Kinetics of extraction and degradation of pectin derived compounds from onion skin wastes in subcritical water

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A B S T R A C T

In this work the valorization of onion skin wastes (OSW) as a source of the pectic oligosaccharides (POS), prebiotic hydrocolloids, using subcritical water (SubW) was thoroughly studied and modeled (using the Panchev's model) in a batch extractor at temperatures up to 165 °C and extraction times up to 180 min. The extraction of pectin derived compounds was notably sensitive to both variables, with the most favorable extraction rates occurring within a severity factor ($\log R_0$) range of 2.8–3.1. The highest recovery, 32 g of OGalA per 100 g of raw material, was achieved at 135 °C for 100 min. This process yielded various families of compounds categorized by their weight average molecular weight (Mw), with 85 kDa being the most prevalent, followed by 27, 17, and 7 kDa. The changes in Mw as a function of time and temperature was modeled using the Emsley equation, which enabled the prediction of POS molecular weight based on extraction conditions, as well as the calculation of the energy of activation for pectin derived compounds degradation (116 ± 2 kJ/mol). Additionally, along with the loss in molecular weight, the presence of degradation products such as formic acid and furfural increased with the intensity of the extraction conditions. In summary, the hydrothermal extraction conducted at temperatures between 125 and 135 °C facilitated the retrieval of POS with MW ranging from 7 to 85 kDa. This stands in contrast to the high MW (>300 kDa) and linear pectin obtained through conventional acid-water extraction processes.

1. Introduction

Pectic oligosaccharides (POS) have emerged as a novel class of prebiotic hydrocolloid due to their ability to regulate microbiota in human intestine, their anti-oxidant properties compared to other commercially available oligosaccharides and their anti-inflammatory and anti-obesity effects (Gerschenson, 2017). The properties of POS make them active ingredients in functional foods. Regular consumption of these foods may offer physiological benefits and aid in reducing the risk of developing chronic diseases (Babbar, Dejonghe, Gatti, Sforza, & Elst, 2016). According to the report Prebiotics Market Size (Global Market Insights, 2023), the prebiotics market size was valued at USD 6.2 billion in 2022, and it is projected to increase up to USD 24 billion in 2032. POS, which are commonly obtained by partial (acid and/or enzymatic) hydrolysis of pectin (Gullón et al., 2013), a complex heteropolysaccharide of galacturonic acid (GalA) and neutral sugars found in the middle lamella of plant cell walls (Ciriminna, Fidalgo, Delisi, Ilharco, & Pagliaro, 2016), include several families of compounds. The most abundant POS are oligogalacturonides (OGalA), followed by others such as galactooligosaccharides (GalOS), rhamnogalacturonoligosaccharides (RhaGalAOS), arabinooligosaccharides (AraOS), xylooligogalacturonides (XylGalAOS) and arabinogalactooligosaccharides (AraGalOS) (Gullón et al., 2013). All of them have the structural feature of not having a degree of polymerization higher than 15 (Wandee, Uttapap, Mischnick, & Rungsardthong, 2021). The prebiotic activity of POS is linked to their distinct structural characteristics (Mao et al., 2019): high branching (comprising neutral sugars like arabinose and galactose) and low molecular weight (attributes commonly associated with the pectin RG-I domain) in contrast to the conventional pectin, which has high molecular weight (features ascribed to the HG domain), and primarily exhibits gel-forming capabilities. The composition and structure of these side branches determine its protective effects (Cui et al., 2021). The authors concluded that side chains play a significant role

in influencing the rheological properties of citrus pectin. Additionally, they observed that these side chains can modify the gut microbiota of obese mice, leading to increased abundance of bacteria with anti-obesogenic effects. Moreover, side chains were found to enhance the immunomodulating activity compared to that of the original linear pectin.

The increasing interest of POS as functional additives in the pharmaceutical and food industries demands new sources and eco-friendly extraction approaches. In this regard, onion skin wastes (OSW) hold great potential, with over 450,000 tons of OSW being discarded annually (Baldassarre et al., 2018), despite its remarkable GalA content (Benito-Román, Alonso-Riaño, Díaz De Cerio, Sanz, & Beltrán, 2022). The composition of this raw material varies depending on the onion cultivar. However, the content of insoluble dietary fiber is consistently at least ten times higher than that of soluble fiber, with pectin being the most abundant type of soluble structural component (Jaime et al., 2002). POS are derived from the depolymerization of pectin through acid hydrolysis (pH 2, >85 °C), that yields mainly the HG domain due to complete hydrolysis of the branched domains (Mao et al., 2019) or enzymatic hydrolysis, which is time consuming but yields branched pectin rich in RG-I and RG-II domains (Baldassarre et al., 2018). As an alternative to the conventional process for producing POS, which typically involves sequential acid hydrolysis and depolymerization, hydrothermal hydrolysis based on subcritical water (SubW) is emerging as an eco-friendly technique. This method enables the extraction and partial depolymerization of pectin in a single reactor, utilizing water as a reagent. SubW refers to water at temperatures ranging from 100 °C (boiling temperature) to 374 °C (critical temperature), which remains in a liquid state due to the application of pressure. The higher ionic strength and lower pH that SubW possesses in contrast to water at ambient conditions, may induce the acid hydrolysis of the bonds between the bioactive compounds and the solid matrix, promoting their release (Plaza & Turner, 2015). Consequently, SubW can facilitate the extraction of pectin from natural matrices, and by controlling the operational parameters, pectin can be tailored into smaller units with varying degrees of polymerization to produce POS. Our research group (Benito-Román et al., 2022) recently demonstrated that SubW can effectively recover pectin branched domains with different molecular weights. However, in practice, accurate control of experimental conditions has emerged as the primary challenge of the SubW extraction process, which can lead to the formation of undesired degradation products (Gómez et al., 2014) and uncontrolled molecular weight reduction of pectin (Klinchongkon, Khuwijitjaru, & Adachi, 2017).

In summary, there is a pressing need to develop optimized processes that enable the consistent and predictable extraction of pectin and pectin-derived products, employing environmentally friendly technologies. Accordingly, the present study aims to examine the hydrothermal extraction kinetics of pectic oligosaccharides from onion skin wastes and to gain a deeper understanding of the degradation process using a batch-type extractor, at temperatures up to 165 °C for 180 min. The extraction kinetics and pectin depolymerization kinetics have been described using the Panchev's model and Emsley equation, respectively. To the best of the authors' knowledge, the Panchev's model has not been previously employed in the literature to describe the extraction kinetics of pectic oligosaccharides using SubW, since experimental design (RSM) serves as a common tool to study the pectin extraction in other studies. The Panchev's model involves two stages: the dissolution of pectin from protopectin, which is the initial pectin content in the raw material, and the degradation of the dissolved pectin. Meanwhile, the Emsley equation has previously found application in explaining the degradation kinetics of other biopolymers exposed to SubW conditions. By leveraging these analytical tools, the objective is to determine the optimal operating conditions to maximize the extraction of pectin-derived compounds and achieve the desired molecular weight distribution using only subcritical water as a reagent.

2. Materials and methods

2.1. Chemicals and materials

Onion (*Allium cepa*) skin wastes (OSW) used in this work corresponded to the cultivar Horcal and were kindly provided by "Embutidos Cardeña" (Burgos, Spain), a local manufacturer of blood sausages. Samples were manually sorted in order to separate the outermost skins, which were air-dried in a room at a controlled temperature (25 °C). Subsequently, they were milled using a SM100 mill (Retsch GmbH, Germany), equipped with a 1 mm sieve. Then, OSW were subjected to a treatment in order to remove flavonoids and other extractives, using an ethanol/water mixture (70/30, v/v) at 37 °C, according to the extraction procedure described by Benito-Román et al. (Benito-Román, Blanco, Sanz, & Beltrán, 2021). After this treatment, OSW were air-dried in a room at controlled temperature (25 °C) and used as raw material for the subcritical water hydrolysis process described in section 2.2. The composition of the OSW was analysed according to the procedure described in section 2.4.1.

D-galacturonic acid monohydrate (GalA, purity >97 %) was obtained from Alfa Aesar (ThermoFischer GmbH, Kandel, Germany). Formic acid (98 %) was purchased from Panreac Química S.L.U. (Barcelona, Spain). Furfural (99 %) was purchased from TCI – Tokyo Chemical Industry CO Ltd (Tokyo, Japan). Sulfuric acid used for the sample hydrolysis was 96 % purity and was provided by Labbox Labware (Barcelona, Spain), whereas the one used for the HPLC mobile phase preparation was 96 % Suprapur provided by Merck KGaA (Darmstadt, Germany). All chemicals were used without further purification. Hydrochloric acid Ph. Eur. (HCl, 37% w/v) was obtained from VWR Chemicals (Radnor, PE, USA).

2.2. Conventional extraction experiments

In the conventional extraction experiments, approximately 25 g of the extractives-free OSW were mixed with 300 mL of distilled water acidified (pH 2) with HCl (37% w/v) into a 1 L beaker. The mixture was stirred and kept at 90 °C for 90 min. Once the mixture was cooled down, it was filtered through a muslin cloth and centrifuged at 3170 g for 10 min at 4 °C, to obtain a clear solution (Benito-Román et al., 2022). The supernatant was analysed in order to determine the GalA content present in oligomeric form according to the procedure described in section 2.4.1. The content in oligomeric GalA of the liquid sample was expressed as *mg of oligomeric GalA/g of OSW* and the GalA extraction yield was calculated by dividing the mass of oligomeric GalA in the liquid by the GalA content in the raw material used for the extraction, times 100.

2.3. Subcritical water hydrolysis experiments

The OSW were subjected to a subcritical water (SubW) hydrolysis process in the 500 mL batch reactor (maximum pressure 7 MPa and maximum temperature, 250 °C), built in stainless steel AISI 316L, with an internal diameter of 7 cm, shown in Fig. 1. In each experiment, 350 mL of water and 15 g of OSW were added to the reactor, which was pressurized by means of N_2 to achieve the desired working pressure (5 MPa). The suspension in the reactor was stirred using a bar driven by a magnetic stirrer placed under the reactor and the system was heated by means of a ceramic electric band heater (2000 W), in order to get a heating rate of 5 °C/min. Samples were periodically collected by opening the valve in line 3 (refer to Fig. 1), which facilitated a reduction in pressure from the working conditions to atmospheric pressure. The vial used for sample collection was immersed in ice to lower the temperature and prevent degradation of the samples.

The effect of the extraction temperature was investigated within the temperature range of 105–165 °C. Samples (5 mL) were collected periodically, with the initial sample (t = 0) obtained upon reaching the extraction temperature, up to a maximum extraction time of 180 min. The liquid sample was analysed in order to determine the GalA content
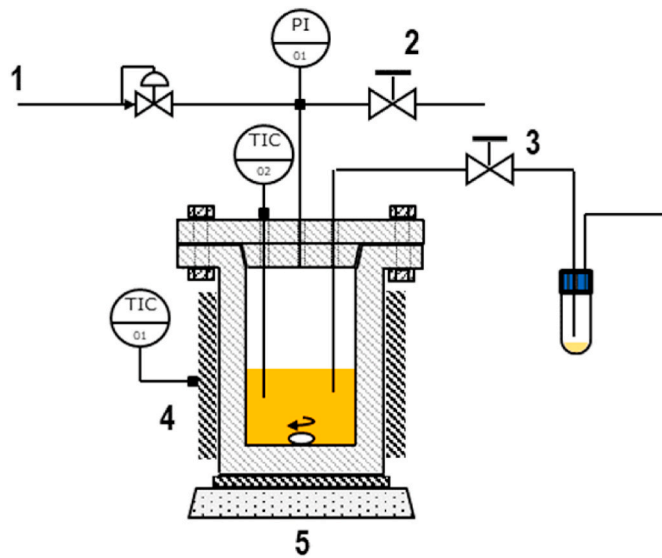
Fig. 1. Subcritical water batch reactor used in this work. Key: (1) N_2 line for pressurization, with pressure regulator; (2) Gas outlet, with purge valve; (3) Sampling circuit, including sampling valve; (4) Heating jacket (ceramic resistance 2000 W), (5) Magnetic stirring plate. Temperature (T) and Pressure (P) Indicators (I) and Controllers (C).

present in oligomeric form according to the procedure described in section 2.4.1, which was expressed as mg of oligomeric GalA/g of OSW. In the liquid sample, the content of degradation products was also determined, and its concentration was expressed as *mg/g of OSW*.

When using SubW as a reaction media, a common tool to evaluate the simultaneous effect of temperature and time is the severity factor (Ruiz et al., 2021) calculated according to Eq. (1), which includes the heating and isothermal periods (Alonso-Riaño, Ramos, Trigueros, Beltrán, & Sanz, 2023) in batch extractors:

$$logR_0 = log\left[\int_0^{t_H} exp\left(\frac{T(t)-100}{14.75}\right)\cdot dt + t\cdot exp\left(\frac{T(t)-100}{14.75}\right) \right] \quad (1)$$

2.4. Samples characterization

2.4.1. OSW characterization: structural components and elemental analysis

The composition of the onion skin wastes was determined following the protocol NREL/TP-510–42618. In brief, solid samples were subjected to acid hydrolysis and then the resulting sugar monomers were determined by HPLC, using the chromatographic system described in Section 2.4.2. Moisture, ash content and lignin (both soluble and insoluble) were also determined according to the above mentioned NREL protocol.

The elemental analysis (C, H, N, S) of the solid samples (raw material and exhausted solid residue after the extraction) was carried out using the FLASH 2000 elemental analyzer (Thermo Scientific, USA). The oxygen content in the samples was determined by difference, considering the ash content of the sample.

2.4.2. Carbohydrates identification

Identification and quantification of sugars and their degradation products in SubW extracts was carried out following protocol NREL/TP-510-42623. For that purpose, a HPLC system equipped with a Biorad Aminex HPX-87 H column (300 × 7.8 mm, Bio-Rad) coupled with a guard column Micro-Guards Cation H^+ (BioRad), with a variable wavelength detector (VWD) and a refractive index detector (RID), using 0.005 M sulfuric acid as mobile phase (0.6 mL/min) was used. The column and detectors were maintained at 40 °C and the total running time was 67 min per injection. Free galacturonic acid (GalA),

monomeric sugars and degradation products such as formic acid (FA) and furfural (Fur) were first determined in the SubW extracts, after centrifugation (3170 g, 15 min, 4 °C) and filtration through a 0.22 μm pore size syringe filter (Scharlab, Spain). Total sugars were determined after the acid hydrolysis of the sample according to the NREL/TP-510-42618 Analytical Procedure. The oligomeric galacturonic acid (OGalA) was determined as the difference between the total galacturonic acid (determined after the acid hydrolysis) and the free galacturonic acid.

2.4.3. Pectic oligosaccharides molecular weight (MW)

The weight-average molecular weights (MW) and polydispersity of the samples were determined employing high-pressure size exclusion chromatography coupled to a refraction index detector (HPSEC-RID). The chromatographic equipment consisted of an Agilent 1260 Infinity II LC system (Agilent Technologies, CA, USA) with guard column (PL Aquagel-OH, 7.5 × 50 mm, 8 μm) and two columns linked in series (PL Aquagel-OH 30 and PL Aquagel-OH 40, 300 mm × 7.5 mm, 8 μm) from Agilent Technologies. Characterization of pectin from OSW and subcritical water hydrolysates was performed at 35 °C. 10 μL of each sample were eluted in isocratic mode with 0.01 M NH_4Ac, at a flow rate of 0.7 mL/min. In addition, a pullulan standard set (0.342–400 kDa) provided by PSS Polymer Standards Service GmbH (Mainz, Germany) was used for calibration and data were analysed with Agilent OpenLab Data Analysis 2.5 software. Standards and samples were filtered through 0.22 μm syringe filters.

2.5. Pectic oligosaccharides extraction modelling

2.5.1. Extraction kinetics

In order to describe the pectic oligosaccharides extraction procedure, the mathematical model proposed by Panchev et al. (Panchev, Kirtchev, & Kratchanov, 1989) was used. This model considers that the extraction process takes place in two stages, as presented in Eq. (2). In the first one, the native pectin present in the plant cell wall (middle lamella) also known as "protopectin", is transformed into soluble pectin. This soluble pectin diffuses to the solution, where in a second stage, can suffer degradation to yield low molecular weight pectin and eventually be transformed in low molecular weight undesired products. Panchev's model assumes that both stages, extraction and degradation, occur simultaneously following a 1st order kinetics, so the extraction conditions will determine which of the two stages becomes dominant over the other.

$$Protopectin \overset{k_{ext}}{\rightarrow} pectin \overset{k_{deg}}{\rightarrow} degraded\ pectin \quad (2)$$
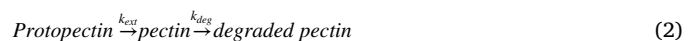
This model assumes that A_0 is the initial pectin content in the raw material (protopectin). It also assumes that Y_p is the content in protopectin at any time in the raw material. The hydrolysis process of protopectin can be described by the differential equation (3), being k_{ext} the rate constant for pectin extraction (which also includes the diffusion constant, besides the transformation of the insoluble pectin into soluble pectin) expressed in min^{-1}.

$$\frac{dY_p(t)}{dt} = -k_{ext}\cdot Y_p(t) \quad (3)$$

The yield of pectin dissolved present in the solution (Y_e), is described by Eq. (4), and considers that the extraction and degradation occur simultaneously, being k_{deg} the rate constant of pectin degradation, expressed in min^{-1}.

$$\frac{dY_e(t)}{dt} = k_{ext}\cdot Y_p(t) - k_{deg}\cdot Y_e(t) \quad (4)$$

After solving the system of equations formed by Eqs. (3) and (4), it is possible to obtain the following expressions describing the changes with time of protopectin in the raw material (Eq. (5)), the obtained pectin in

the solution (Eq. (6)), and the yield of degraded pectin (Y_d) (Eq. (7)).

$$Y_p(t) = A_0 \cdot e^{-k_{ext} \cdot t} \tag{5}$$

$$Y_e(t) = A_0 \cdot \frac{k_{ext}}{k_{deg} - k_{ext}} \cdot \left(e^{-k_{ext} \cdot t} - e^{-k_{deg} \cdot t} \right) \tag{6}$$

$$Y_d(t) = A_0 \cdot \left(1 + \frac{k_{deg}}{k_{ext} - k_{deg}} \cdot e^{-k_{ext} \cdot t} + \frac{k_{ext}}{k_{deg} - k_{ext}} \cdot e^{-k_{deg} \cdot t} \right) \tag{7}$$

The mass balance (Eq. (8)), considers that the initial protopectin A_0 is the sum of the protopectin present in the raw material plus the dissolved pectin plus the degraded pectin at any time:

$$A_0 = Y_p(t) + Y_e(t) + Y_d(t) \tag{8}$$

Finally, from Eq. (6) it is possible to calculate the time required (Eq. (9)) to reach the maximum concentration of pectin dissolved (Eq. (10)) under given extraction conditions.

$$t_{max} = \frac{ln\left(k_{ext}/k_{deg} \right)}{k_{ext} - k_{deg}} \tag{9}$$

$$Y_{e,max} = A_0 \cdot \left(\frac{k_{deg}}{k_{ext}} \right)^{\left(\frac{k_{deg}}{k_{ext}} \right)} \Big/ \left(1 - \frac{k_{deg}}{k_{ext}} \right) \tag{10}$$

2.5.2. Molecular weight degradation

The changes in the POS molecular weight during the SubW extraction was evaluated using the Emsley model (Eq. (11)), which is a modification of the Ekenstam equation often used to model the pectin molecular weight change (Klinchongkon, Khuwijitjaru, & Adachi, 2017). In this equation, the changes in the degree of polymerization of the GalA chains in comparison with the initial values ($1/DP - 1/DP_0$) is described as a function of the time.

$$\frac{1}{DP} - \frac{1}{DP_o} = \frac{k_{1_0}}{k_2} \cdot \left(1 - e^{-k_2 \cdot t} \right) \tag{11}$$

In Eq. (11), DP refers to the degree of polymerization at time t, DP_0 is the initial degree of polymerization, k_{10} is the initial degradation rate constant, k_2 is the rate of k_1 changing, being k_1 the degradation rate constant that can be calculated according to Eq. (12):

$$k_1 = k_{1_0} \cdot e^{-k_2 \cdot t} \tag{12}$$

The degree of polymerization (DP) is calculated according to Eq. (13), where M_n is the number-average molecular weight of pectin, 194.14 is the molecular weight of GalA and 18.02 the molecular weight of water.

$$DP = \frac{M_n}{194.14 - 18.02} \tag{13}$$

Finally, the dependence of the kinetic constants with temperature is described by the Arrhenius equation (14), where A is the frequency factor (which accounts for both the frequency of collisions between reactant molecules and the probability that the molecules collide in the right geometry to produce an activated complex), E_a is the energy of activation (kJ/mol), T is the temperature (K) and R is the universal gas constant (8.3145 J/mol·K).

$$ln\left(k_{1_0} \right) = ln\left(A \right) - E_a/R \cdot T \tag{14}$$

2.6. Statistical analysis

All the statistical calculations were done using Statgraphics 19-X64. To estimate the kinetic parameters, both on extraction modelling and molecular weight loss, non-linear regression was performed by using the Marquardt algorithm (Statgraphics 19-X64), considering the following parameters: maximum iterations 1000, stopping criterion 0.00001,

maximum function calls 200 and confidence level 95%. In addition, experimental results were then compared to those of the model prediction through the values of the Root Mean Square Deviation (RMSD), calculated according to Eq. (15):

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n} \left(Response_{exp} - Response_{calc} \right)^2}{N}} \tag{15}$$

where N is the number of experimental data.

3. Results and discussion

3.1. Raw material composition

The composition of the raw material utilized in this study is outlined in Table 1. It is evident that the primary structural components present in the raw material are pectin (26.6 ± 0.9 g/100 g of raw material), along with cellulose and lignin.

According to the literature, the final composition of onion skin waste varies significantly depending on the onion cultivar. Generally, the insoluble dietary fibre content in this raw material is reported to be 10 times higher than soluble dietary fibre (Vojvodić, Komes, Vovk, Belščak-Cvitanović, & Bušić, 2016), and in some onion cultivars, it can be even higher, up to 14 times (Benítez et al., 2011) or even 39 times higher (Jaime et al., 2002). These studies have observed a decrease in galactose content and a reduction in pectic galactose and arabinose content in the outer brown leaves of onions, as cell wall soluble components decrease. Considering the composition of the raw material and the temperature range proposed in this study (105–165 °C), it is anticipated that pectin will be the main component extracted, as other structural components require temperatures of around 200 °C to be hydrolysed and released (Cocero et al., 2018).

3.2. Effect of the working conditions on the extraction of OGalA

Temperature, pressure, solvent-to-raw-material ratio, and time represent the primary process parameters that govern any SubW extraction experiment (Basak & Annapure, 2022), although it is known that the parameter that has the least effect among the four is pressure (Alonso-Riaño, Sanz, Benito-Román, Beltrán, & Trigueros, 2021). However, when the target compound is pectin, the yield and the reaction rates are predominantly influenced by temperature (Das & Arora, 2021). Table S1 compiles key findings from various authors who have studied pectin extraction from diverse raw materials using SubW in batch reactors. All these authors investigated the temperature's effect, consistently identifying it as a critical parameter. However, the results regarding the impact of the solvent-to-raw-material ratio were inconclusive, whereas some researchers showed that increasing the solvent-to-raw material ratio increased the extraction yield (Ma, Jing, Wang, Xu, & Hu, 2020; X. Wang & Lü, 2014), others found no significant effect (Li, Fan, Wu, Jiang, & Shi, 2019; Peighambardoust, Jafarzadeh-Moghaddam, Pateiro, Lorenzo, & Domínguez, 2021). In the present study, a ratio of 23 mL/g was selected, aligning with ratios used in existing literature. The chosen temperature range for the extraction experiments spanned from 105 to 165 °C. It is worth noting that, in

Table 1
Composition of onion skin wastes (OSW) used in this work.

Component	mg/100g OSW
Extractives	10.4 ± 0.7
Glucan	39.3 ± 2.1
Pectin	26.6 ± 0.9
Soluble lignin	9.5 ± 0.2
Insoluble lignin	3.3 ± 0.1
Protein	2.6 ± 0.1
Galactose + Arabinose + Xylose	4.5 ± 0.4

SubW extraction of polysaccharides, temperatures should typically not exceed 180–200 °C, as temperatures beyond 200 °C can lead to biomass solubilization and complete polysaccharide degradation (Cocero et al., 2018).

According to the results presented in Fig. 2, temperature promotes the extraction of pectin up to 135 °C, yielding the best results at 135 °C (extraction time 80 min) and 125 °C (extraction time 150 min) when approximately 90 mg of OGalA/g of OSW were extracted, representing nearly six times the extraction yield achieved in the conventional extraction process (15.3 ± 0.6 mg of OGalA/g OSW). This result leads to the conclusion that SubW effectively enhances the extraction of OGalA. Furthermore, it was observed that temperatures below 125 °C resulted in lower extraction yields, which gradually increased over time. Temperatures exceeding 135 °C reduced the time required to reach the maximum extraction yield, but concurrently decreased the yield as the temperature rose. This suggests that, as temperature rises, the degradation rate of pectin exceeds the extraction rate. The literature review reveals that the extraction of pectin using SubW from various raw materials has been extensively investigated, with most authors citing optimal extraction temperatures within the 120–150 °C range, as indicated in Table S1. The choice of the extraction temperature is notably influenced by the specific raw material under consideration. For instance, while citrus peels typically necessitate temperatures around 120 °C, apple pomace requires temperatures closer to 140 °C. Generally, the consensus among researchers is that temperatures lower than the optimum, yield poor extraction results, while temperatures exceeding the optimal lead to the hydrolysis and rapid degradation of pectin. This changes in the extraction yield with temperature can be linked to changes in the ionic product of water (K_w): it increases from 10^{-14} at room temperature to 10^{-12} at 110 °C and to $6 \cdot 10^{-12}$ at 165 °C, favouring the hydrolysis reactions.

As evidenced by the data presented in Table S1, comparing the results is challenging because authors employ different combinations of temperature and time in their optimal experiments. To establish a clear and standardized basis for comparison, the severity factor can be utilized. The severity factor ($\log R_0$) is an adimensional number, commonly used in hydrothermal processes, that considers the combined influence of temperature and time. It is calculated according to Eq. (1). In the case of pectic oligosaccharides extracted from OSW (Fig. 3), the best results are achieved when the severity factor falls within the narrow range of 2.9–3.1. Further increases in the severity factor lead to a sharp decline in the OGalA yield. Conversely, milder conditions that lead to a lower severity factor are not harsh enough to promote the hydrolysis of the protopectin, leading to consistently low extraction yields.

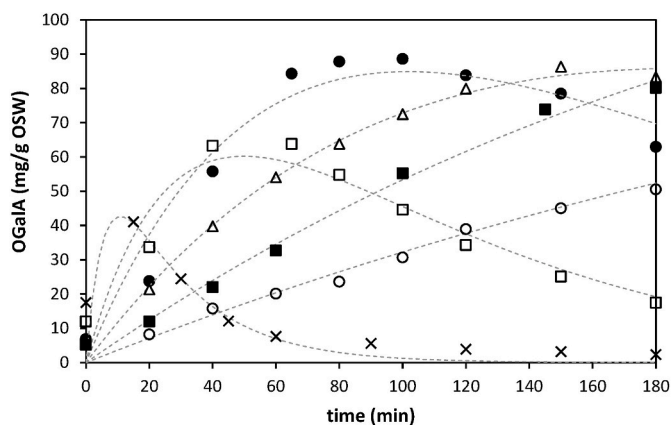The severity factor is not commonly used in the literature to discuss

Fig. 2. Quantity of oligomeric GalA extracted as a function of both temperature and extraction time. The dashed lines correspond to the extraction curve generated using the Panchev's model. Key: ○, 105 °C; ■, 115 °C; △, 125 °C; ●, 135 °C; □, 145 °C; ✕, 165 °C.
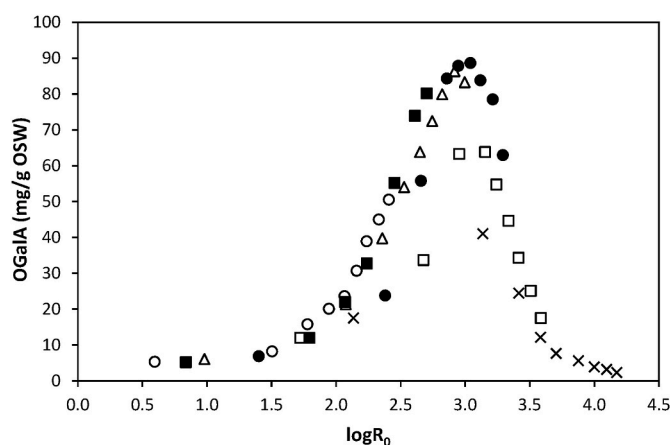

Fig. 3. Oligomeric GalA extracted as a function of the severity factor ($\log R_0$). Key: ○, 105 °C; ■, 115 °C; △, 125 °C; ●, 135 °C; □, 145 °C; ✕, 165 °C.

results in the SubW extraction process of pectin, despite the authors try different combinations of temperature and time from which can be easily calculated the severity factor, as will be shown next. For instance, Rincón et al. (Rincon et al., 2021) carried out the extraction of pectin from bay-tree pruning in a lab-scale accelerated solvent extraction system Dionex™ ASE™ 350 (Thermo Fisher Scientific Inc., USA), selecting conditions that corresponded to a severity factor ranging from 0.7 to 3.07. The optimal result in terms of polymeric precipitated fraction was 160 °C and 5 min ($\log R_0 = 2.47$), but the highest GalA content was detected in 140 °C, 20 min ($\log R_0 = 2.48$), 160 °C, 10 min ($\log R_0 = 2.77$) and 140 °C, 15 min ($\log R_0 = 2.35$). Klinchongkon et al. (Klinchongkon, Khuwijitjaru, & Adachi, 2018), who studied the hydrolysis of pectin from passion fruit, incorporated the severity factor into the discussion of their results (100–160 °C, heating rates 3.5–7 °C/min). Their findings indicated that higher severity conditions resulted in pectin with lower viscosity and distinct solution properties. Also Klinchongkon et al. (Klinchongkon, Khuwijitjaru, Wiboonsirikul, & Adachi, 2017) studied the extraction of oligosaccharides from passion fruit peels discovering that galacturonan (oligomeric GalA) was most abundant at temperatures below 200 °C. They observed that the highest value of galacturonan was 133–138 mg/g raw material at $\ln R_0$ of 3.4 (150 °C, 4.5 min of heating time) and 5.1 (175 °C, 5.5 min of heating time), followed by a dramatic decrease at $\ln R_0$ of 8.4 and above; these authors calculated $\ln R_0$ from the temperature data recorded every 30 s during the heating and cooling processes. Martínez et al. (Martínez, Yáñez, Alonsó, & Parajó, 2010) studied the hydrothermal extraction of pectic oligosaccharides from orange peel wastes using a 3.75 L stainless steel Parr reactor (L/S ratio of 12 kg of water/kg of dry feedstock, and working temperature in the range 140–200 °C). These authors obtained the highest yield (25.1%) at 160 °C after a heating period of 17 min ($\log R_0 = 2.46$). Subsequent increments in the severity treatment led to a sharp decline in the OGalA yield, reaching near-zero values at temperatures exceeding 190 °C ($\log R_0 = 3.42$). Pińkowska et al. (Pińkowska, Wolak, Krzywonos, & Złocińska, 2021) employed sugar beet pulp as a source of pectin and conducted the hydrothermal treatment in a batch reactor. The maximum yield (13.6%) was obtained at 120 °C and 20 min ($\log R_0 = 1.9$), being the temperature range studied 100–140 °C. Gómez et al. (Gómez, Gullón, Yáñez, Parajó, & Alonso, 2013) observed an almost constant concentration in OGalA in the range 150–165 °C ($\log R_0 = 2.18$–2.22), but they selected as the best conditions 160 °C ($\log R_0 = 2.51$; 18.3 g OGalA/100 g raw material). Notably, significant variations exist in the selection of operating conditions to maximize OGalA extraction, although the general trend indicates an increase in yield with rising severity, followed by a sharp decrease upon reaching specific conditions. This inflection point is dependent on both the reactor configuration and the specific raw material, with citrus peels and other raw materials

seemingly necessitating milder conditions than onion skin waste to facilitate pectin release, possibly due to differences in composition and structure.

3.2.1. Kinetic study of the pectic oligosaccharides extraction

As highlighted in Table S1, a common practice in the extraction of pectin from natural sources involves the use of experimental design strategies, such as response surface methodology. Although this approach might be valuable for selecting optimal extraction conditions, it may overlook critical information regarding the extraction mechanism. Hence, the current study proposes a comprehensive kinetic analysis, focusing on the modelling of the pectic oligosaccharide extraction process using the Panchev's model. This approach aims to yield consistent and reproducible data about the extraction of oligomeric GalA (OGalA). The results presented in Table 2 demonstrate the efficacy of this model in fitting the experimental data, as depicted in Fig. 1.

Our experimental results confirm the presence of three distinct extraction regions that might yield different types of pectins. Firstly, the **high-temperature region (145–165 °C)** leads to a rapid degradation of the extracted pectin. Elevated temperatures, in this case, accelerate the degradation of the extracted pectin rather than enhancing the extraction yield, as deduced from the kinetic constants presented in Table 2. These findings are consistent with those of (Zhang et al., 2022), who demonstrated that at high temperatures, the degradation of pectic polysaccharides predominates. They established 140 °C as the temperature point beyond which pectin degradation is promoted rather than pectin extraction, probably due to the increase of the ionization constant of water, which increases the acidity of the SubW. Conversely, in the **low temperature region (105–115 °C)** it is possible to observe an increase in the extraction rate of pectin with rising temperature and extraction time ($k_{ext} > k_{deg}$). This trend aligns with conventional extraction experiments, where even at temperatures as high as 94 °C, extraction prevails over degradation, as reported by Sebaoui et al. (Sebaoui, Moussaoui, Kadi, Michaud, & Delattre, 2017) when extracting pectin from wasted citrus lemon. In the **central region (125–135 °C)**, comparable k_{ext} and k_{deg} indicate that extraction and degradation occur simultaneously at similar rates. Consequently, a cautious selection of the extraction temperature, in combination with the duration of extraction, is necessary to optimize both the extraction rate and the molecular weight of the pectin. In this regard, the selection of the extraction temperature depends on the intended final use of the extracted pectin (Basak & Annapure, 2022). The activation energy (E_a) of pectin dissolution was determined to be 78 ± 2 kJ/mol, whereas the activation energy for pectin degradation resulted to be 131 ± 7 kJ/mol. The higher activation energy value observed for the degradation process indicates that temperature exerts a more pronounced influence on degradation rather than on extraction, in line with the findings that indicate that higher temperatures will promote the degradation rather than the extraction (Fraeye et al., 2007). These results support the importance of cautiously selecting extraction conditions to prevent uncontrolled degradation of the extracted pectin.

Comparing the model results with existing literature is challenging due to the limited utilization of the Panchev's model in SubW extraction experiments of pectin. This model, however, has found application in describing the extraction kinetics of pectin in conventional extraction

experiments involving acidified water (Sebaoui et al., 2017; Xu et al., 2014). Xu et al. (Xu et al., 2014) extracted pectin form grapefruit peel trying different extraction techniques (ultrasound assisted extraction, conventional extraction and room temperature extraction) reporting k_{ext} constants of 0.0743, 0.048 and 0.0274 min^{-1} and k_{deg} of 0.00173, 0.00169 and 0.0015 min^{-1} respectively for each extraction process and pectin yield (%). The activation energies reported were 18.62 kJ/mol with ultrasounds and 9.69 kJ/mol without ultrasound. Sebaoui et al. (Sebaoui et al., 2017) reported an increase of k_{ext} with temperature, that decreased as pH increased above 1.80. At optimal pH (1.80), k_{ext} was established to be varied from 0.03184 to 0.5384 min^{-1} and k_{deg} from 0.02152 to 0.00463 min^{-1}. The activation energy at optimal pH was estimated at 9.41 kJ/mol. The extraction was carried out from lemon (*Citrus limon* L.) wastes and the best conditions were 94 °C and 60 min (25% yield). It can be observed that the energy of activation of the SubW extraction process is higher than the observed for the conventional process, which indicates that the extraction in SubW is strongly affected by the temperature.

From the results obtained using the Panchev's model, it was also possible to calculate the highest expected yield (Eq. (10)) and the time required to achieve it (Eq. (9)) as it is reported in Table 2. It is possible to see that the best predicted results were obtained at 115 °C, requiring an impractical extraction time exceeding 500 min. Temperatures within the range of 125–135 °C yielded similar extraction yields (approximately 90 mg OGalA/g of raw material) with extraction times of 189 and 102 min, respectively. Optimal extraction temperature should thus be selected within this range, considering the presence of degradation products (to be eliminated in subsequent downstream stages) and the molecular weight of the extracted pectin.

3.3. Degradation of pectic oligosaccharides during the SubW extraction experiments

The degradation of the POS can be assessed through the analysis of the concentration of degradation products and the distribution of molecular weights in the recovered POS.

3.3.1. Degradation products formed

According to the literature, in SubW extraction experiments, increases in the extraction temperature promote hydrolysis reactions that lead to the degradation of pectin and the formation of undesirable by-products. It is also known that GalA is a highly reactive compound (greater than its hexose counterparts) that degrades very fast in SubW (Wang, Kobayashi, & Adachi, 2009), yielding mainly formic acid and furfural (Benito-Román, Sanz, & Beltrán, 2024). The results presented in Fig. 4 show the concentration of these two degradation compounds as a function of the severity factor.

Regarding formic acid (Fig. 4a), its concentration tends to rise as the severity factor increases until it reaches a maximum at approximately $logR_0 = 3.4$. After that, there is a rapid decline in the concentration of formic acid, which could possibly indicate the progression towards other degradation products. In contrast, a completely different trend was observed for furfural (Fig. 4b), which consistently increased with the increase of the severity of the extraction conditions. Furfural is a common degradation product that results from the degradation of the C5

Table 2
Kinetic parameters of the pectin extraction from onion skin wastes in subcritical water.

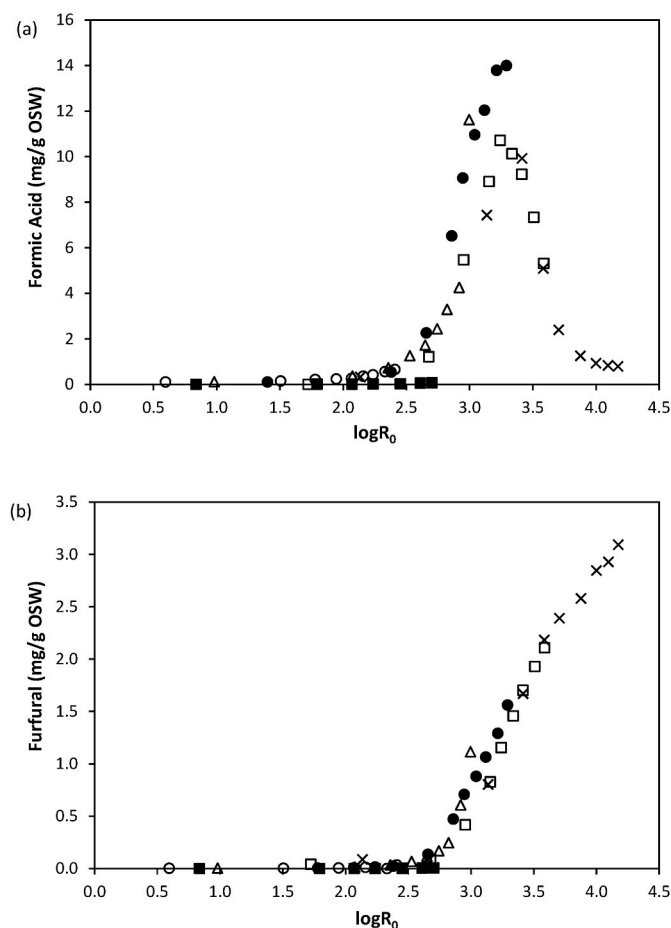| T (°C)	$k_{ext} \cdot 10^3$ (min^{-1})	$k_{deg} \cdot 10^3$ (min^{-1})	R^2	RMSD	t_{max} (min)	C_{max} (mg/g OSW)	$yield_{max}$ (%)
105	1.38 ± 0.13	1.09 ± 0.11	0.992	2.3	697	94	35.3
115	2.4 ± 0.2	1.4 ± 0.9	0.990	2.2	533	125	47.0
125	4.6 ± 0.2	6.0 ± 0.5	0.992	2.4	189	86	32.2
135	8.5 ± 0.8	11 ± 1	0.945	3.7	102	85	31.9
145	13 ± 1	30 ± 2	0.887	5.1	50	60	22.6
165	43 ± 12	168 ± 25	0.785	5.8	11	43	16.0

Fig. 4. Degradation products – a), formic acid; b), furfural - concentration as a function of the severity factor in a hydrothermal process for the recovery of POS from onion skin wastes. Key: ○, 105 °C; ■, 115 °C; △, 125 °C; ●, 135 °C; □, 145 °C; ×, 165 °C.

sugars, through dehydration reactions (Zhou & Zhang, 2016).

Formic acid emerges as the primary degradation product following the hydrothermal treatment of orange peel waste (Martínez et al., 2010). This compound surges at temperatures exceeding 160 °C, reaching a maximum at 190 °C ($logR_0 = 3.42$) (1 g/L), starting a low decrease after further increases in temperature (200 °C, $logR_0 = 3.64$). Additionally, the authors identified acetic acid, which was formed more gradually than formic acid, reaching its maximum concentration (0.4 g/L) at 200 °C. Unfortunately, they did not specify the initial amount of raw material used, making it impossible to calculate degradation product concentrations in comparable units to those presented in our study (amount formed as a function of the amount of raw material). A similar trend was detected for 5-Hydroxymethylfurfural (HMF), but concentration was half that of acetic acid. Pińkowska et al. (Pińkowska et al., 2021) observed the formation of carboxylic acids (formic acid, lactic acid, levulinic acid, oxalic acid) and furfurals (furfural and 5-HMF) under certain hydrothermal conditions when utilizing sugar beet pulp as raw material. They found that the content of carboxylic acids steadily increased over the entire temperature and holding time range, reaching 7.46 g/100 g raw material (140 °C, 30 min, $logR_0 = 2.65$). In contrast, they found that furfural was undetectable at temperatures below 120 °C, but its content increased at 130 and 140 °C with the rise in extraction temperature and time, reaching the highest value of 2.69 g/100 g raw material (140 °C, 30 min). These authors also highlighted that these degradation products could have formed through the decomposition of uronic acids, pentoses, and hexoses. Uronic acids, in particular GalA and GluA, were found to be more susceptible to react and form degradation

products (such as organic acids or furfural) than pentoses and hexoses under identical subcritical water conditions, although they are structurally related (Urbisch, Einhorn-Stoll, Kastner, Drusch, & Kroh, 2018). According to Gómez et al. (Gómez et al., 2013), when lemon peel waste was used as raw material, formic acid concentration was approximately 0.2 g/L at 160 °C ($logR_0 = 2.51$). Furfural concentration steadily increased with temperature reaching a maximum at 180 °C ($logR_0 = 3.02$). Additionally, acetic acid increased in concentration (from 0.3 to 0.6 g/L) at temperatures in the range of 170–180 °C, when using lemon peel wastes as a raw material.

3.3.2. Depolymerization of pectin derived compounds: molecular weight distributions and modelling

The results depicted in Fig. 5 show that pectin derived compounds extracted from OSW using SubW exhibits a multimodal distribution. Furthermore, it is noteworthy that the response of the low molecular weight fractions increased as the extraction process advances, indicating the increased presence of lower molecular weight fractions, which could be primarily attributed to the presence of POS. In the example shown in Fig. 5, corresponding to the extraction conducted at 135 °C, it is possible to see that initially the highest molecular weight fraction (>50 kDa) represented roughly 55% of the initial samples. However, this fraction decreases down to 25–30% in samples collected at 120 and 180 min, indicative of an ongoing depolymerization process with extraction time, as the presence of intermediate fractions (7 and 27 kDa) increases. In the sample obtained after 180 min, a decrease in the lowest molecular weight populations is observed, phenomena that can be attributed to the complete degradation of the monomers to form organic acids or furfural (Zhao, Lu, Xu, Zhu, & Wang, 2021), that have a molecular weight <0.1 kDa. This result is consistent with the observed increase in the concentration of degradation compounds (such as formic acid and furfural) as the severity of the extraction conditions increases, as depicted in Fig. 4. All in all, further works focused of the fractionation and isolation of these families are required to assess the prebiotic properties of the low molecular weight families.

This phenomenon is widely observed in SubW extraction processes for pectin: the presence of multimodal distributions and an augmented proportion of low molecular weight populations with increasing extraction severity. Pereira Dias et al. (Pereira Dias et al., 2020) reported chromatograms with four distinct peaks in a broad time range, indicative of the coexistence of high and low MW populations. Similarly, Pedraza-Guevara et al. (Pedraza-Guevara et al., 2021) reported a complex MW distribution characterized by multiple peaks, with the 57–240 kDa range consistently representing 66% of the total pectin content in unripe papaya. In the case of pectin extracted from cacao pod husk (Muñoz-Almagro, Valadez-Carmona, Mendiola, Ibáñez, & Villamiel, 2019), complex chromatograms were also presented, regardless the
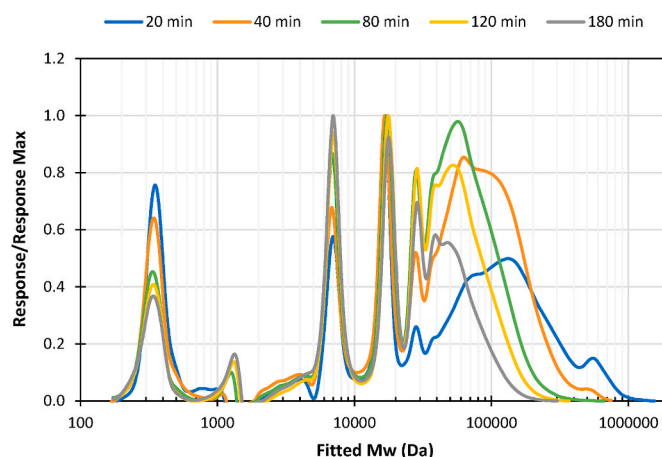

Fig. 5. GPC profiles at different extraction times (at 135 °C).

extraction process employed: in this sense, those authors reported that the SubW extraction process, generated up to 5 peaks (the most significant at 61.2 kDa (41%), followed by 750 kDa peak (38%), alongside two minor peaks above 805 kDa and at 7.9 kDa), whereas the conventional citric acid extraction process resulted in 4 peaks (with a predominant fraction (>50%) exceeded 805 kDa, followed by two fractions of 125 and 8.9 kDa.

Based on the diverse observed populations, an average molecular weight (MW) was calculated considering the weight attributed to each fraction in the distribution. This calculation facilitated the visualization of the progression of the average MW over the extraction, represented in Fig. 6. According to Fig. 6, within the lower temperature range (<125 °C), the initial stages of the extraction experiments demonstrated an increase in the molecular weight of pectic oligosaccharides, followed by a gradual decline that started at a severity factor ($logR_o$) of 2. On contrary, at higher temperatures, the degradation of pectin derived compounds occurred at an accelerated rate, leading to the detection of only low molecular weight species (<1 kDa). Similar findings were reported by Klinchongkon et al. (Klinchongkon et al., 2018), who indicated a decrease in molecular weight with increasing severity of the SubW treatment. Ma et al. (Ma et al., 2020) reported a molecular weight of 11.5 kDa for the pectin extracted from fresh sunflower heads. These authors attributed the relatively low MW of the extracted pectin to potential pectin hydrolysis and decomposition, likely resulting from the elevated temperatures employed during the SubW treatment. These authors reported a high polydispersity index for the recovered pectin (2.49), suggesting a broad MW distribution not previously documented in other studies.

Subsequently, the results were modeled using the Emsley equation (Eq. 11). Fig. 7 illustrates the variations in the degree of polymerization of the GalA chains in comparison with the initial values ($1/DP–1/DP_0$) over reaction time at various reaction temperatures. On one hand, the figure demonstrates the model's capacity to effectively predict and align with the experimental data, and on the other, that the ratio $1/DP–1/DP_0$ consistently increased with prolonged residence time, but differences were observed with the temperature. At low temperatures, the decrease in the degree of polymerization occurred gradually, suggesting a slow reduction in the molecular weight of pectin. However, as the temperature increased, the rate of depolymerization accelerated, as evidenced in Fig. 7 (135–145 °C), exhibiting a different trend at the highest temperature (165 °C). At this temperature, pectin depolymerization occurred rapidly within the first 60 min of the experiment, after which it remained constant, indicating no further reduction in molecular weight. This observation aligns with the kinetic constants for the Emsley model reported in Table 3.
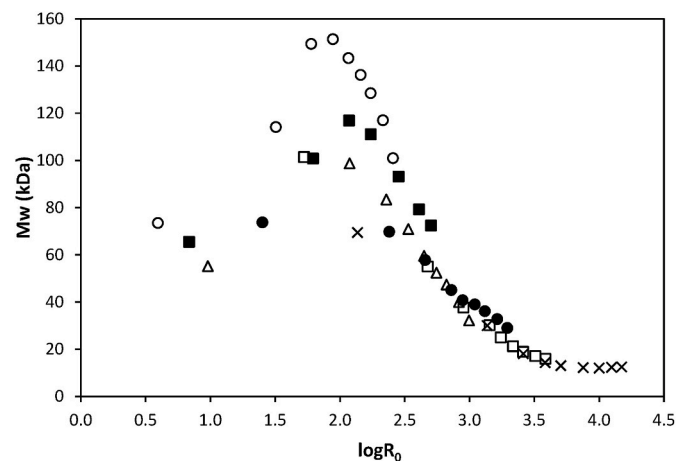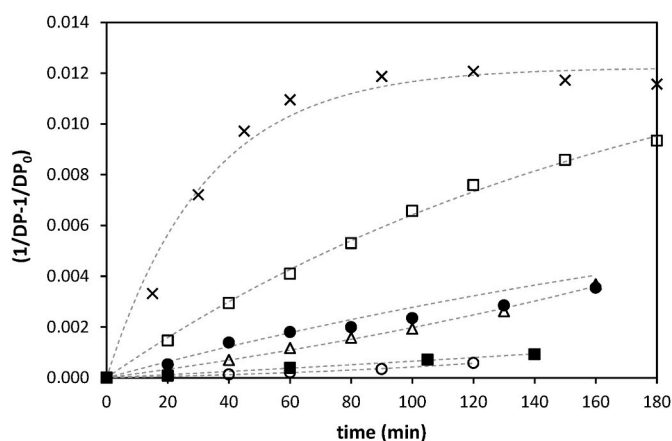

Fig. 7. Evolution with the extraction time of the ratio of broken GalA units vs. the total GalA units at different temperatures. Dashed lines represent the depolymerization curve obtained with the Emsley equation. Key: ○, 105 °C; ■, 115 °C; △, 125 °C; ●, 135 °C; □, 145 °C; ✕, 165 °C.

Table 3

Kinetic parameters of pectin depolymerization in subcritical water.

T (°C)	$k_{10} \cdot 10^5$ (min^{-1})	$k_2 \cdot 10^3$ (min^{-1})	DP_0	Mn_0 (kDa)	R^2	RMSD ($\cdot 10^4$)
105	0.25 ± 0.02	−9.9 ± 1.4	860	151	0.996	1.1
115	0.61 ± 0.06	−1.6 ± 0.1	664	117	0.996	1.4
125	1.6 ± 0.1	−4.0 ± 0.7	561	97	0.997	3.1
135	3.1 ± 0.2	3.7 ± 0.9	553	96	0.995	2.0
145	8.4 ± 0.3	5.5 ± 0.6	576	101	0.998	1.4
165	38 ± 4	31 ± 4	395	69	0.973	5.7

Table 3 present the kinetic constants calculated for the Emsley model at each respective temperature. It is possible to see that the calculated values for k_{10} exhibit a notable increase with rising temperature, potentially associated with the temperature's capacity to induce the hydrolysis of pectin. This phenomenon aligns with similar findings reported by Klinchongkon et al. (Klinchongkon, Khuwijitjaru, & Adachi, 2017) when employing this model to simulate the degradation of passion fruit pectin in SubW. A deeper analysis of the kinetic constant can be done by comparing k_1 (degradation rate constant, calculated using Eq. (12), form the values of k_{10} and k_2) and k_{10} (initial degradation rate constant). The differences observed between k_1 and k_{10}, representing the variation in the rate constant throughout the reaction process, can be attributed to the heterogeneous composition of the raw material (Emsley et al., 1997). Unlike in a simple chemical reaction, in the SubW hydrolysis of OSW, the composition of the raw material undergoes continuous changes as the reaction progresses, leading to alterations in the molecular weight distribution of the pectin. These differences in compositions as the reaction proceeds, explain the need to obtain a kinetic constant that changes. This heterogeneity results in a complex mixture of components, each exhibiting distinct rates of reaction. In Fig. S1 (supplementary material) the value of k_1 for each temperature versus time is presented. At temperatures <135 °C, k_1 increases with time, whereas at higher temperatures, k_1 decreases, a decrease which is faster the higher the temperature. This fact is reflecting the changes in the composition in the raw material as the extraction process happens, that affects the degradation of pectic-materials.

Furthermore, the temperature-dependent relationship of these kinetic constants was determined using the Arrhenius equation. In our investigation, the activation energy for the depolymerization reaction of pectin was determined to be 116 ± 2 kJ/mol, which resulted to be higher than that of other pectins obtained from other raw materials in the literature, as the reported by Klinchongkon et al. (Klinchongkon, Khuwijitjaru, & Adachi, 2017), which resulted to be 62.8 kJ/mol from

Fig. 6. Average molecular weight as a function of the severity factor. Key: ○, 105 °C; ■, 115 °C; △, 125 °C; ●, 135 °C; □, 145 °C; ✕, 165 °C.

passion fruit. According to these authors, passion fruit pectin exhibited a greater susceptibility to hydrolysis compared to cellulose, as evidenced by its nearly two-fold lower activation energy for pectin hydrolysis compared to cellulose.

Then, the MW distribution of the conventionally extracted pectin from OWS, extracted by SubW and a commercial pectin (citrus) were represented in Fig. 8. Striking disparities in their MW patterns were evident: the conventional extraction process yielded pectins with a single, high MW population, while the SubW-extracted pectin exhibited as many as four distinct populations, all of which featured lower MW values compared to conventionally extracted pectin. This trend is consistent and has been observed by various researchers working with different source materials. Wang and Lü (Wang & Lü, 2014) compared pectin extracted from apple pomace by SubW to commercial pectin: the MW (64.2 vs. 539.1 kDa), galacturonic acid content (48 vs. 66%), degree of esterification (60.2 vs. 85.5%) were lower than the SubW obtained pectins, but the neutral sugars content was higher, which might be indicating higher degree of branching in pectin extracted by SubW. Peighambardoust et al. (Peighambardoust et al., 2021) reported that the MW of the SubW extracted pectin was significantly lower than that obtained in the conventionally extracted pectin (23.51 kDa vs. 102.27 kDa). This divergence in MW was attributed to the unique physical properties of SubW, which promotes hydrolysis reactions. Li et al. (Li et al., 2019) reported similar results: the molecular weight of SubW jackfruit peel pectin was 113.3 kDa, which was significantly lower than that of conventionally extracted pectin 174.3 kDa. Chen et al. (Chen, Fu, & Luo, 2015) extracted sugar beet pectin with MW of 89.4 kDa through SCWE (liquid/solid ratio 44.03, extraction temperature 120.72 °C, extraction time 30.49 min and extraction pressure 10.70 MPa, maximum pectin yield 24.6%), which was also lower than that extracted through organic acid.

3.4. Onion skin solid residue after extraction

Elemental analysis (CHNS) has unveiled variations in the composition of the exhausted onion skin solid residues obtained after SubW hydrolysis at different temperatures, as detailed in Table 4. Notably, the carbon content increases with temperature, concomitant with a decrease in oxygen content. This trend is likely associated with dehydration reactions that occur during the SubW treatment, in accordance with findings by Zhou and Zhang (Zhou & Zhang, 2016). As previously reported, an increase in the severity of extraction conditions corresponds to an increased concentration of furfural, which is a product of dehydration reactions.
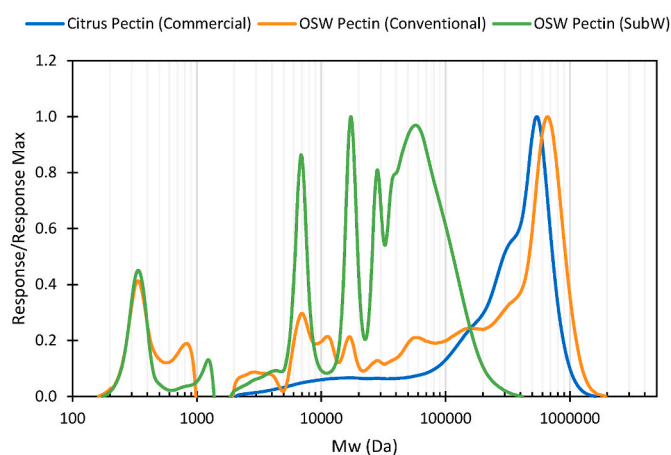
From the elemental composition results presented in Table 4, the H/C and O/C ratios were calculated. The H/C ratio, which reflects the relative proportion of chemical species with double bonds in the samples, decreases at the highest temperatures tried, indicating the dissolution of molecules containing double bonds as the temperature increases. Conversely, the O/C ratio continuously decreases with temperature, implying a higher carbon content in the solid residues after extraction, in alignment with the observed promotion of dehydration reactions. The Van Krevelen diagram serves as a valuable tool for illustrating the H/C ratio versus O/C ratio, offering a visual representation of the primary reaction pathways, typically involving dehydration or decarboxylation, connecting the biomass raw material with its resultant products (Qian, Wang, & Savage, 2020). The dehydration reactions involve the removal of two hydrogen atoms and one oxygen atom simultaneously, thus a line connecting the raw material and the product with a slope of two could be indicative of a dehydration process. On the contrary, decarboxylation involves the removal of COO from a carboxyl group (-COOH), leading to products with higher H/C ratios and lower O/C ratios compared to the original raw material. This results in a connecting line with a negative slope, typically around −1. According to the results presented in Fig. 9, two different scenarios emerge based on the SubW extraction temperature: at temperatures below 135 °C, the primary reaction pathway is decarboxylation, which aligns with the pectin extraction previously demonstrated in this study. In contrast, at temperatures higher than 135 °C, dehydration becomes the dominant process. It is worth noting that there are notable deviations from the ideal decarboxylation and dehydration reactions slope, suggesting the presence of additional reaction pathways such as gasification or condensation.

Additionally, the Higher Heating Value (HHV) of both the solid residue and the raw material, was evaluated using Eq. (16) (Salak, Daneshvar, Abedi, & Furukawa, 2013). HHV serves as an indicator of the enthalpy associated with the complete combustion of a fuel (Friedl, Padouvas, Rotter, & Varmuza, 2005).

$$HHV\left(\frac{MJ}{kg}\right) = [151.2C + 499.7H + 45.0S - 47.7O + 27.0N] \cdot 2.326 \cdot 10^{-3}$$

(16)

According to the results presented in Table 4, HHV increases with temperature until a maximum registered at 165 °C due to the high C content, resulting 16.7 ± 0.1 MJ/kg, similar to the value reported by Benito-Román et al. (Benito-Román et al., 2022) in a semi-continuous process but at 180 °C (16.4 ± 0.2 MJ/kg). Salak et al. (Salak et al., 2013) reported an increase of the HHV with temperature to reach a maximum at 270 °C (residence time, 5 min; HHV 16.99 MJ/kg, severity factor $\log R_0 = 5.7$). According to these results, it is possible to consider the solid residue as a fuel after the complete removal of extractives and pectin.

4. Conclusions

This study has successfully demonstrated the technical feasibility of a hydrothermal process employing subcritical water for the recovery of pectin derived compounds from onion skin waste. Careful selection of operating conditions was crucial to prevent the degradation of the pectin derived compounds extracted, as evidenced by the observed loss in molecular weight and the emergence of degradation byproducts such as formic acid and furfural. The modeling of the extraction kinetics and the depolymerization of the extracted compounds was conducted using Panchev's model and the Emsley equation, respectively. It has been established that there exists a narrow window of working conditions that facilitate the recovery of POS within a reasonable timeframe: specifically, at temperatures ranging from 125 °C (150 min, extraction time) to 135 °C (80 min, extraction time), corresponding to a severity factor ($\log R_0$) within the range of 2.9–3.1. Any further increase in

Fig. 8. GPC profiles for the MW distribution of different pectins: green line, OSW pectin obtained by SubW at 135 °C for 80 min; orange line OSW pectin obtained by conventional extraction process; blue line, commercial citrus pectin.

Table 4

Elemental composition of the solid residues after the subcritical water treatment. The composition of the raw material is also shown.

T (°C)	C	H	N	O	S	H/C	O/C	HHV (MJ/kg)
Raw material	36.1 ± 0.1	5.67 ± 0.15	0.38 ± 0.02	48.8 ± 0.5	nd	1.88 ± 0.06	0.90 ± 0.02	13.92 ± 0.41
105	36.9 ± 0.1	5.90 ± 0.09	0.33 ± 0.02	49.4 ± 0.2	nd	1.92 ± 0.03	0.89 ± 0.01	14.23 ± 0.27
115	36.7 ± 0.1	5.87 ± 0.07	0.32 ± 0.01	48.6 ± 0.3	nd	1.92 ± 0.03	0.88 ± 0.01	14.25 ± 0.07
125	37.0 ± 0.0	5.89 ± 0.03	0.32 ± 0.01	48.4 ± 0.2	nd	1.91 ± 0.01	0.87 ± 0.01	14.53 ± 0.04
135	37.4 ± 0.0	5.94 ± 0.01	0.28 ± 0.01	47.4 ± 0.2	nd	1.91 ± 0.01	0.85 ± 0.01	14.90 ± 0.17
145	38.9 ± 0.1	5.85 ± 0.03	0.37 ± 0.02	45.0 ± 0.1	nd	1.80 ± 0.01	0.77 ± 0.01	15.52 ± 0.13
165	41.6 ± 0.2	5.80 ± 0.04	0.41 ± 0.02	42.8 ± 0.2	nd	1.68 ± 0.02	0.69 ± 0.01	16.71 ± 0.11

nd: not detected.
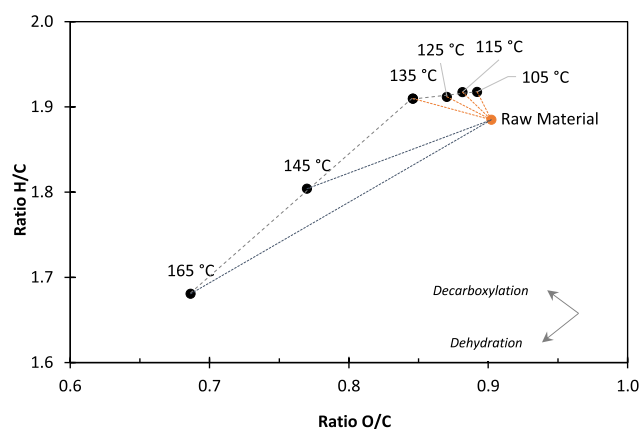
Fig. 9. Van Krevelen diagram (O/C vs H/C elemental ratios) showing the composition of the raw material and the solid residues after the hydrothermal treatment to recover pectin.

temperature tilts the balance towards the degradation stage, resulting in a net degradation of the extracted compounds. Overall, the hydrothermal process enables the production of several families of pectin-derived compounds based on their molecular weight (up to 100 kDa), which necessitate further fractionation processing to isolate the low molecular weight POS fraction obtained so their prebiotic effect can be assessed, at temperatures between 125 and 135 °C, in contrast to the high molecular weight (>300 kDa) obtained through conventional acid-water extraction processes. The elemental analysis of the solid residue obtained after the extraction, unveiled significant variations in the extraction mechanism. At temperatures below 135 °C, decarboxylation was predominant, while at higher temperatures, dehydration reactions became increasingly prominent. In summary, this work opens up the possibility of new studies to obtain these or other compounds using the hydrothermal processing of onion skin wastes and other agroindustrial by-products, coupled with a fractionation and purification step.

CRediT authorship contribution statement

Ó. Benito-Román: Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **R. Melgosa:** Writing – review & editing, Formal analysis. **A.E. Illera:** Writing – review & editing. **M.T. Sanz:** Writing – review & editing, Project administration, Funding acquisition, Data curation. **S. Beltrán:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2024.109957.

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