of antioxidants. The different extractions showed significant differences ($p < 0.05$) in both methods. The IC_{50} value of DPPH radical scavenging rate was higher in the case of CAE pectins than in UAE samples, providing a lower ability of scavenging DPPH radical in the former. However, the reducing power was lower in CAE than in UAE pectin. According to these data, extraction by the assistance of ultrasound gave rise to pectin with better antioxidant activity than the conventional treatment. These results seem also to be related to the different structures, as above indicated, and probably to the content of GalA, since the extracted pectins by UAE presented higher amount of GalA than the other pectin samples. It has been postulated that the favorable structure of pectin towards reducing power was attributed to the presence of abundant -OH and/or -COOH groups [56].

3.6. In vitro anti-diabetic activity

Diabetes mellitus is a metabolic disease likely caused by defective insulin secretion and more likely by oxidative injury and dysfunction of β cells [56]. This metabolic disorder constitutes a major challenge with regards to the life quality and imposes a consistent economic burden on the global health care systems [57]. Faced with this challenge, the scientists throughout the world turn to phytochemicals to avoid the adverse effects associated with conventional hypoglycemic drugs. For instance, natural products have gained the attention of many researchers as alternative and complementary to chemically synthesized drugs [58]. Date fruits have demonstrated antidiabetic effects. The mechanism is not yet perfectly known but it could be ascribed to an increase in insulin output and a decrease in glucose absorption in the intestine [59]. In this context, date pectin could play an important role in this property since pectins from different sources have demonstrated to have antidiabetic effect [61].

3.6.1. Glucose adsorption capacity

Glucose adsorption is a capacity of dietary fiber that could lead to decreased postprandial blood glucose levels. This *in vitro* measurement is a useful index to predict the effect of dietary fibres on glucose levels in the gastrointestinal tract *in vivo* [60]. Results showed that date pectins were effective in adsorbing glucose at any glucose concentrations, increasing their adsorption along with the glucose concentration in the medium (10 to $200\text{ mmol}\cdot\text{L}^{-1}$) (Fig. 4A). These results suggest the ability of date pectins to attenuate available glucose in the intestinal tract. Regarding the extraction method, pectins obtained by UAE had the highest capacity to adsorb glucose ($4.0 \pm 0.2\text{ mmol}\cdot\text{g}^{-1}$), as compared to pectins obtained by conventional acid extraction ($2.6 \pm 0.2\text{ mmol}\cdot\text{g}^{-1}$) at $200\text{ mmol}\cdot\text{L}^{-1}$ of glucose, probably due to the higher Mw and related viscosity of UAE samples. Glucose adsorption capacity is dependent on some physicochemical properties such as viscosity, microstructure, particle size, and soluble dietary fiber content [60]. Dietary fibres with higher surface area and more porous microstructure may have stronger capacity to adsorb glucose [61,62]. Michel et al. [63] observed that two different date extracts reduced the serum glucose levels in induced diabetic rats. Similarly, Ahmed et al. [64] revealed important hypoglycemic effects of Aseel dates in the treatment of diabetes. However, no previous data on pectin from date have been reported so far.

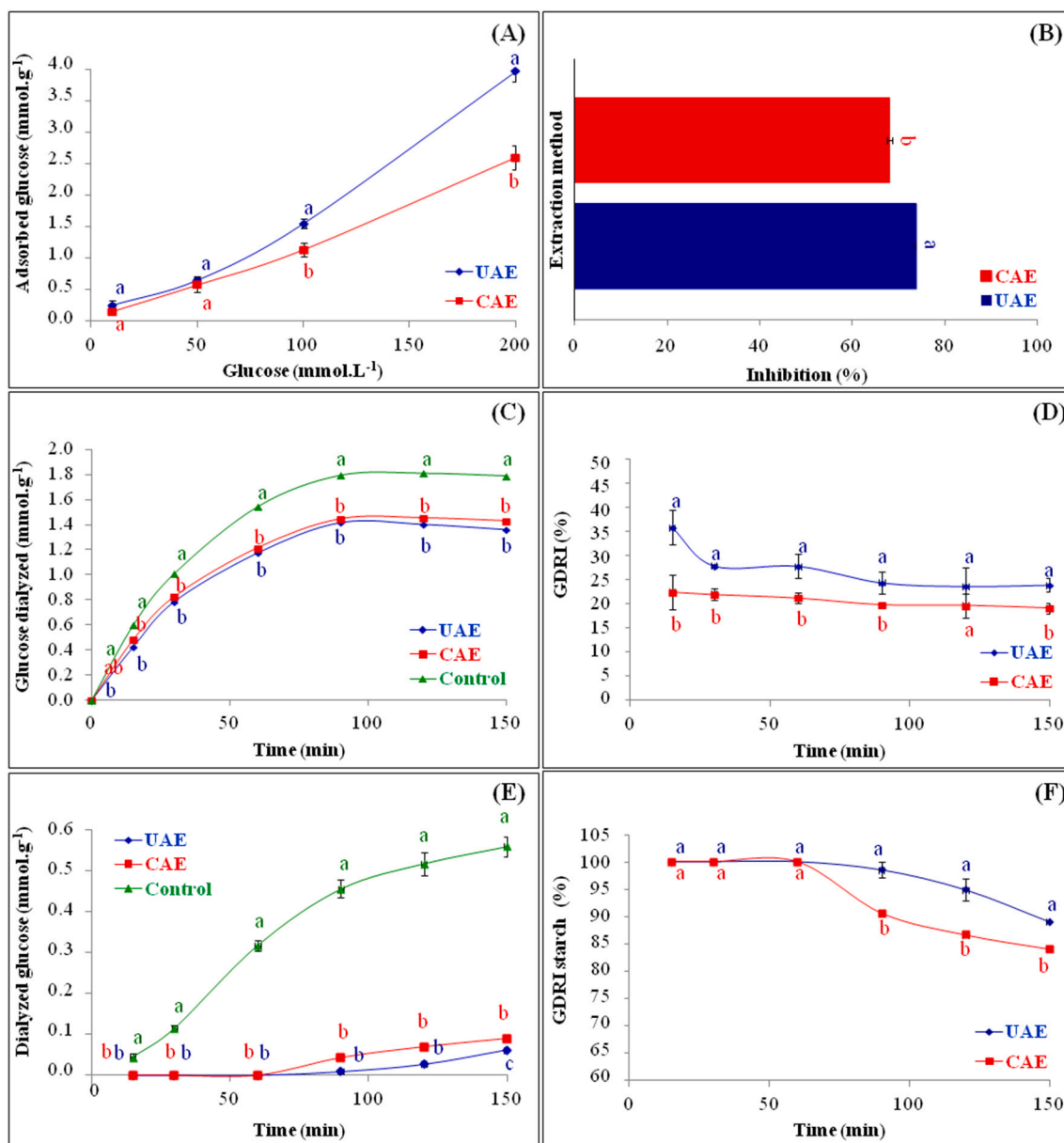


Fig. 4. Effect of date fruit pectins on glucose adsorption capacity (mmol g⁻¹) (A), α -amylase inhibition (B), glucose diffusion kinetics (0–150 min) (C), glucose diffusion retardation index (GDMI) (D), starch hydrolysis kinetics (0–150 min) (E), and GDMI for glucose release from starch (F). The results are reported as mean $\pm$ SD ($n = 3$). Results with different letters significantly ($p < 0.05$) differ according to ANOVA and Tukey's multiple range test.

3.6.2. *In vitro* α -amylase inhibition

One of the therapeutic approaches in diabetes treatment is the reduction of the hyperglycemic conditions by inhibiting carbohydrate-digesting enzymes [65]. According to various *in vivo* studies, inhibition of α -amylase is assumed to be one of the most effective approaches for diabetes care. Natural α -amylase inhibitors are being investigated as new candidates to control hyperglycemia in diabetic patients, for they do not cause severe side effects [66]. The *in vitro* α -amylase study, shown as % inhibition in Fig. 4B, revealed that date pectins were able to inhibit α -amylase, pectins obtained by UAE possessing significantly higher ($p < 0.05$) inhibitory effect than pectins obtained by CAE. El Abed et al. [67] displayed that an aqueous ethanolic extract from dates has a powerful inhibition of the enzymes related to Type 2 diabetes, since they found that date extracts exhibit a strong inhibitory activity against digestive enzymes, confirming its ability to regulate glucose absorption in the intestinal tracts of rats. Considering pectin, this polysaccharide obtained from citrus has been demonstrated to decrease starch digestion rate due

to numerous factors, not only related to the rheological properties but also to the interaction of pectin with the involved enzyme that modify its conformation probably acting as a barrier between the enzyme and the starch [62]

3.6.3. *In vitro* glucose dialysis retardation capacity

The retardation of glucose transportation across small intestinal mucosa is another major way to lower the rise of postprandial blood glucose [68]. Dietary fibres reduced diffusion of sugars from the intestinal lumen to the brush border of the small intestine [69]. It could be well simulated by *in vitro* dialysis membrane [60]. As shown in Fig. 3C, the diffusion of glucose was time-dependent, date pectins could significantly decrease the amount of glucose dialyzed ($p < 0.05$) regarding control, whereas no differences were found due to extraction. GDMI is an indicator to predict the delayed effect of fibres on glucose diffusion in the intestinal tract [68]. Maximal GDMI values were reached after 15 min for pectins obtained by ultrasound-assisted and conventional acid

extractions (35.87 and 22.53%, respectively) (Fig. 4D). Date pectins GDRI values showed that they might slow the diffusion of glucose and thus reduce the level of serum postprandial glucose.

3.6.4. *In vitro* starch digestibility

The effect of date pectins on the starch digestibility was evaluated and presented in Fig. 4E and F. This assay allowed evaluating the effect of pectin samples on both the glucose release from starch and its subsequent diffusion. CAE and UAE date pectins exhibited high capacity to reduce the starch digestibility, producing during the first 60 min a 100% inhibition of glucose production and its diffusion. After 90 min, pectins obtained by ultrasound-assisted extraction presented higher capacity to delay the starch digestibility than that pectins obtained by conventional acid extraction. The decrease of starch digestion rate could be due to the enzyme binding to pectin, hindering the access the enzyme to the starch; or the increased viscosity of the starch suspensions in the presence of pectin that reduces its accessibility to starch, as above indicated. [61,70].

Therefore, UAE seems to be an alternative process to the traditional chemical methods to produce pectin polysaccharides with enhanced hypoglycemic properties [71]. Few in-depth studies exist documenting the relationship between UAE conditions and the structure or functional properties of pectins. More concretely these are the first studies on the systematic extraction of pectin from dates by UAE and on the *in vitro* evaluation of its antidiabetic properties. Although a deeper understanding of this relationship issue is still required [72], Muñoz-Almagro et al. [73] revised the role of pectin as an antidiabetic agent, and showed the intricate mechanisms that can be involved. In the present paper, it seems clear that the higher content of GalA, HG and Mw, together with a lower amount of glucose, could have exerted a positive control on the *in vitro* antidiabetic properties.

4. Conclusions

This innovative investigation tries to highlight the valorization of an Algerian common date (*Phoenix dactylifera* L.) variety (Degla-Beida) as a potential source to produce pectins by a simple, fast, energy efficient, scalable and eco-friendly technique. A high correlated quadratic polynomial mathematical model was developed and its significance was investigated. Under the optimal conditions, experimental yield was very close to the predicted value. Systematic characterization of obtained pectin from date fruits, newly explored in the present work, revealed their excellent physicochemical, techno-functional and biological properties. The different extraction conditions here used demonstrate different applications of pectin considering the diverse structural characteristic of the obtained molecules. Thus, pectins obtained by conventional extraction could be applied as food ingredient offering new structures to the increasing market of pectin. However, pectins from date extracted by the assistance of ultrasound present interesting antioxidant and antidiabetic properties. Although the intricate involved mechanisms deserve further investigation, antidiabetic tests highlighted the ultrasound obtained pectin as a potential better antidiabetic agent than that extracted without ultrasound.

Valorization approach developed in the present research provides a platform for waste recovery. In addition, it can provide benefits for farmers and food industry by enabling them to process the underutilized date fruits and develop a high-quality value-added product to enhance resource efficiency, which is among sustainable development goals in a context of circular economy.

CRedit authorship contribution statement

CRedit authorship contribution statement: **Kahina Djaoud** and **Nerea Muñoz-Almagro**: Investigation, Methodology, Writing - original draft, review & editing. **Khodir Madani** and **Lila Boulekbache-Makhlouf**: Supervision. **Vanesa Benítez**, **M Ángeles Martín-Cabrejas**

and Mar Villamiel: Funding acquisition, Supervision, Writing - original draft, review & editing.

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References

- [1] A. Younas, S.A. Naqvi, M.R. Khan, M.A. Shabbir, M.A. Jatoti, F. Anwar, M. Inam-Ur-Raheem, N. Saari, R.M. Aadil, Functional food and nutra-pharmaceutical perspectives of date (*Phoenix dactylifera* L.) fruit, *J. Food Biochem.* 44 (9) (2020), e13332.
- [2] FAOSTAT, FAOSTAT Database, Food and Agriculture Organization of the United Nations, Roma, 2021 <https://www.fao.org/faostat/fr/#data/QV>.
- [3] K. Djaoud, L. Boulekbache-Makhlouf, M. Yahia, H. Mansouri, N. Mansouri, K. Madani, A. Romero, Dairy dessert processing: effect of sugar substitution by date syrup and powder on its quality characteristics, *J. Food Process. Preserv.* 44 (5) (2020), e14414.
- [4] N. Echegaray, B. Gullón, M. Pateiro, R. Amarowicz, J.M. Misihairabgwi, J. M. Lorenzo, Date fruit and its by-products as promising source of bioactive components: a review, *Food Rev. Int.* (2021) 1–22.
- [5] S. Maqsood, O. Adiamo, M. Ahmad, P. Mudgil, Bioactive compounds from date fruit and seed as potential nutraceutical and functional food ingredients, *Food Chem.* 308 (2020), 125522.
- [6] J. Cui, C. Zhao, L. Feng, Y. Han, H. Du, H. Xiao, J. Zheng, Pectins from fruits: relationships between extraction methods, structural characteristics, and functional properties, *Trends Food Sci. Technol.* 110 (2021) 39–54.
- [7] L. Khedmat, A. Izadi, V. Mofid, S.Y. Mojtahedi, Recent advances in extracting pectin by single and combined ultrasound techniques: a review of techno-functional and bioactive health-promoting aspects, *Carbohydr. Polym.* 229 (2020), 115474.
- [8] S.A. Ibrahim, A.A. Ayad, L.L. Williams, R.D. Ayivi, R. Gyawali, A. Krastanov, S. O. Aljaloud, Date fruit: a review of the chemical and nutritional compounds, functional effects and food application in nutrition bars for athletes, *Int. J. Food Sci. Technol.* 56 (4) (2021) 1503–1513.
- [9] N. Muñoz-Almagro, A. Ruiz-Torralba, P. Méndez-Albiñana, E. Guerra-Hernández, B. García-Villanova, R. Moreno, M. Villamiel, A. Montilla, Berry fruits as source of pectin: conventional and non-conventional extraction techniques, *Int. J. Biol. Macromol.* 186 (2021) 962–974.
- [10] S. Huang, Z.-C. Tu, X.-M. Sha, H. Wang, Y.-M. Hu, Z.-Z. Hu, Gelling properties and interaction analysis of fish gelatin–low-methoxyl pectin system with different concentrations of Ca²⁺, *LWT* 132 (2020), 109826.
- [11] M. Marić, A.N. Grassino, Z. Zhu, F.J. Barba, M. Brncić, S.R. Brncić, An overview of the traditional and innovative approaches for pectin extraction from plant food wastes and by-products: ultrasound-, microwave-, and enzyme-assisted extraction, *Trends Food Sci. Technol.* 76 (2018) 28–37.
- [12] A.N. Grassino, J. Halambek, S. Djaković, S.R. Brncić, M. Dent, Z. Grabarić, Utilization of tomato peel waste from canning factory as a potential source for pectin production and application as tin corrosion inhibitor, *Food Hydrocoll.* 52 (2016) 265–274.
- [13] B.B.V. Guandalini, N.P. Rodrigues, L.D.F. Marczak, Sequential extraction of phenolics and pectin from mango peel assisted by ultrasound, *Food Res. Int.* 119 (2019) 455–461.
- [14] C.M. Galanakis, Functionality of food components and emerging technologies, *Foods* 10 (1) (2021) 128.
- [15] A. Jovanović, P. Petrović, V. Đorđević, G. Zdunić, K. Šavikin, B. Bugarski, Polyphenols extraction from plant sources, *Lekovite Sirovine* (37) (2017) 45–49.
- [16] K. Djaoud, L. Arkoub-Djermoune, H. Remini, S. Sait, M. Tazarourte, S. Hadjal, A. Romero, K. Madani, L. Boulekbache-Makhlouf, Syrup from common date variety (*Phoenix dactylifera* L.): optimization of sugars extraction and their quantification by high performance liquid chromatography, 2019.
- [17] S. Nesrine, O. Ouadia, B. Amina, A.H. Nadia, K. Omar, A. Abdelakder, Effect of pectin extract of date (*Phoenix dactylifera* L.) on erythrocytes oxidative damage and hematological parameters induced by lead in males rats, *J. Appl. Environ. Biol. Sci.* 6 (10) (2016) 41–49.
- [18] N. Rajendran, B. Harikumar, Thampi, Pectin—extraction from underground stem of banana and its structural, rheological, and textural analyses and grading, *J. Food Process. Preserv.* 45 (4) (2021), e15332.
- [19] N. Muñoz-Almagro, F. Rico-Rodríguez, P.J. Wilde, A. Montilla, M. Villamiel, Structural and technological characterization of pectin extracted with sodium citrate and nitric acid from sunflower heads, *Electrophoresis* 39 (15) (2018) 1984–1992.

- [20] N. Muñoz-Almagro, F. Rico-Rodríguez, M. Villamiel, A. Montilla, Pectin characterisation using size exclusion chromatography: a comparison of ELS and RI detection, *Food Chem.* 252 (2018) 271–276.
- [21] R. De la Peña Armada, M. Villanueva-Suárez, I. Mateos-Aparicio, High hydrostatic pressure processing enhances pectin solubilisation on apple by-product improving techno-functional properties, *Eur. Food Res. Technol.* 246 (2020) 1691–1702.
- [22] M.T. Pacheco, M. Villamiel, R. Moreno, F.J. Moreno, Structural and rheological properties of pectins extracted from industrial sugar beet by-products, *Molecules* 24 (3) (2019) 392.
- [23] X. Chen, Y. Qi, C. Zhu, Q. Wang, Effect of ultrasound on the properties and antioxidant activity of hawthorn pectin, *Int. J. Biol. Macromol.* 131 (2019) 273–281.
- [24] V. Benítez, M. Rebollo-Hernanz, S. Hernanz, S. Chantres, Y. Aguilera, M.A. Martín-Cabrejas, Coffee parchment as a new dietary fiber ingredient: functional and physiological characterization, *Food Res. Int.* 122 (2019) 105–113.
- [25] I.G. Moorthy, J.P. Maran, S. Muneeswari, S. Naganyashree, C. Shivamathi, Response surface optimization of ultrasound assisted extraction of pectin from pomegranate peel, *Int. J. Biol. Macromol.* 72 (2015) 1323–1328.
- [26] A. Hernoux-Villière, U. Lassi, J.-M. Léveque, An original ultrasonic reaction with dual coaxial frequencies for biomass processing, *Ultrason. Sonochem.* 20 (6) (2013) 1341–1344.
- [27] K. Ponnurugan, N.A. Al-Dhabi, J.P. Maran, K. Karthikeyan, I.G. Moorthy, N. Sivarajasekar, J.J.B. Manoj, Ultrasound assisted pectic polysaccharide extraction and its characterization with waste heads of *Helianthus annuus*, *Carbohydr. Polym.* 173 (2017) 707–713.
- [28] Y. Xu, L. Zhang, Y. Bailina, Z. Ge, T. Ding, X. Ye, D. Liu, Effects of ultrasound and/or heating on the extraction of pectin from grapefruit peel, *J. Food Eng.* 126 (2014) 72–81.
- [29] R.C. Skinner, J.C. Gigliotti, K.-M. Ku, J.C. Tou, A comprehensive analysis of the composition, health benefits, and safety of apple pomace, *Nutr. Rev.* 76 (12) (2018) 893–909.
- [30] M. Yates, M.R. Gomez, M.A. Martín-Luengo, V.Z. Ibañez, A.M.M. Serrano, MultivalORIZATION of apple pomace towards materials and chemicals. Waste to wealth, *J. Clean. Prod.* 143 (2017) 847–853.
- [31] Y. Lin, F. An, H. He, F. Geng, H. Song, Q. Huang, Structural and rheological characterization of pectin from passion fruit (*Passiflora edulis* f. *flavicarpa*) peel extracted by high-speed shearing, *Food Hydrocoll.* 114 (2021), 106555.
- [32] J.C. Amorim, L.C. Vriesmann, C.L. Petkowicz, G.R. Martinez, G.R. Noleto, Modified pectin from Theobroma cacao induces potent pro-inflammatory activity in murine peritoneal macrophage, *Int. J. Biol. Macromol.* 92 (2016) 1040–1048.
- [33] O. Yulianti, L. Matia-Merino, K.K. Goh, J. Mawson, M.A. Williams, C. Brennan, Characterization of gold kiwifruit pectin from fruit of different maturities and extraction methods, *Food Chem.* 166 (2015) 479–485.
- [34] W. Wang, X. Ma, P. Jiang, L. Hu, Z. Zhi, J. Chen, T. Ding, X. Ye, D. Liu, Characterization of pectin from grapefruit peel: a comparison of ultrasound-assisted and conventional heating extractions, *Food Hydrocoll.* 61 (2016) 730–739.
- [35] N. Yang, Y. Li, F. Xing, X. Wang, X. Li, L. Li, J. Yang, Y. Wang, M. Zhang, Composition and structural characterization of pectin in micropropagated and conventional plants of *Premna puberula* Pamp, *Carbohydr. Polym.* 260 (2021), 117711.
- [36] F. Dranca, M. Vargas, M. Oroian, Physicochemical properties of pectin from *Malus domestica* 'Fálticeni' apple pomace as affected by non-conventional extraction techniques, *Food Hydrocoll.* 100 (2020), 105383.
- [37] J. Chen, H. Cheng, Z. Zhi, H. Zhang, R.J. Linhardt, F. Zhang, S. Chen, X. Ye, Extraction temperature is a decisive factor for the properties of pectin, *Food Hydrocoll.* 112 (2021), 106160.
- [38] Y. Wandee, D. Uttapap, P. Mischnick, Yield and structural composition of pomelo peel pectins extracted under acidic and alkaline conditions, *Food Hydrocoll.* 87 (2019) 237–244.
- [39] E.E. Santos, R.C. Amaro, C.C.C. Bustamante, M.H.A. Guerra, L.C. Soares, R.E. S. Froes, Extraction of pectin from agroindustrial residue with an ecofriendly solvent: use of FTIR and chemometrics to differentiate pectins according to degree of methyl esterification, *Food Hydrocoll.* 107 (2020), 105921.
- [40] M. Szymanska-Chargot, A. Zdunek, Use of FT-IR spectra and PCA to the bulk characterization of cell wall residues of fruits and vegetables along a fraction process, *Food Biophys.* 8 (1) (2013) 29–42.
- [41] M.T. Oloye, J.M. Jabar, A.O. Adetuyi, L. Lajide, Extraction and characterization of pectin from fruit peels of *Irvingia gabonensis* and pulp of *Cola milleni* and *Theobroma cacao* as precursor for industrial applications, *Biomass Convers. Biorefin.* (2021) 1–9.
- [42] A. Baum, M. Dominiak, S. Vidal-Melgosa, W.G. Willats, K.M. Søndergaard, P. W. Hansen, A.S. Meyer, J.D. Mikkelsen, Prediction of pectin yield and quality by FTIR and carbohydrate microarray analysis, *Food Bioprocess Technol.* 10 (1) (2017) 143–154.
- [43] J.M. Fuentes-Alventosa, G. Rodríguez-Gutiérrez, S. Jaramillo-Carmona, J. Espejo-Calvo, R. Rodríguez-Arcos, J. Fernández-Bolaños, R. Guillén-Bejarano, A. Jiménez-Araujo, Effect of extraction method on chemical composition and functional characteristics of high dietary fibre powders obtained from asparagus by-products, *Food Chem.* 113 (2) (2009) 665–671.
- [44] S. Baissis, H. Ghanem, D. Fahoul, A. Lekbir, Comparison of structure and emulsifying activity of pectin extracted from apple pomace and apricot pulp, *World J. Dairy Food Sci.* 5 (1) (2010) 79–84.
- [45] M. Akhtar, E. Dickinson, J. Mazoyer, V. Langendorff, Emulsion stabilizing properties of depolymerized pectin, *Food Hydrocoll.* 16 (3) (2002) 249–256.
- [46] F. Abbès, W. Kchaou, C. Blecker, M. Ongena, G. Lognay, H. Attia, S. Besbes, Effect of processing conditions on phenolic compounds and antioxidant properties of date syrup, *Ind. Crop. Prod.* 44 (2013) 634–642.
- [47] J. Leroux, V. Langendorff, G. Schick, V. Vaishnav, J. Mazoyer, Emulsion stabilizing properties of pectin, *Food Hydrocoll.* 17 (4) (2003) 455–462.
- [48] P.A. Williams, C. Sayers, C. Viebke, C. Senan, J. Mazoyer, P. Boulenguer, Elucidation of the emulsification properties of sugar beet pectin, *J. Agric. Food Chem.* 53 (9) (2005) 3592–3597.
- [49] M.Z. Alam, M.S. Alhebsi, S. Ghnimi, A. Kamal-Eldin, Inability of total antioxidant activity assays to accurately assess the phenolic compounds of date palm fruit (*Phoenix dactylifera* L.), *NFS J.* 22 (2021) 32–40.
- [50] K. Djaoud, M. Daglia, A.J. Sokeng, F. Kermiche, L. Arkoub, K. Madani, L. B. Makhoul, RP-HPLC-PDA-ESI-MS/MS screening of bioactive compounds from Degla-Beida dates: conventional and green extraction technologies, *Ann. Univ. Dunarea Jos Galati Fascicle VI: Food Technol.* 44 (1) (2020).
- [51] O. Djaoudene, M.B. Bey, H. Louaiche, Physicochemical characteristics and nutritional compositions of some date (*Phoenix dactylifera* L.) fruit cultivars, <sb: contribution><sb:title>Acta Univ. Cibiensis Ser. E</sb:title></sb: contribution><sb: host><sb: issue><sb: series><sb: title>Food Technol.</sb: title></sb: series></sb: issue></sb: host> 23 (2) (2019) 129–138.
- [52] A. Messaoudi, M. Dekmouche, Z. Rahmani, C. Bensaci, Phenolic profile, antioxidant potential of date (*Phoenix dactylifera* Var. Degla Baidha and Deglet-Nour) seeds from Debila region (Oued Souf, Algeria), <sb: contribution><sb: title>Asian J. Res.</sb:title> </sb: contribution><sb: host><sb: issue><sb: series><sb: title>Chem.</sb:title></sb: series></sb: issue></sb: host> 14 (1) (2021) 37–41.
- [53] G.O. Isopencu, A. Stoica-Guzun, C. Busuioic, M. Stroescu, I.M. Deleanu, Development of antioxidant and antimicrobial edible coatings incorporating bacterial cellulose, pectin, and blackberry pomace, *Carbohydr. Polym. Technol. Applic.* 2 (2021), 100057.
- [54] M. Kumar, J. Potkule, M. Tomar, S. Punia, S. Singh, S. Patil, S. Singh, T. Ilakiya, C. Kaur, J.F. Kennedy, Jackfruit seed slimy sheath, a novel source of pectin: studies on antioxidant activity, functional group, and structural morphology, *Carbohydr. Polym. Technol. Applic.* 2 (2021), 100054.
- [55] C. Tan, D. Li, H. Wang, Y. Tong, Y. Zhao, H. Deng, Y. Kong, C. Shu, T. Yan, X. Meng, Effects of high hydrostatic pressure on the binding capacity, interaction, and antioxidant activity of the binding products of cyanidin-3-glucoside and blueberry pectin, *Food Chem.* 344 (2021), 128731.
- [56] M.S. Refat, R.Z. Hamza, A.M.A. Adam, H.A. Saad, A.A. Gobouri, F.S. Al-Harbi, F. A. Al-Salmi, T. Altalhi, S.M. El-Megharbel, Quercetin/zinc complex and stem cells: a new drug therapy to ameliorate glycometabolic control and pulmonary dysfunction in diabetes mellitus: structural characterization and genetic studies, *PLoS one* 16 (3) (2021), e0246265.
- [57] L. Magueresse-Battistoni, H. Vidal, D. Naville, Environmental pollutants and metabolic disorders: the multi-exposure scenario of life, *Front. Endocrinol.* 9 (2018) 582.
- [58] N. Lammari, F. Froio, M. Louaer, M.C. Cristiano, C. Bensouici, D. Paolino, O. Louaer, A.H. Meniai, A. Elaissari, <sb: contribution><sb: title>Poly (ethyl acrylate-co-methyl methacrylate-co-trimethylammoniumethyl methacrylate chloride) (Eudragit RS100) nanocapsules as nanovector carriers for Phoenix dactylifera L.</sb: title></sb: contribution><sb: host><sb: issue><sb: series><sb: title>seeds oil: a versatile antidiabetic agent</sb:title></sb: series></sb: issue></sb: host>, *Biomacromolecules* 21 (11) (2020) 4442–4456.
- [59] M.I. Hussain, M. Farooq, Q.A. Syed, Nutritional and biological characteristics of the date palm fruit (*Phoenix dactylifera* L.)—a review, *Food, Bioscience* 34 (2020), 100509.
- [60] J. Qi, Y. Li, K.G. Masamba, C.F. Shoemaker, F. Zhong, H. Majeed, J. Ma, The effect of chemical treatment on the in vitro hypoglycemic properties of rice bran insoluble dietary fiber, *Food Hydrocoll.* 52 (2016) 699–706.
- [61] S. Dhital, M.J. Gidley, F.J. Warren, Inhibition of α -amylase activity by cellulose: kinetic analysis and nutritional implications, *Carbohydr. Polym.* 123 (2015) 305–312.
- [62] N. Muñoz-Almagro, M. Vendrell-Calatayud, P. Méndez-Albiñana, R. Moreno, M. P. Cano, M. Villamiel, Extraction optimization and structural characterization of pectin from persimmon fruit (*Diospyros kaki* Thunb. var. Rojo brillante), *Carbohydr. Polym.* 272 (2021), 118411.
- [63] T. Michel, M. Halabalaki, A.-L. Skaltsounis, New concepts, experimental approaches, and dereplication strategies for the discovery of novel phytoestrogens from natural sources, *Planta Med.* 79 (07) (2013) 514–532.
- [64] S. Ahmed, R.A. Khan, S. Jamil, S. Afroz, Antidiabetic effects of native date fruit Aseel (*Phoenix dactylifera* L.) in normal and hyperglycemic rats, *Pak. J. Pharm. Sci.* 30 (5) (2017).
- [65] K. Arun, S. Thomas, T. Reshmitha, G. Akhil, P. Nisha, Dietary fibre and phenolic-rich extracts from *Musa paradisiaca* inflorescence ameliorates type 2 diabetes and associated cardiovascular risks, *J. Funct. Foods* 31 (2017) 198–207.
- [66] B. Liu, Z. Kang, W. Yan, Synthesis, stability, and antidiabetic activity evaluation of (–)-epigallocatechin gallate (EGCG) palmitate derived from natural tea polyphenols, *Molecules* 26 (2) (2021) 393.
- [67] H. El Abed, M. Chakroun, I. Fendri, M. Makni, M. Bouaziz, N. Drira, H. Mejdoub, B. Khemakhem, Extraction optimization and in vitro and in vivo anti-postprandial hyperglycemia effects of inhibitor from *Phoenix dactylifera* L. parthenocarpic fruit, *Biomed. Pharmacother.* 88 (2017) 835–843.
- [68] X. Meng, C. Wu, H. Liu, Q. Tang, X. Nie, Dietary fibers fractionated from gardenia (*Gardenia jasminoides* Ellis) husk: structure and in vitro hypoglycemic effect, *J. Sci. Food Agric.* 101 (2020) 3723–3731.

- [69] A. Lovegrove, C. Edwards, I. De Noni, H. Patel, S. El, T. Grassby, C. Zielke, M. Ulmius, L. Nilsson, P. Butterworth, Role of polysaccharides in food, digestion, and health, *Crit. Rev. Food Sci. Nutr.* 57 (2) (2017) 237–253.
- [70] Y. Bai, P. Wu, K. Wang, C. Li, E. Li, R.G. Gilbert, Effects of pectin on molecular structural changes in starch during digestion, *Food Hydrocoll.* 69 (2017) 10–18.
- [71] L.N. Gerschenson, E.N. Fissore, A.M. Rojas, A.M.I. Encalada, E.F. Zukowski, R.A. H. Coelho, Pectins obtained by ultrasound from agroindustrial by-products, *Food Hydrocoll.* 118 (2021), 106799.
- [72] S. Zhang, G.I. Waterhouse, F. Xu, Z. He, Y. Du, Y. Lian, P. Wu, D. Sun-Waterhouse, Recent advances in utilization of pectins in biomedical applications: a review focusing on molecular structure-directing health-promoting properties, *Crit. Rev. Food Sci. Nutr.* (2021), <https://doi.org/10.1080/10408398.2021.1988897>.
- [73] N. Muñoz-Almagro, A. Montilla, M. Villamiel, Role of pectin in the current trends towards low-glycaemic food consumption, *Food Res. Int.* 140 (2021), 109851, <https://doi.org/10.1016/j.foodres.2020.109851-34>.