# Microwave vs. conventional extraction of pectin from *Malus domestica* 'Fălticeni' pomace and its potential use in hydrocolloid-based films

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**Abstract**

Conventional extraction (CE) and microwave-assisted extraction (MAE) were compared in terms of efficiency and quality of pectin in two separate processes aimed to extract pectin from *Malus domestica* 'Fălticeni' apple pomace. A similar extraction yield in a shorter extraction time was observed for the microwave-assisted procedure as compared to CE, while the galacturonic acid content and the degree of esterification of pectin were similar for both methods. Apple pectin extracted from this plant source by both methods had high galacturonic acid content, degree of esterification and molecular weight. Considering the high efficiency of microwave-assisted extraction and the composition of the obtained pectin, microwave-assisted apple pectin extracted under optimal conditions was used to produce edible films in combination with hydroxypropyl methylcellulose (HPMC). Films formulated with pectin from microwave extraction had significant lower oxygen permeability as compared to plasticized pure HPMC films, which makes microwave

extracted pectin suitable for film-forming applications in which a good barrier to oxygen is required.

**Keywords:** pectin; extraction; *Malus domestica* 'Fălticeni'; edible film

## 1. Introduction

The statistical data regarding crop production recorded by the Food and Agriculture Organization of the United Nations (FAO) shows a significant growth of production quantity for apples in the last few years. From this production, it was estimated that about 10 million tons of pomace are discarded each year as waste by the processing industries (Chen & Lahaye, 2021). The waste consists of 5–10% liquid sludge and 25–30% solid pomace, which has high moisture content (70-75%) and is rich in carbohydrates and other nutrients thus being highly susceptible to microbial activity (Dhillon et al., 2013). Because apple pomace has high pectin content, which accounts for 4.6-20.9% on a dry-weight basis (Zhao et al., 2020), and also contains other cell wall polysaccharides (xyloglucans, cellulose and hemicellulose), pectin production is considered its best use with large economic benefits (Luo et al., 2020). Apple pomace was reported to cover about 14% of the source materials for pectin extraction, while citrus peel is the main source (85%) of worldwide pectin production (Chen et al., 2021; Ciriminna et al., 2016). However, as pectin market reached 77,611 tonnes in 2019 and was estimated to expand at a CAGR (compound annual growth rate) of 5.1% between 2020 and 2025 (IMARC Group, 2019), other wastes discarded from agricultural, agro industry and food industry may be considered to expand the production of pectin and create a more sustainable supply (Reichembach & Petkowicz, 2021).

The apple hybrid *Malus domestica* 'Fălticeni' was developed through the free pollination of the Jonathan apple variety in the north-eastern region of Fălticeni, Romania, with the purpose

of obtaining an increased apple production (Dranca & Oroian, 2018a). By processing 'Fălticeni' apples into juice, the evaluation of the resulting apple pomace as a suitable pectin source became of interest. We conducted early studies on the influence of extraction conditions (acid type and pomace particle size) on pectin yield and purity (Dranca & Oroian, 2018a) and studied the outcome of the application of various techniques for pectin extraction from this plant source. Some of these extraction techniques, which include ultrasound-assisted extraction (Dranca & Oroian, 2019c), sequential ultrasound-assisted extraction – heating treatment (Dranca & Oroian, 2019b) and enzyme-assisted extraction (Dranca et al., 2020; Dranca & Oroian, 2019a), resulted in an extraction yield below that obtained in early studies focused on a comparison between mineral and organic acid extraction of pectin from *Malus domestica* 'Fălticeni' pomace (Dranca & Oroian, 2018a). Considering this outcome and also previous studies that showed that microwave-assisted extraction can lead to high extraction yields in a short processing time (Rodsamran & Sothornvit, 2019a; Sucheta et al., 2020; Thu Dao et al., 2021), this extraction technique was applied to improve the extraction of pectin from the selected plant source.

Important structural characteristics such as the distribution of galacturonic acid (GalA) units, the composition of neutral monosaccharides and the degree of methyl- and/or acetyl-esterification of GalA units in the main pectic domains (homogalacturonan, rhamnogalacturonan-I, and rhamnogalacturonan-II) were thoroughly studied for pectin extracted from various plant sources. The determination of GalA content, neutral monosaccharides composition, degree of methylation, as well as of the molecular weight are a fundamental part of pectin analysis because these properties form the basis for its various food and non-food applications (Adetunji et al., 2017). Furthermore, water absorption capacity, the interactions with other compounds, the rheological properties and the ability to form gels are all dependent on the degree of esterification and the botanical origin of the polysaccharide (Pancerz et al., 2019). Studies on the

physicochemical properties of pectin from apple pomace highlighted a GalA content of minimum 58.6%, a degree of esterification between 52.51 and 76.4%, 14.3-31.1% neutral monosaccharide content, and a molecular weight of 331-899 kDa (Dranca & Oroian, 2018b). Apple pectin was found suitable for use as thickening agent, but less suitable for emulsification by comparison to sugar beet pectin and citrus pectin (Dranca et al., 2020; Schmidt et al., 2015).

Apart from its uses as gelling, stabilizing, or thickening agent in the food industry, pectin is also considered a suitable polymer matrix for the development of edible films due to its gelling properties, edibility, biodegradability and biocompatibility (Espitia et al., 2014). Research on the use of pectin to produce edible films intended as food packaging considered the various sources for pectin extraction, including industrial waste, and also other components (polymers, plasticizers, essential oils) that can be blended with pectin to achieve the desired properties of the edible film. In this sense, Baron et al. (2017) developed films based on chitosan and orange peel pectin in different proportions. Citrus pectin-based films with clove bud essential oil have been also evaluated (Nisar et al., 2018). Pectin from mango peel waste was combined with low methoxyl pectin to formulate a film with applications as drug delivery system or edible film (Chaiwarit et al., 2020). Pineapple peel pectin extract solution was proposed as natural plasticizer to produce films, which act as good water vapor barrier and have antioxidant properties (Rodsamran & Sothornvit, 2019b). Rodsamran & Sothornvit (2019c) incorporated coconut water and lime peel extract into lime peel films that were effective in delaying soybean oil oxidation during a 30 day storage period. Other recent studies on pectin-based film were focused on the evaluation of sweet potato starch-lemon waste pectin with nanoparticles (Dash et al., 2019), commercial pectin-based films combined with corn flour, orange peel, muesli or beetroot powder (Sucheta et al., 2019), and citrus pectin-fish gelatin films (Bermúdez-Oria et al., 2019; Jridi et al., 2020). However, to the best

of our knowledge the studies on the evaluation of films based on pectin obtained from apple pomace are scarce.

This study aimed to extract pectin from *Malus domestica* 'Fălticeni' apple pomace by microwave-assisted extraction (MAE) as compared by conventional citric acid extraction (CE) to find the most efficient technique in terms of extraction yield and pectin quality (galacturonic acid content, degree of esterification and molecular weight), and to evaluate the potential film-forming application of the pectin obtained by MAE. The use of pectin from *Malus domestica* 'Fălticeni' apple pomace to produce films in combination with hydrocolloids such as hydroxypropyl methylcellulose (HPMC) has the potential to improve the mechanical and barrier properties and the thermal stability of the blended film, which can be used as packaging that provides to food products protection against external stress during storage.

## 2. Materials and methods

### 2.1. Materials

The apple pomace used for the extraction was obtained from the manufacturing process of juice using 'Fălticeni' apples, in a small scale unit; the resulting by-product was dried to constant weight in a laboratory oven with air circulation ZRD-A5055 (Zhicheng Analysis Instrument, China) at 60 °C and then powdered in a processor. The separation of apple pomace powder according to particle size was made with a sieve shaker model AS 200 (Retsch GmbH, Germany), and the pomace with particle sizes of 125–200 μm was used in the extraction.

The reagents used for pectin extraction, physicochemical analysis and film preparation were of analytical grade and were purchased from Merck KGaA (Germany) and Panreac Química SLU (Castellar del Vallès, Barcelona, Spain). HPLC grade acetonitrile was also purchased from Merck KGaA (Germany). Ethyl alcohol used for pectin precipitation and purification was

purchased from Redox Research & Analytic (Bucharest, Romania). Pullulan standards were purchased from Shodex (Japan).

### 2.2. Procedure of pectin extraction and purification

Conventional citric acid extraction of pectin was performed, as follows: apple pomace powder (10 g) was mixed with water acidified with citric acid (pH of 1.5, 2 or 2.5) in a solid-to-liquid ratio of 1:10, and then exposed to heating in a water bath JP Selecta Precisdig (J.P. SELECTA, Barcelona, Spain) at different temperatures (70, 80 or 90 °C) and heating time (60, 120 or 180 min).

Microwave-assisted extraction of pectin was performed according to the following procedure: apple pomace powder (10 g) was mixed with acidified water (pH of 1.5, 2 or 2.5) in a solid-to-liquid ratio of 1:10, 1:15 or 1:20, and then exposed to microwaves in a MO17DW oven (Gorenje, Velenje, Slovenia) at different power levels (280, 420 or 560 W) and different exposure time (60, 90 or 120 s).

After each extraction procedure was performed, pectin was separated from the mixture by centrifugation (40 min at 4000 rpm), followed by the precipitation of the supernatant with cold ethyl alcohol in a 1:1 ratio (v/v). The mixture was kept for 12 h under refrigeration (4-6 °C) to complete the precipitation, and then was centrifuged (40 min at 4000 rpm) to separate the wet pectin from the liquid. Finally, wet pectin was purified by consecutive washing (3 times) with ethyl alcohol and dried to a constant weight at a temperature of 50 °C in an oven with air circulation.

The extraction yield (as % of dry matter) was determined with the equation:

$$Pectin\ yield\ (\%) = \frac{weight\ of\ dried\ pectin\ (g)}{weight\ of\ dried\ pomace\ powder\ (g)} \times 100. \quad (1)$$

### 2.3. Physicochemical characteristics of pectin samples

The degree of esterification (DE) of pectin was determined by the titrimetric method (Franchi et al., 2014) and the galacturonic acid (GalA) content was analyzed according to the sulfamate/*m*-hydroxydiphenyl method (Melton & Smith, 2001). For both methods the procedure for sample preparation and analysis was described previously (Dranca & Oroian, 2019a).

The monosaccharide composition of pectin samples was measured by the HPLC method described by Yang et al. (2005) with the modifications reported by Zhang et al. (2013). The pectin sample (2 mg) was hydrolyzed with a solution of 2 M trifluoroacetic acid at 110 °C for 8 h, the was cooled to room temperature and neutralized with 0.3 M NaOH. From this solution, 400 μL were placed in a tube and mixed with 450 μL of 0.3 M NaOH, 450 μL of 0.5 M methanol solution of 1-phenyl-3-methyl-5-pyrazolone (PMP), and 50 μL of 2 mM lactose solution (internal standard). The mixture was heated at 70 °C for 30 min to allow the components to react, then was cooled down and neutralized with 450 μL of 0.3 M HCl. Finally, the resulting solution was extracted three times by chloroform (1 mL) and the supernatant was filtered through 0.45 μm PTFE membranes before it was injected into the chromatographic instrument. The HPLC system (Shimadzu, Kyoto, Japan) used for the analysis was equipped with a Zorbax Eclipse Plus C18 column (150 × 4.6 mm, 5 μm i.d.; Agilent Technologies, California, USA) and coupled on-line with a UV SPD-M-20A detector (Shimadzu, Kyoto, Japan). The mobile phase was a solution of 0.05 M sodium phosphate (pH 6.9) with 15% acetonitrile (buffer A) and 40% acetonitrile (buffer B) with the following gradient elution: 0-15% (0-16 min), 15–25% (16-48 min) and 25-0% (48-64 min) buffer B. The flow rate was 0.6 mL/min and UV detection was made at 250 nm.

The determination of weight-average molecular weight was made according to the HPSEC method that we have previously described (Dranca et al., 2020). For the analysis, a HPLC system (Shimadzu, Kyoto, Japan) equipped with a LC-20 AD liquid chromatograph, SIL-20A auto

sampler, CTO-20AC column oven, a Yarra 3µm SEC-2000 column (300 × 7.8 mm; Phenomenex, California, USA) and KJ0-4282 SecurityGuard column protection (Phenomenex, California, USA) and coupled on-line with a RID-10A refractive index detector (Shimadzu, Kyoto, Japan) was used. The mobile phase was a solution of 0.1 M sodium nitrate containing 0.024% sodium azide as a bactericide and the flow rate was of 0.6 mL/min. Pectin solutions (0.3% w/w) were filtered through 0.45 µm membranes and injected into the chromatographic system in a volume of 100 µL. The calibration was performed using pullulan standards (Shodex, Japan). Data collection and subsequent processing were performed using the LC solution software version 1.21 (Shimadzu, Kyoto, Japan).

A FT-IR Spectrum Two spectrometer (Perkin Elmer Co., Norwalk, Connecticut, USA) was used to analyze the structure of pectin extracted by the two different methods. The spectra were recorded in the transmission mode in the 4000-400 $cm^{-1}$ mid-infrared region with a resolution of 4 $cm^{-1}$. SpectraGryph software (ver. 1.2.11) was used to display the collected spectra.

### 2.4. Film preparation

Films were prepared by the casting method. To this end, solutions (2% w/w) of commercial pectin (CP) or pectin obtained by MAE (MP) under optimal extraction conditions were prepared by dissolving the polysaccharide into ultrapure water under magnetic stirring at 40 °C and 250 rpm for 3 h. The pectin solutions were mixed in a ratio of 1:1 (w/w) with a 2% (w/w) HPMC solution that was prepared at 80 °C, under continuous stirring (250 rpm) for 4 h; the HPMC solution was cooled to 30 °C prior to the addition of pectin solution. Glycerol was added to the mixture in a polymer:glycerol ratio of 0.9:0.1 (w/w). As control samples, films without pectin containing HPMC and glycerol (HPMC:glycerol ratio of 0.9:0.1, w/w) were also prepared. All film-forming dispersions were degassed using a vacuum pump and then were poured into Teflon plates (150 mm

189 diameter) with a surface solid density of 5.6 mg of solids/cm$^2$. Drying was made under controlled
190 conditions (25 °C, 40% relative humidity) for 48 h and the resulting films were conditioned until
191 constant weight in a desiccator with oversaturated magnesium nitrate solution, at 25 °C, prior to
192 any analysis.
193
194 **2.5. Characterization of the films**
195 To analyze the mechanical behavior, the pre-conditioned films were cut into 100 mm × 25
196 mm pieces for which the thickness was measured in 6 points with an electronic digital micrometer
197 (Comecta S.A., Barcelona, Spain). Tensile properties testing was performed with a TA.XT plus
198 texture analyzer (Stable Micro Systems, Surrey, UK) by mounting the ends of the film in the
199 extension grip of the analyzer and stretching the samples at a rate of 10 mm/min until breaking.
200 Eight repetitions were made for each film formulation. Tensile properties were characterized in
201 terms of tensile strength (TS), elastic modulus (EM) and percentage of elongation at break (%E)
202 (Talón, Vargas, et al., 2019).
203 Water vapor permeability (WVP) of the films was determined by the method described by
204 Talón et al. (2019), which presents some modifications to the ASTM E96-95 gravimetric method
205 (ASTM, 1995). Measurements were performed in triplicate at 25 °C and at 53-100% relative
206 humidity gradient. The oxygen permeability (OP) of the films was determined according to the
207 ASTM Standard Method D3985-05 (ASTM, 2010), as detailed by Talón et al. (2019).
208 Measurements were performed in triplicate at 25 °C and at 53% relative humidity gradient.
209 Thermal resistance of the films was evaluated using a TGA 1 Star System (Mettler Toledo,
210 Switzerland) by placing approximately 3 mg of the film in a ceramic crucible and subjecting it to
211 heating from 25 to 500 °C at a heating rate of 10 °C min$^{-1}$ in nitrogen atmosphere (20 mL/min).

For each film, three repetitions were performed for reliability. Sample weight vs. temperature curves were recorded using the Star software, ver. 9.01 (Mettler Toledo, Switzerland).

### 2.6. Experimental design and statistical analysis

A Box-Behnken response surface experimental design was used to study and optimize the effect of the extraction conditions (independent variables) of the applied extraction methods – temperature (T), pH and time (t) for conventional citric acid extraction (Table 1) and microwave power (P), pH, solid-to-liquid ratio (SLR) and time (t) for microwave-assisted extraction (Table 2) – on the extraction yield, the galacturonic acid content and degree of esterification of pectin (dependent variables). Modeling and optimization was made with Design Expert v11 software (trial version, Stat-Ease, Minnesota, USA).

To predict the evolution of extraction efficiency a second-order (quadratic) polynomial response surface model was applied to fit the experimental results obtained by Box-Behnken design using the equation:

$$y = b_0 + \sum_{i=1}^{n}\left(b_i x_i\right) + \sum_{i=1}^{n}\left(b_{ii} x_{ii}^2\right) + \sum_{ij=1}^{n}\left(b_{ij} x_i x_j\right) \quad (2)$$

where: $y$ is the predicted response (extraction yield, galacturonic acid content or degree of esterification), $x_i$ stands for the coded levels of the design variable (temperature, pH and time for CE and microwave power, pH, solid-to-liquid ratio and time for MAE), $b_0$ is a constant, $b_i$ – linear effects, $b_{ii}$ – quadratic effects and $b_{ij}$ – interaction effects. The parameters were optimized simultaneously using the desirability function approach to achieve the highest yield, galacturonic acid content and degree of esterification (Montgomery, 2005).

The results of the analysis of physicochemical properties of pectin at optimal extraction conditions, as well as of the analysis of films properties were submitted to analysis of variance

(ANOVA) using Statgraphics Centurion XVI software (Statgraphics Technologies, Inc., Virginia, USA). Fisher′s least significant difference (LSD) procedure was used at the 95% confidence level.

Table 1. Box-Behnken design with experimental results and predicted response for conventional extraction of pectin

| Run | Independent variables | | | Experimental results | | | Predicted response | | |
|---|---|---|---|---|---|---|---|---|---|
| | pH | T, °C | t, min | Yield (%) | GalA (g/100 g) | DE (%) | Yield (%) | GalA (g/100 g) | DE (%) |
| 1 | 2 | 80 | 120 | 15.65 | 97.62 | 83.33 | 15.66 | 97.62 | 83.33 |
| 2 | 2 | 70 | 180 | 11.24 | 68.88 | 85.74 | 11.05 | 73.51 | 85.76 |
| 3 | 1.5 | 90 | 120 | 38.91 | 64.80 | 66.94 | 39.14 | 64.04 | 66.12 |
| 4 | 2.5 | 80 | 180 | 9.78 | 98.31 | 93.06 | 10.21 | 92.91 | 92.22 |
| 5 | 1.5 | 80 | 180 | 33.22 | 46.89 | 64.96 | 33.78 | 42.97 | 67.05 |
| 6 | 2 | 80 | 120 | 15.65 | 97.62 | 83.33 | 15.66 | 97.62 | 83.33 |
| 7 | 2 | 90 | 60 | 18.62 | 93.08 | 81.03 | 18.82 | 88.45 | 81.02 |
| 8 | 2 | 80 | 120 | 15.65 | 97.62 | 83.33 | 15.66 | 97.62 | 83.33 |
| 9 | 2.5 | 80 | 60 | 6.82 | 77.64 | 94.14 | 6.26 | 81.56 | 92.05 |
| 10 | 2.5 | 90 | 120 | 13.46 | 97.68 | 92.82 | 13.83 | 98.39 | 94.93 |
| 11 | 2 | 70 | 60 | 10.39 | 98.99 | 79.90 | 11.18 | 94.31 | 81.17 |
| 12 | 1.5 | 80 | 60 | 35.15 | 57.65 | 60.83 | 34.73 | 63.05 | 61.67 |
| 13 | 2.5 | 70 | 120 | 4.08 | 86.92 | 95.03 | 3.86 | 87.69 | 95.85 |
| 14 | 1.5 | 70 | 120 | 30.94 | 54.30 | 71.22 | 30.58 | 53.59 | 69.11 |
| 15 | 2 | 90 | 180 | 22.72 | 95.85 | 83.26 | 21.94 | 97.53 | 81.99 |

Table 2. Box-Behnken design with experimental results and predicted response for microwave-assisted extraction of pectin

| Run | Independent variables | | | | Experimental results | | | Predicted response | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | P, W | pH | SLR, g/mL | t, s | Yield (%) | GalA (g/100 g) | DE (%) | Yield (%) | GalA (g/100 g) | DE (%) |
| 1 | 560 | 1.5 | 1:15 | 90 | 38.06 | 44.70 | 65.91 | 38.05 | 49.28 | 68.76 |
| 2 | 420 | 2 | 1:15 | 90 | 12.79 | 83.59 | 71.70 | 12.79 | 83.59 | 71.70 |
| 3 | 420 | 2 | 1:10 | 60 | 7.05 | 63.82 | 78.80 | 6.67 | 64.51 | 78.69 |
| 4 | 420 | 2 | 1:20 | 120 | 18.91 | 56.02 | 71.98 | 20.37 | 58.10 | 72.77 |
| 5 | 560 | 2.5 | 1:15 | 90 | 4.63 | 94.37 | 88.79 | 3.24 | 86.49 | 93.93 |
| 6 | 420 | 2 | 1:10 | 120 | 8.80 | 99.53 | 88.73 | 11.30 | 93.48 | 86.57 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 7 | 420 | 2 | 1:20 | 60 | 10.27 | 70.11 | 69.96 | 8.85 | 78.93 | 72.80 |
| 8 | 280 | 2.5 | 1:15 | 90 | 2.59 | 56.66 | 92.30 | 3.67 | 54.85 | 90.12 |
| 9 | 280 | 1.5 | 1:15 | 90 | 20.43 | 37.44 | 65.85 | 22.89 | 48.09 | 61.38 |
| 10 | 420 | 2 | 1:15 | 90 | 12.79 | 83.59 | 71.70 | 12.79 | 83.59 | 71.70 |
| 11 | 420 | 2.5 | 1:10 | 90 | 2.98 | 72.99 | 95.53 | 2.95 | 66.70 | 96.02 |
| 12 | 560 | 2 | 1:15 | 120 | 24.17 | 94.68 | 84.06 | 22.73 | 95.07 | 81.26 |
| 13 | 420 | 2.5 | 1:20 | 90 | 4.19 | 72.35 | 87.80 | 4.26 | 69.06 | 84.11 |
| 14 | 420 | 1.5 | 1:20 | 90 | 26.41 | 34.12 | 68.85 | 31.69 | 34.23 | 63.22 |
| 15 | 420 | 2 | 1:15 | 90 | 12.79 | 83.59 | 71.70 | 12.79 | 83.59 | 71.70 |
| 16 | 280 | 2 | 1:15 | 120 | 12.12 | 64.30 | 78.38 | 12.55 | 62.09 | 78.00 |
| 17 | 280 | 2 | 1:15 | 60 | 4.52 | 81.16 | 70.07 | 7.29 | 74.59 | 71.74 |
| 18 | 420 | 1.5 | 1:10 | 90 | 24.37 | 60.44 | 64.45 | 25.64 | 57.55 | 67.01 |
| 19 | 420 | 2 | 1:15 | 90 | 12.79 | 83.59 | 71.70 | 12.79 | 83.59 | 71.70 |
| 20 | 560 | 2 | 1:15 | 60 | 10.93 | 78.39 | 80.41 | 11.84 | 74.43 | 79.66 |
| 21 | 560 | 2 | 1:10 | 90 | 5.64 | 89.94 | 94.19 | 8.09 | 98.94 | 89.35 |
| 22 | 420 | 1.5 | 1:15 | 120 | 45.15 | 37.24 | 60.82 | 40.38 | 32.20 | 65.22 |
| 23 | 420 | 2 | 1:15 | 90 | 12.79 | 83.59 | 71.70 | 12.79 | 83.59 | 71.70 |
| 24 | 420 | 2.5 | 1:15 | 120 | 5.41 | 50.56 | 95.35 | 7.23 | 61.39 | 95.52 |
| 25 | 420 | 2 | 1:15 | 90 | 12.79 | 83.59 | 71.70 | 12.79 | 83.59 | 71.70 |
| 26 | 420 | 1.5 | 1:15 | 60 | 30.41 | 42.75 | 64.35 | 26.17 | 35.33 | 64.64 |
| 27 | 280 | 2 | 1:20 | 90 | 11.22 | 77.64 | 68.62 | 6.36 | 72.05 | 73.92 |
| 28 | 420 | 2.5 | 1:15 | 60 | 2.94 | 41.67 | 92.18 | 5.29 | 50.11 | 88.24 |
| 29 | 280 | 2 | 1:10 | 90 | 6.15 | 83.35 | 76.13 | 4.26 | 88.88 | 76.19 |
| 30 | 560 | 2 | 1:20 | 90 | 17.78 | 96.94 | 71.54 | 17.25 | 94.82 | 71.94 |

## 3. Results and discussion

### 3.1. Comparison between extraction techniques: CE vs. MAE

The model used to predict the evolution of pectin yield, galacturonic acid content and degree of esterification for both CE and MAE was a second-order (quadratic) polynomial response surface model that was selected because of the higher $R^2$, adjusted $R^2$, and predicted $R^2$ and the low *p*-value ($p < 0.05$). The results of ANOVA, presented in Table 3 and 4, showed that the quadratic model can explain and predict most of the variation of pectin yield ($R^2 = 0.998$ for CE and $R^2 = 0.951$), galacturonic acid content ($R^2 = 0.964$ for CE and $R^2 = 0.923$), and degree of esterification ($R^2 = 0.985$ for CE and $R^2 = 0.923$) of extracted pectin. The second order polynomial equations that describe the combined effect of temperature (*T*), pH and time (*t*) for CE and

255 microwave power (*P*), pH, solid-to-liquid ratio (*SLR*) and time (*t*) for MAE on the extraction yield,
256 galacturonic acid content and degree of esterification of pectin are shown in the equations below.
257 For conventional extraction:
258 $$\text{Yield (\%)} = 15.65 + 4.63 \times T - 13.008 \times pH + 0.74 \times t + 0.35 \times T \times pH + 0.81 \times T \times t +$$
259 $$1.22 \times pH \times t + 0.34 \times T^2 + 5.84 \times pH^2 - 0.25 \times t^2 \quad (3)$$
260 $$\text{GalA content (g/100 g)} = 97.61 + 5.28 \times T + 17.11 \times pH - 2.18 \times t + 0.06 \times T \times pH + 8.21$$
261 $$\times T \times t + 7.85 \times pH \times t - 1.30 \times T^2 - 20.38 \times pH^2 - 7.11 \times t^2 \quad (4)$$
262 $$\text{DE (\%)} = 83.33 - 0.98 \times T + 13.88 \times pH + 1.39 \times t + 0.51 \times T \times pH - 0.90 \times T \times t - 1.30 \times$$
263 $$pH \times t + 1.20 \times T^2 - 3.03 \times pH^2 - 2.05 \times t^2 \quad (5)$$
264
265 For microwave-assisted extraction:
266 $$\text{Yield (\%)} = 12.79 + 3.68 \times P - 13.506 \times pH + 2.81 \times SLR + 4.03 \times t - 3.89 \times P \times pH + 1.76$$
267 $$\times P \times SLR + 1.40 \times P \times t - 0.206 \times pH \times SLR - 3.06 \times pH \times t + 1.72 \times SLR \times t - 0.99 \times P^2 + 5.16$$
268 $$\times pH^2 - 2.804 \times SLR^2 + 1.80 \times t^2 \quad (6)$$
269 $$\text{GalA content (g/100 g)} = 83.58 + 8.207 \times P + 10.99 \times pH - 5.24 \times SLR + 2.03 \times t + 7.61$$
270 $$\times P \times pH + 3.17 \times P \times SLR + 8.28 \times P \times t + 6.41 \times pH \times SLR + 3.602 \times pH \times t - 12.44 \times SLR \times t$$
271 $$+ 3.93 \times P^2 - 27.84 \times pH^2 + 1.14 \times SLR^2 - 10.98 \times t^2 \quad (7)$$
272 $$\text{DE (\%)} = 71.7 + 2.79 \times P + 13.47 \times pH - 4.92 \times SLR + 1.96 \times t - 0.89 \times P \times pH - 3.78 \times$$
273 $$P \times SLR - 1.16 \times P \times t - 3.03 \times pH \times SLR + 1.67 \times pH \times t - 1.97 \times SLR \times t + 3.05 \times P^2 + 3.79 \times$$
274 $$pH^2 + 3.09 \times SLR^2 + 2.909 \times t^2 \quad (8)$$
275 Table 3. ANOVA for yield, galacturonic acid content and degree of esterification of pectin from
276 conventional extraction

| Source | Sum of squares | DF | Mean square | *F*-value | *P*-value |
|---|---|---|---|---|---|
| (A) Pectin yield, % | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Model | 1667.07 | 9 | 185.23 | 348.95 | < 0.0001 |
| Temperature | 171.60 | 1 | 171.60 | 323.28 | < 0.0001 |
| pH | 1353.77 | 1 | 1353.77 | 2550.30 | < 0.0001 |
| Time | 4.48 | 1 | 4.48 | 8.45 | 0.03 |
| Temperature × pH | 0.49 | 1 | 0.49 | 0.93 | 0.37 |
| Temperature × time | 2.63 | 1 | 2.63 | 4.95 | 0.07 |
| pH × time | 5.99 | 1 | 5.99 | 11.29 | 0.02 |
| $R^2$ | | | 0.998 | | |
| (B) Galacturonic acid content, g/100 g | | | | | |
| Model | 4771.47 | 9 | 530.16 | 14.91 | 0.004 |
| Temperature | 223.83 | 1 | 223.83 | 6.29 | 0.05 |
| pH | 2342.49 | 1 | 2342.49 | 65.87 | 0.0005 |
| Time | 38.05 | 1 | 38.05 | 1.07 | 0.34 |
| Temperature × pH | 0.016 | 1 | 0.016 | 0.0005 | 0.98 |
| Temperature × time | 270.25 | 1 | 270.25 | 7.60 | 0.04 |
| pH × time | 246.90 | 1 | 246.90 | 6.94 | 0.04 |
| $R^2$ | | | 0.964 | | |
| (C) Degree of esterification, % | | | | | |
| Model | 1632.53 | 9 | 181.39 | 38.39 | 0.0004 |
| Temperature | 7.68 | 1 | 7.68 | 1.63 | 0.25 |
| pH | 1542.90 | 1 | 1542.90 | 326.58 | < 0.0001 |
| Time | 15.46 | 1 | 15.46 | 3.27 | 0.13 |
| Temperature × pH | 1.07 | 1 | 1.07 | 0.22 | 0.65 |
| Temperature × time | 3.26 | 1 | 3.26 | 0.68 | 0.44 |
| pH × time | 6.79 | 1 | 6.79 | 1.44 | 0.28 |
| $R^2$ | | | 0.985 | | |

277

278

279 Table 4. ANOVA for yield, galacturonic acid content and degree of esterification of pectin from

280 microwave-assisted extraction

| Source | Sum of squares | DF | Mean square | *F*-value | *P*-value |
|---|---|---|---|---|---|
| (A) Pectin yield, % | | | | | |
| Model | 3076.13 | 14 | 219.72 | 20.81 | < 0.0001 |
| Power | 162.68 | 1 | 162.68 | 15.40 | 0.0014 |
| pH | 2189.25 | 1 | 2189.25 | 207.31 | < 0.0001 |

| | | | | | |
|---|---|---|---|---|---|
| SLR | 95.08 | 1 | 95.08 | 9.00 | 0.009 |
| Time | 195.53 | 1 | 195.53 | 18.52 | 0.0006 |
| Power × pH | 60.80 | 1 | 60.80 | 5.76 | 0.029 |
| Power × SLR | 12.46 | 1 | 12.46 | 1.18 | 0.29 |
| Power × time | 7.94 | 1 | 7.94 | 0.75 | 0.39 |
| pH × SLR | 0.17 | 1 | 0.1700 | 0.01 | 0.90 |
| pH × time | 37.60 | 1 | 37.60 | 3.56 | 0.07 |
| SLR × time | 11.86 | 1 | 11.86 | 1.12 | 0.30 |
| $R^2$ | | | 0.951 | | |
| (B) Galacturonic acid content, g/100 g | | | | | |
| Model | 10414 | 14 | 743.86 | 13 | < 0.0001 |
| Power | 808.27 | 1 | 808.27 | 14.12 | 0.0019 |
| pH | 1450.06 | 1 | 1450.06 | 25.34 | 0.0001 |
| SLR | 329.55 | 1 | 329.55 | 5.76 | 0.02 |
| Time | 49.73 | 1 | 49.73 | 0.86 | 0.36 |
| Power × pH | 231.84 | 1 | 231.84 | 4.05 | 0.06 |
| Power × SLR | 40.40 | 1 | 40.40 | 0.70 | 0.41 |
| Power × time | 274.55 | 1 | 274.55 | 4.80 | 0.04 |
| pH × SLR | 164.79 | 1 | 164.79 | 2.88 | 0.11 |
| pH × time | 51.90 | 1 | 51.90 | 0.90 | 0.35 |
| SLR × time | 619.99 | 1 | 619.99 | 10.83 | 0.004 |
| $R^2$ | | | 0.9238 | | |
| (C) Degree of esterification, % | | | | | |
| Model | 2941.94 | 14 | 210.14 | 13 | < 0.0001 |
| Power | 93.80 | 1 | 93.80 | 5.80 | 0.029 |
| pH | 2179.45 | 1 | 2179.45 | 134.85 | < 0.0001 |
| SLR | 290.87 | 1 | 290.87 | 18 | 0.0007 |
| Time | 46.22 | 1 | 46.22 | 2.86 | 0.11 |
| Power × pH | 3.19 | 1 | 3.19 | 0.19 | 0.66 |
| Power × SLR | 57.30 | 1 | 57.30 | 3.55 | 0.079 |
| Power × time | 5.43 | 1 | 5.43 | 0.33 | 0.57 |
| pH × SLR | 36.78 | 1 | 36.78 | 2.28 | 0.15 |
| pH × time | 11.22 | 1 | 11.22 | 0.69 | 0.41 |
| SLR × time | 15.64 | 1 | 15.64 | 0.96 | 0.34 |
| $R^2$ | | | 0.9239 | | |

281

282

283 The extraction methods were compared in terms of pectin yield, GalA content and DE and
284 the changes recorded for these parameters in function of the extraction conditions are shown in Fig.
285 1 and 2. For conventional extraction, the 3D graphs show that the changes in pH, temperature and

time led to significant variations of extraction yield, resulting in a higher pectin yield than that reported in other studies focused on the extraction of apple pectin. The maximum extraction yield (38.91% at a pH of 1.5, temperature of 90 °C and 120 min) that was achieved in this study by CE was higher than that of 19.8% reported for the enzymatic extraction of pectin from apple pomace (Wikiera et al., 2016). Furthermore, the pectin yield determined for apple pomace from 'Fălticeni' variety was higher than the yield achieved when Royal (16.65%) and Golden (18.79%) apple varieties were used as pectin sources (Kumar & Chauhan, 2010). By comparison to the conventional extraction process, MAE resulted in a maximum pectin yield of 38.06% at a microwave power of 560 W, pH of 1.5, SLR of 1:15 g/mL and extraction time of 90 s. Although this value was close to the maximum yield obtained by CE, MAE has the major advantage of a shorter extraction time. It can be observed (Fig. 2) that the improvements of extraction yield were mainly determined by the increase of microwave power and extraction time; this observation regarding the influence of these process parameters on pectin yield was previously made in the study by Bagherian et al. (2011). While the rate of heat transfer is rather low in the case of conventional extraction and thus the method requires a longer time to achieve temperatures that promote cell disruption, the vibration of polar water molecules under the exposure to microwaves causes an instantaneous volumetric heating in the cells (Sucheta et al., 2020). This explains why in our study the increase of microwave power (for MAE) and temperature (for CE) had a positive influence on pectin yield. For both methods, it was observed a positive evolution of the extraction yield with the decrease of pH; this extraction parameter significantly influenced ($p < 0.001$) the pectin yield. Better results for MAE were observed when the SLR was above 1:15 g/mL, confirming the indication of an incomplete extraction at low SLR previously made by Lefsih et al. (2017).

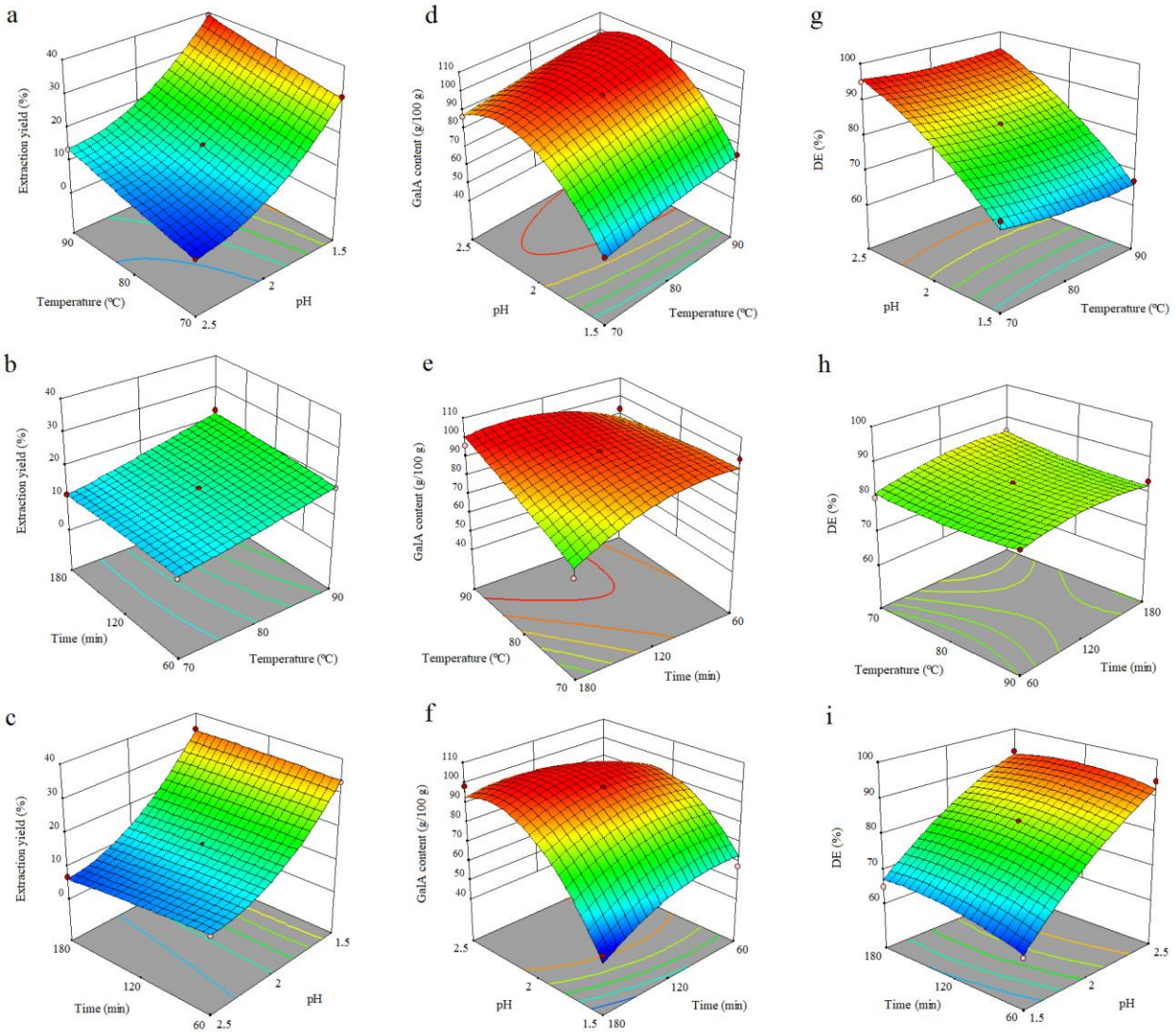
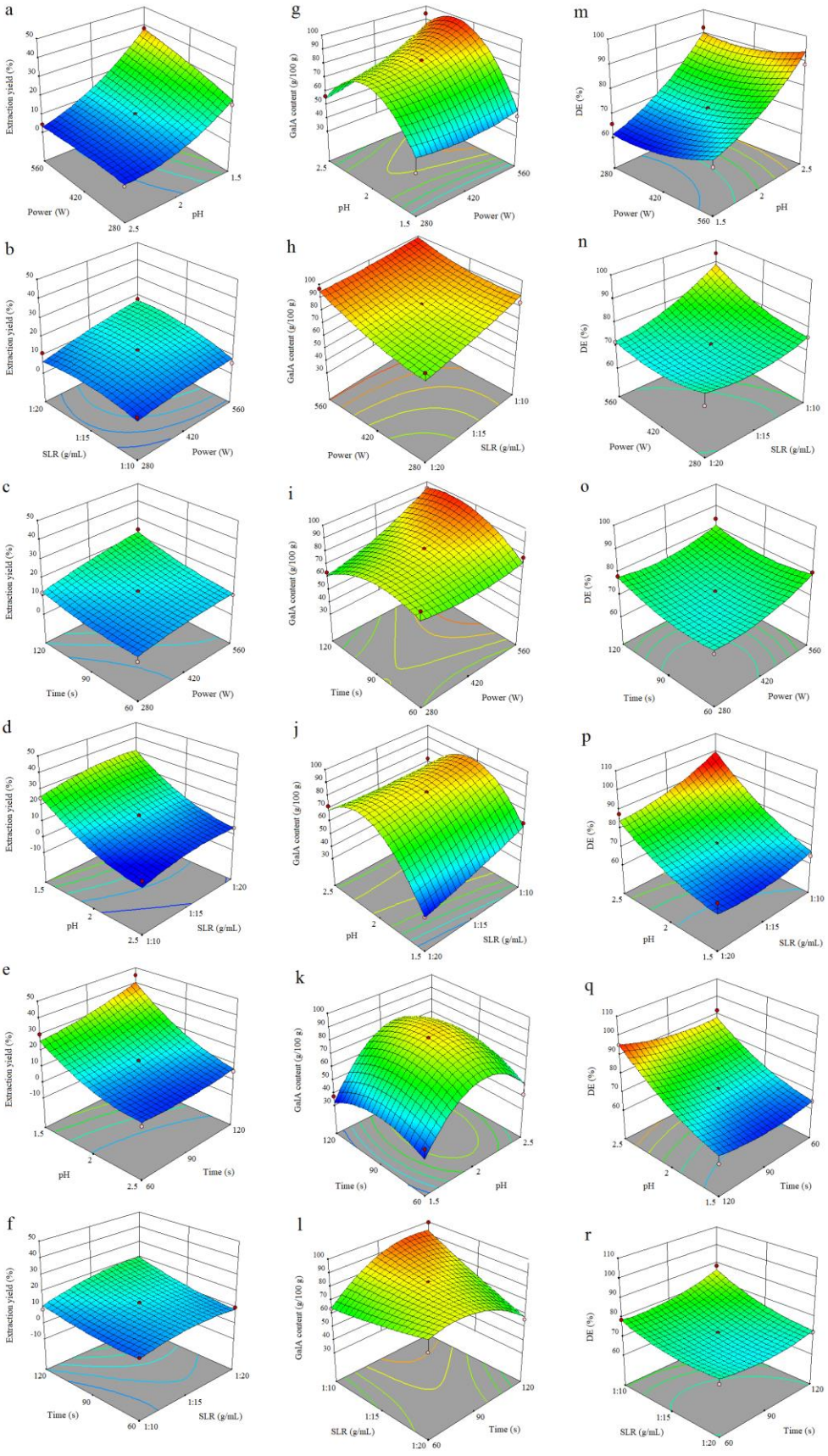



**Fig. 1.** Response surface plots showing the effect of the conventional extraction parameters on the pectin yield (**a**–**c**), the galacturonic acid content (**d**–**f**), and the degree of esterification (**g**–**i**).


a
Extraction yield (%)
Power (W)
pH
b
Extraction yield (%)
SLR (g/mL)
Power (W)
c
Extraction yield (%)
Time (s)
Power (W)
d
Extraction yield (%)
pH
SLR (g/mL)
e
Extraction yield (%)
pH
Time (s)
f
Extraction yield (%)
Time (s)
SLR (g/mL)
g
GalA content (g/100 g)
pH
Power (W)
h
GalA content (g/100 g)
Power (W)
SLR (g/mL)
i
GalA content (g/100 g)
Time (s)
Power (W)
j
GalA content (g/100 g)
pH
SLR (g/mL)
k
GalA content (g/100 g)
Time (s)
pH
l
GalA content (g/100 g)
SLR (g/mL)
Time (s)
m
DE (%)
Power (W)
pH
n
DE (%)
Power (W)
SLR (g/mL)
o
DE (%)
Time (s)
Power (W)
p
DE (%)
pH
SLR (g/mL)
q
DE (%)
pH
Time (s)
r
DE (%)
SLR (g/mL)
Time (s)

314

**Fig. 2.** Response surface plots showing the effect of the microwave-assisted extraction parameters on the pectin yield (**a**–**f**), the galacturonic acid content (**g**–**l**), and the degree of esterification (**m**–**r**).

The GalA content of pectin had values between 46.89 g/100 g (pH of 1.5, temperature of 80 °C and 180 min extraction time) and 98.99 g/100 g (pH of 2, temperature of 70 °C and 60 min extraction time) for pectin extracted by CE and between 34.12 g/100 g (microwave power of 420 W, pH of 1.5, SLR of 1:20 g/mL and 90 s) and 99.53 g/100 g (microwave power of 420 W, pH of 2, SLR of 1:10 g/mL and 120 s) for pectin from MAE. The highest GalA content determined in this study was above the value of 67.14% reported by Kumar & Chauhan (2010) for pectin extracted with citric acid from apple pomace resulted by processing apple of the Royal variety and the 80.9% galacturonic acid content determined for commercial apple pectin (Wikiera et al., 2016). By comparing the measured GalA content between the two extraction techniques, it can be observed that pectin from the conventional method of extraction had an overall higher content of this chemical component than pectin extracted by MAE. A similar finding was made by Rodsamran & Sothornvit (2019a) for pectin obtained from lime peel by microwave heating extraction when its composition was compared to that of pectin extracted from the same plant material through a conventional extraction. While the authors did not explain what determined the slight decrease of GalA content for pectin from microwave extraction, they argued that this process was efficient to extract lime pectin without quality loss. Regarding the factors that determined this difference between the extraction methods, Fig. 2 (g, j & k) shows that the lowest values of GalA content were determined by an MAE at a pH of 1.5; ANOVA indicated a significant influence ($p < 0.001$) of this process parameter on the GalA content of pectin from MAE. An opposite evolution of GalA content with the pH was observed by Su et al. (2019), who linked a low pH value to the release of

water-soluble pectin with high GalA content as a result of an increased depolymerization of cellulose and hemicellulose. Microwave power had a positive effect, while the increase of SLR led to lower GalA content. Extraction time had no influence on the GalA content of both pectin from MAE and CE. As in the case of MAE, the GalA content of pectin from CE was significantly influenced by pH ($p < 0.001$) and not by temperature and extraction time.

The degree of esterification presented variation depending on the extraction technique, as follows: for CE between 60.83% (pH of 1.5, temperature of 80 °C and 60 min) and 95.03% (pH of 2.5, temperature of 70 °C and 120 min) and for MAE between a minimum of 60.82% (microwave power of 420 W, pH of 1.5, SLR of 1:15 g/mL and 120 s) and a maximum DE of 95.53% (microwave power of 420 W, pH of 2.5, SLR of 1:10 g/mL and 90 s). These values indicate that both techniques led to the extraction of high methoxyl (HM) pectin (DE>50%) from *Malus domestica* 'Fălticeni' apple pomace. Regarding the influence of the extraction parameters on the DE of pectin, it was observed a significant influence ($p < 0.001$) of the pH for both CE and MAE, and the evolution of DE with the pH of extraction had the same tendency that was recorded for the GalA content (the DE was higher as the pH increased). Fig. 1 shows an almost linear increase of the DE of pectin extracted by the conventional method with the increase of the pH, which was in agreement with the results of previous studies (Raji et al., 2017; Oliveira et al., 2016). The positive influence of the pH on the DE of pectin extracted by MAE was also observed in other studies (Su et al., 2019; Hosseini et al., 2016b; Hosseini, Khodaiyan, & Yarmand, 2016a). Another parameter that presented significant influence ($p < 0.001$) on the DE of pectin from MAE was the SLR, for which a decrease determined the extraction of pectin with higher DE (Fig. 2). The DE of pectin from MAE was also influenced ($p < 0.05$) by microwave power, and the positive impact that this process parameter manifested on DE showed that the extraction occurred without the deesterification of galacturonic acid chains observed in other studies (Kazemi et al., 2019).

### 3.2. Extraction optimization

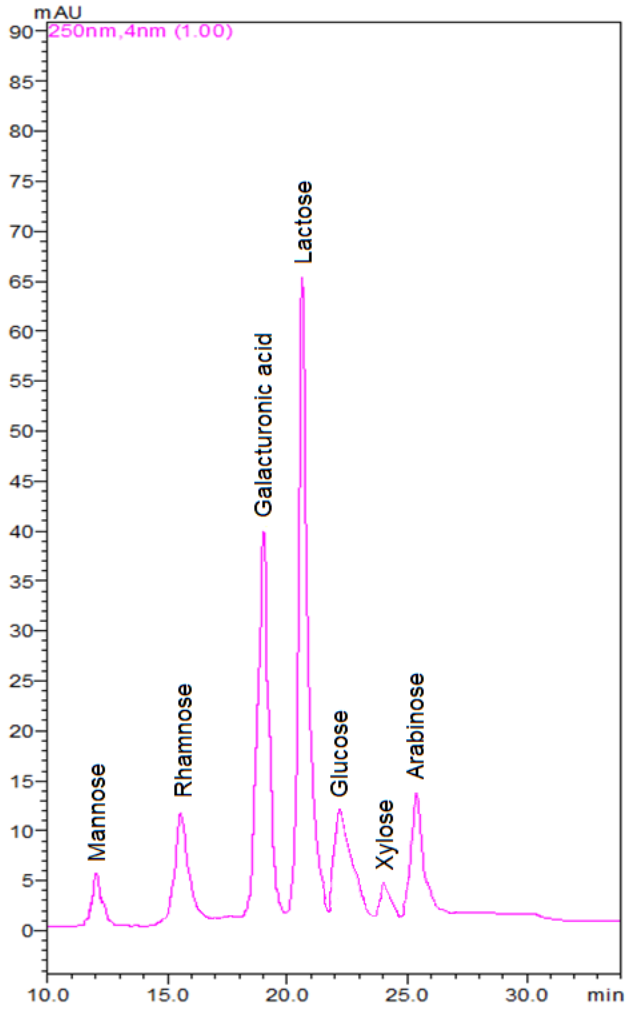
The extraction conditions were optimized in order to reach simultaneously a maximum pectin yield, GalA content and degree of esterification. For the conventional citric acid extraction method, an extraction at a temperature of 90 °C, pH of 1.92 and time of 147 min and 43 s was estimated to result in an extraction yield of 23.26%, GalA content of 99.25 g/100 g and DE of 81.18%. Response surface methodology was also used to optimize the conditions of MAE (microwave power, pH, SLR and time) in order to maximize the yield, GalA content and DE of pectin. The applied model estimated a pectin yield of 24%, GalA content of 91.82 g/100 g and DE of 88.52% for an extraction at a microwave power of 560 W, pH of 2.2, SLR of 1:10 g/mL and 120 s.

### 3.3. Physicochemical characteristics of pectin at optimal extraction conditions

The pectin that was extracted from *Malus domestica* 'Fălticeni' apple pomace by CE and MAE under the optimal conditions of extraction that were presented in Section 3.2 were characterized in terms of monosaccharide composition, molecular weight and structure (by means of FT-IR spectroscopy).

The HPLC chromatogram obtained from the analysis of the monosaccharide composition of MAE pectin extracted under optimal conditions is presented in Fig. 3. The monosaccharide composition of the pectin samples, expressed as mol%, is presented in Table 5. From these values it can be observed that, after galacturonic acid, arabinose, glucose and rhamnose were the most abundant monosaccharides. Based on the content determined for each monosaccharide it can be concluded that for both CE and MAE the extracted crude pectin consisted of a mixture of homogalacturonan and rhamnogalacturonan with neutral side chains mainly composed of arabinan,

galactan and arabinogalactan (Wang, Chen, & Lü, 2014). Mannose, which was determined in lower quantities, may derive from non-pectic polysaccharides (hemicellulose) bound to pectin side chains (Wang et al., 2016). By comparison to pectin from MAE, pectin from CE had a lower content of galacturonic acid, but had a higher content of neutral monosaccharides (arabinose, glucose, rhamnose, mannose, and xylose). Gharibzahedi et al. (2019) reported a higher molar ratio of GalA in report with other monosaccharides for pectin extracted from fig skin by MAE as compared to hot water extraction. In addition to galacturonic acid, arabinose and rhamnose, Cho et al. (2019) also determined a high content of galactose and glucose in the pectin extracted from apple peel. Luo et al. (2020) also reported high concentrations of galactose (4.22-5.03 wt%) and glucose (2.94-4.21 wt%) in apple pectin. The concentration of glucose in our pectin samples was similar to that reported by these studies.




399

400 **Fig. 3.** HPLC-DAD chromatogram at 250 nm for the monosaccharide components of MAE

401 pectin extracted under optimal conditions.

402

403 Table 5. Monosaccharide composition and molecular weight of pectin extracted by conventional

404 extraction (CE) and microwave-assisted extraction (MAE) in optimal conditions. Mean values

405 and standard deviation, in brackets.

| Parameter | Pectin from CE | Pectin from MAE |
|---|---|---|
| Galacturonic acid, %mol | 78.22 (0.27)b | 86.21 (0.16)a |

| | | |
|---|---|---|
| Arabinose, %mol | 7.51 (0.02)a | 4.66 (0.05)b |
| Mannose, %mol | 1.84 (0.03)a | 1.48 (0.01)b |
| Rhamnose, %mol | 4.81 (0.02)a | 3.10 (0.05)b |
| Glucose, %mol | 6.37 (0.08)a | 3.71 (0.04)b |
| Xylose, %mol | 1.16 (0.02)a | 0.97 (0.01)b |
| Molecular weight, g/mol | $2.63 \times 10^5$ (0.07)a | $2.64 \times 10^5$ (0.07)a |

406 [a-b]Different letters in the same line indicate significant differences among samples ($p < 0.05$)

407

408 The HPLC-SEC chromatograms obtained from the analysis of the weight-average
409 molecular weight ($M_w$) of pectin extracted by CE and respectively MAE under optimal extraction
410 conditions are presented in Fig. 4. The values determined for the $M_w$ of these samples are shown
411 in Table 5. By considering the complete range of $M_w$ distribution determined by the HPSEC
412 analysis, for pectin from CE it was calculated an average value of $2.63 \times 10^5$ g/mol, while for $M_w$
413 of pectin from MAE the average value was $2.64 \times 10^5$ g/mol. It is important to also consider that
414 both extraction procedures (CE and MAE) involved the use of citric acid, for which higher
415 molecular distributions and generally no degradation in the structure of the extracted pectin were
416 observed (Mao et al., 2019). The degradation of some of the neutral monosaccharides in the RG-I
417 side chains of pectin due to a high intensity microwave treatment that was reported by other authors
418 (J.-S. Yang et al., 2019; Xu et al., 2018) was therefore not observed in this study. For pectin
419 extracted from apple peel Cho et al. (2019) determined a similar value ($2.6 \times 10^5$ g/mol) for the
420 extraction with 0.1 M tartaric acid and reported higher $M_w$ for apple pectin extracted with malic
421 acid ($4.5\text{-}4.7 \times 10^5$ g/mol) and citric acid ($5.3\text{-}10.7 \times 10^5$ g/mol).

422

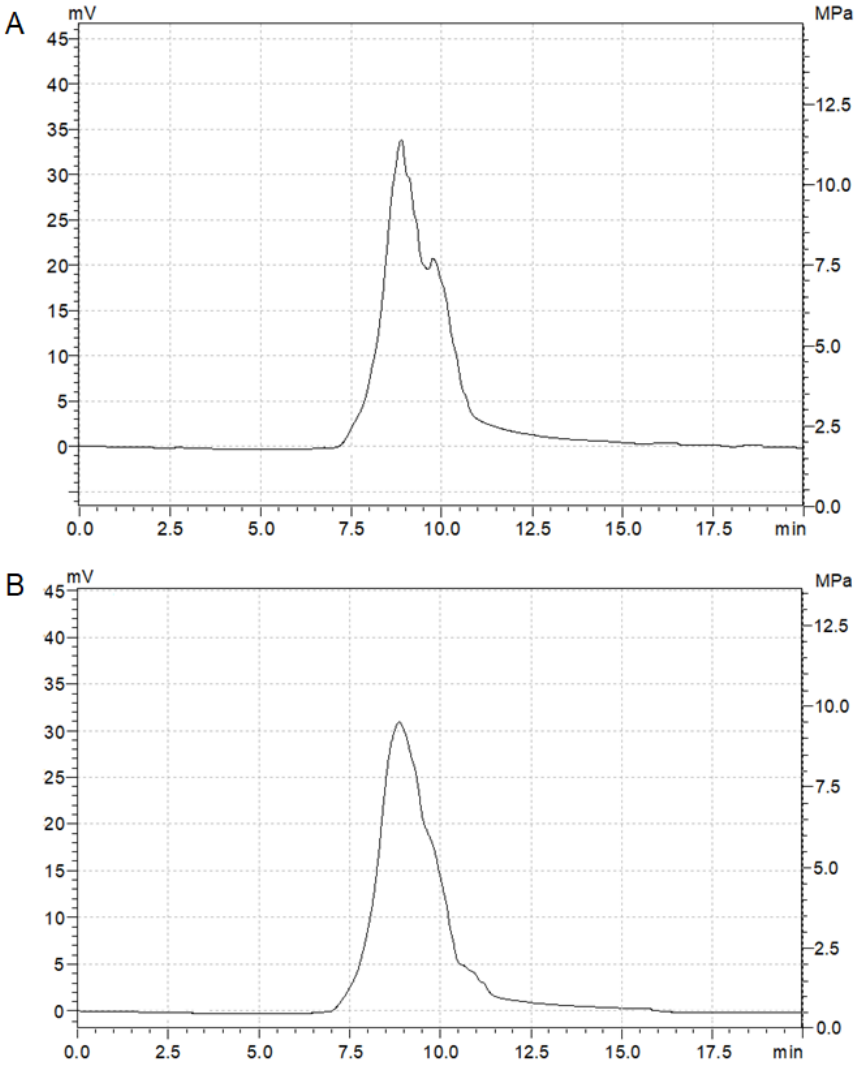



**Fig. 4.** HPLC-SEC chromatograms obtained for *(A)* CE pectin and *(B)* MAE pectin samples extracted under optimal conditions.

FT-IR spectroscopy was used as a mean to study the functional groups that make up the composition of the pectin samples. Fig. 5 shows the similar spectra collected for pectin from the conventional method of extraction and pectin from MAE. The broad absorption area between 3600 and 3000 $cm^{-1}$ corresponded to stretching vibrations of the hydroxyl groups (O–H), and specifically to the vibrational modes of inter- and intramolecular hydrogen bonds of the

galacturonic acid polymer (Y. Chen et al., 2014). The absorption peak at 2934 $cm^{-1}$ was attributed to stretching vibrations of C–H (CH, $CH_2$ and $CH_3$). The peak at 1734 $cm^{-1}$ corresponded to C=O stretching of ester carbonyl, while 1612 $cm^{-1}$ was attributed to C=O stretching of free carboxyl groups (Dranca et al., 2020; Rodsamran & Sothornvit, 2019a). The ratio between the peak area at 1734 $cm^{-1}$ and the sum of the peak areas at 1734 $cm^{-1}$ and 1612 $cm^{-1}$ could be used for the quantification of the degree of esterification (Pappas et al., 2004). Based on the absorption spectra, both pectin samples were high-esterified, which was in accordance with the results of the determination of DE by the titrimetric method. Carboxylate groups also presented a weaker symmetric stretching band at 1439 $cm^{-1}$ (Dranca & Oroian, 2019a). Between 1200 and 800 $cm^{-1}$ the intense peaks were attributed to specific functional groups that are characteristic to pectin polysaccharides (the region between 1200 and 950 $cm^{-1}$ was indicated to be the fingerprint area of carbohydrates; 1227 $cm^{-1}$ was correlated to vibrations of C–C bond in the ring structure of the polysaccharide) or to the vibrations in the glycosidic bonds and pyranoid rings (1014 $cm^{-1}$ to pyranose and 829.5 $cm^{-1}$ to α-*D*-mannopyranose) (Dranca et al., 2020; Dranca & Oroian, 2019a; Gharibzahedi et al., 2019). The presence of mannose in the crude pectin extracts was also confirmed and quantified through the HPLC analysis of monosaccharide composition.


**Fig. 5.** FT-IR spectra of pectin extracted from *Malus domestica* 'Fălticeni' apple pomace by conventional extraction (CE) and microwave-assisted extraction (MAE) under optimal conditions.

### 3.4. Films characterization

Pectin extracted from *Malus domestica* 'Fălticeni' apple pomace by the MAE method, in the optimized extraction conditions presented in section 3.2, was chosen to develop edible films on the basis of the above mentioned physicochemical properties together with the higher efficiency of the extraction method as compared to the conventional extraction method. Previous studies showed that pectin films can become rigid and brittle (Nur Hanani, 2018; Tung et al., 2016), and for this reason the high molecular weight polymer HPMC was chosen to develop blended films with pectin as a mean to improve the mechanical strength. The properties of films prepared with HPMC and pectin from this source (HPMC-MP) in equal ratios were compared to films without pectin (HMPC) and films prepared with HPMC and commercial pectin (HPMC-CP) and the results are

presented and discussed below. According to the specification sheet provided by the manufacturer, commercial pectin used in HPMC-CP films had high GalA content (>74%). The analysis of the physicochemical properties of this pectin sample showed that the GalA content (81.40 g/100 g), DE (88.50%), methoxyl content (4.83%), equivalent weight (515), and molecular weight ($1.19 \times 10^5$) were lower in comparison to those of pectin extracted from *Malus domestica* 'Fălticeni' apple pomace (Dranca et al., 2020).

The mechanical properties (strength and elasticity) of edible films are preliminary characteristics that are investigated and controlled in order to ensure the integrity of the product under the influence of external stress (Jridi et al., 2020; Hosseini et al., 2016). Tensile strength, elongation at break (%E) and elastic modulus (EM) of HPMC-pectin films and HPMC films are presented in Table 6. Films containing pectin were significantly less stretchable than pure HPMC films. Tensile strength and EM of HPMC-CP and HPMC-MP films were higher while %E values were lower than those reported for films prepared with mango pectin and commercial low methoxyl pectin (Chaiwarit et al., 2020) and pectin films incorporated with gamma-aminobutyric acid (Meerasri & Sothornvit, 2019). The differences in terms of tensile properties between HPMC-CP and HMPC-MP films can be attributed to the different extraction procedures and degree of methylation, as it was previously observed by Meerasri & Sothornvit (2019). As commercial pectin and pectin extracted by MAE had very similar degree of esterification (88.50% and 88.52%, respectively), in this case is seems that tensile properties are mostly influenced by the extraction procedure. Glycerol also has a significant influence on the mechanical properties of the films, as the plasticizer molecules intersperse and intercalate among and between HPMC and pectin chains. This restructuration of the polymer matrix determines increased chain mobility, thus reducing the resistance to applied stress and increasing the stretchability of the film (Razavi et al., 2015).

Table 6. Tensile properties, oxygen and water vapor permeability and TGA parameters of edible films of pectin (commercial pectin, CP or microwave-extracted, MP) and hydroxypropyl methylcellulose (HPMC). Mean values and standard deviation, in brackets.

| Parameter | HPMC | HPMC-CP | HPMC-MP |
|---|---|---|---|
| Tensile strength, MPa | 48(5)b | 56(6)a | 29(4)c |
| Elastic modulus, MPa | 1439(104)c | 1835(99)a | 1449(105)b |
| Elongation at break, % | 12(3)a | 4.2(0.8)b | 2.2(0.3)c |
| Oxygen permeability, cc mm $m^{-2}$ $atm^{-1}$ d $ay^{-1}$ | 81.99(0.15)a | 0.6(0.03)b | 3.7(0.08)b |
| Water vapor permeability, g mm $kPa^{-1}$ $h^{-1}$ $m^{-2}$ | 59.1(0.4)b | 64.3(0.4)a | 64.9(0.4)a |
| $T_0$, °C | 289.01(0.04)b | 288.67(0.07)b | 294.11(0.08)a |
| $T_{max}$, °C | 321.8(0.3)c | 322.25(0.08)b | 323.8(0.3)a |
| % Mass loss | 79.2(0.09)a | 62.02(0.4)c | 71.4(0.5)b |

[a-c]Different letters in the same line indicate significant differences among formulations ($p < 0.05$)

Barrier properties such as oxygen permeability and water vapor permeability can directly affect the quality of the coated product and its shelf life (Akhtar et al., 2013). The values determined for the oxygen and water vapor permeability of the films investigated in this study are shown in Table 6. OP of HPMC films was higher than that of films prepared with HPMC and pectin in equal ratios, which indicated a significant improvement of the oxygen barrier capacity of films due to the incorporation of pectin. The improvement of the barrier properties against oxygen was probably due to the formation of intermolecular hydrogen bonds between pectin chains and HPMC as it was previously observed for pectin and nanochitosan films (Ngo et al., 2020). The increased

interactions between pectin and HPMC lead to a decrease of oxygen permeability. Good oxygen barrier properties are characteristic to hydrophilic films, thus the decrease of oxygen permeability through the addition of pectin in film formulation was in agreement with the higher water vapor permeability obtained in the blended films as compared to pure HPMC films. A similar trend was observed for edible films formulated with high methoxyl apple pectin and chitosan blends (Younis & Zhao, 2019) and can be explained by the higher water affinity of pectin as compared to other hydrocolloids (Shahrampour et al., 2020). Another factor that affects the water vapor permeability of edible films is the hygroscopic nature of glycerol; the addition of glycerol in the formulation of the blended films determines an increase of the water content, and consequently increased mobility of the polymer molecules (Mu et al., 2012).

The thermal stability of the films was tested by thermogravimetric analysis, and the determined TGA parameters are presented in Table 6. Films containing pectin exhibited the first mass loss step below 240 °C (first derivative curve, DTGA; Supplementary data), which was attributed to the evaporation of the residual water from the films (Talón, Lampi, et al., 2019). For HPMC-CP films the high mass loss rate between 160 and 240 °C suggested a strong water-bonding capability of the commercial pectin used for this formulation (Tan et al., 2020). In the case of HPMC-MP films, the first step of moisture loss from the film was followed by a stage of thermal decomposition that occurred between 240 and 280 °C and was attributed to the decomposition of glycerol used as plasticizer (Ezati & Rhim, 2020; Shankar & Rhim, 2015). The main mass loss step corresponded to the thermal degradation of the two polymers, pectin and HPMC. The onset temperature ($T_0$) and the peak temperature of the maximum degradation rate ($T_{max}$) were 288.67 and 322.25 °C for HPMC-CP films and 294.11 and 323.83 °C for HPMC-MP films containing pectin extracted from *Malus domestica* 'Fălticeni' apple pomace by MAE. The slight increase of the thermal stability of the blended films by comparison to HPMC films can be attributed to the

formation of hydrogen bonds between the $H^+$ and $OH^-$ groups of pectin and HPMC; this finding was in line with the conclusions drawn from a study of the physicochemical and antimicrobial properties of a composite film based on black mulberry pulp pectin (Sharifi & Pirsa, 2021). The temperature of degradation of HPMC-CP and HPMC-MP films was higher than that reported for pure pectin films and pectin/silver nanoparticles composite films (222.5 °C) (Shankar et al., 2016) and pectin films containing essential oil (231.53-232.21 °C) (Nisar et al., 2018). Beyond 360 °C all polymer chains were decomposed. The mass loss was higher for HPMC-MP films (71.4%) when compared to HPMC-CP films (62.02%).

## 4. Conclusions

The decrease in pH and the heating of the extraction mixture, as determined by the increase of temperature in the case of the conventional process (CE) and by the increase on microwave power in the case of microwave-assisted extraction (MAE), had a positive influence on the pectin yield. The pH had the same positive influence on the degree of esterification, but an opposite effect on the galacturonic acid content of pectin obtained by CE and MAE. The optimization of the extraction conditions allowed further investigation into the physicochemical properties of pectin from the two methods of extraction. Apple pectin from *Malus domestica* 'Fălticeni' consisted of a mixture of homogalacturonan and rhamnogalacturonan with arabinan and/or arabinogalactan-rich side chains and had high molecular weight.

Films formulated with HPMC and pectin obtained by MAE (HPMC-MP) showed improved thermal stability and had lower oxygen permeability as compared to pure HPMC films. The latter makes these films specially suitable for food application in which a high oxygen barrier is required. However, the overall mechanical and barrier properties and thermal stability of HMPC-MP films were not significantly improved as compared to the blended films formulated with commercial

549 pectin. The differences in terms of mechanical properties were attributed in part to the different
550 extraction methods applied to obtain the pectin used for film formulations, while barrier properties
551 and thermal stability were more determined by the hydrogen bonds between pectin and HPMC.
552 Therefore, more research on the use of different pectin ratios and its behavior in blends with
553 different hydrocolloids and plasticizers are required in order to optimize the use of microwave-
554 assisted extracted pectin from *Malus domestica* 'Fălticeni' as a component of edible films.
555
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562
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