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The effect of heat processing on the functional properties of pectin contained in olive mill wastewater

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ABSTRACT

The purpose of this study was to evaluate the effect of prolonged heat processing (180 min at 50–80 °C) on the functional and rheological properties of pectin, derived from olive mill wastewater (OMW). It was shown that a low temperature blanching of OMW at 60 °C, activates endogenous pectin methyl esterase and promotes demethylation, despite the high concentration of phenols. Activation of the enzyme resulted in enhanced solubilization and subsequent partial degradation of pectin. The induced degradation impaired pectin grade and resulted in loss of gelling functionality. An alternative heating process at 80 °C resulted in negligible enzyme induced degradation of the pectin and improved gelling properties of the recovered material, despite the lower solubilization of the pectin. The obtained results contribute to a better understanding of the temperature effect on pectin functional properties and can be utilized in order to optimize pectin recovery from OMW.

1. Introduction

Olive Mill Wastewater (OMW) is the by-product of the olive oil production process that is generated in different forms and compositions. It is an acidic mixture (3< pH value <5.9) comprised of 83–94 g water, 4–16 g organics (sugars, nitrogenous compounds, volatile acids, fats, polyphenols and fibres) and 0.4–2.5 g/100 g inorganic compounds (mainly potassium salts and phosphates) (Niaounakis & Halvadakis, 2004). Vierhuis, Korver, Schols, and Voragen (2003) studied the structural features of the soluble polysaccharides present in the OMW, indicating that they are mainly composed of pectic material. Lately, this undervalued agricultural by-product has been considered as a raw material for the recovery of pectin containing material with potential application as gelling agent in food industry. The extraction of this material demands sequential processing of the wastewater and the contained cell wall material (Galanakis, Tornberg, & Gekas, submitted for publication).

During processing, cell walls undergo modifications in terms of their physical state, macrostructure, microstructure, and composition, as well as structure-dependent changes in their functional and material properties (Kunzek, Kabbert, & Gloyna, 1999). For example, fruit and vegetables are softened during thermal processing, due to enzymatic and non enzymatic changes in pectin (Vu, Smout, Sila, Van Loey, & Hendrickx, 2006). For the evaluation of these changes, examination of hydration, rheological (external mechanical stress) and thermal (external thermal stress) characteristics is important (Kunzek et al., 1999).

The influence of external stress during processing has been examined predominantly in the case of heat treatments (Kunzek et al., 1999). Definitely, it has long been known that preheating of vegetables to above 50 °C, in a so-called low temperature blanching, activates endogenous pectin methyl esterase (PME) and results in a firmer final product through subsequent high temperature processing (Van Buren, Moyer, Wilson, Robinson, & Hand, 1960). This effect has been extensively studied and shown to occur in a number of vegetables (Bartolome & Hoff, 1972). A recent verification is referred by Anthon and Barrett (2006) who showed that 60 min thermal treatment at 60 °C is adequate for green beans and tomato endogenous PME activation. With regard to the olive fruit, information about the action of PME is limited. Besides, Vierhuis et al. (2001) proposed that the action of the enzyme is restricted during processing by the high concentration of phenolic compounds present in the olive pulp.

The thermal induced activation of PME causes a decrease in the degree of methylation (DM) of pectin and consequent acceleration of different reactions such as cross linking with calcium ions,

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increased hydration at the demethylated sites, decreased susceptibility for β-elimination and enhanced shielding and repulsion forces by the electric charges within the biopolymer matrix of the cell walls (Tijskens, Waldron, Ng, Ingham, & Van Dijk, 1997). But cross-linking of pectin with calcium, which is promoted on demethylation, is known to retard solubilization of cell wall pectin by ionic-pectin-gel interaction (Sajjaanantakul, Van Buren, & Downing, 1993). Moreover, low methoxy pectins are more susceptible to degradation by endo-polygalacturonase and pectic acid lyase, a process that can lead to a dramatic decrease in viscosity of the final product (Stoforos, Crelier, Robert, & Taoukis, 2002).

Chemical β-elimination is one of the non enzymatic degradation mechanisms in pectins. The rate of this reaction is accelerated with increasing DM, temperature and pH (Diaz, Anthon, & Barrett, 2007). Moreover, prolonged high temperature treatments can result in the β-elimination cleavage and solubilization of pectins (Anthon & Barrett, 2006). Lower DM promotes depolymerization by acid hydrolysis instead of β-elimination at elevated temperatures (Fraeye et al., 2007). In general, any modification in the structural characteristics of pectin may lead to alterations in the functional properties of the system and new applications (Sila, Smout, Elliot, Van Loey, & Hendrickx, 2006). For example, as the product is subjected to further thermal processing, pectin breakdown leads to a decrease in pectin molecular weight, resulting in a loss of pectin functionality (Diaz et al., 2007).

The purpose of the current work is to investigate if PME activity exists in pectin from OMW and to study its time-temperature dependence. Furthermore, the effect of prolonged heat processing (180 min at 50–80 °C) on the functional and rheological properties of pectin, derived from OMW was studied with the goal of improving the gelling properties of the pectin material, and to understand the mechanisms that undergo the thermal induced pectin deesterification, solubilization and degradation.

2. Experimental

2.1. Materials

Samples of OMW were collected from a local three phase olive mill production plant (Chania, Greece). The three phase continuous centrifugation system involves the steps of: crushing the olives, mixing the olive paste and centrifuging it in a decanter with water addition. The used extraction process requires 10–20 L fresh water/100 kg of olives processed to separate the olive oil from the crushed olive cake and the wastewater. Crushing and kneading temperature was kept below 30 °C, while the residence period of the OMW in the sequential extractor was 40 min. Fresh samples were collected from the output of the decanter and kept in plastic containers in the freezer (−20 °C) until usage.

2.2. OMW heat treatment

Aliquots (150 mL) of OMW samples were placed into a 250 mL glass bottle and closed with a plastic lid. The bottle was placed into a circulating water bath and incubated at different temperatures (25, 50, 55, 60, 65, 70 and 80 °C). At various time intervals (0, 30, 60, 120 and 180 min), 2 mL aliquots of the incubation mixture was removed with a pipette, transferred to small sealed plastic vials and directly held on ice in order to stop the activity of PME. After the completion of the heating procedure, samples were diluted and assayed to methanol determination. The 180 min thermal treated OMW mixtures were further processed for the recovery of the alcohol insoluble residue. All the experiments as well as all the determinations were made in duplicates. Fig. 1 shows a schematic overview of the research strategy.

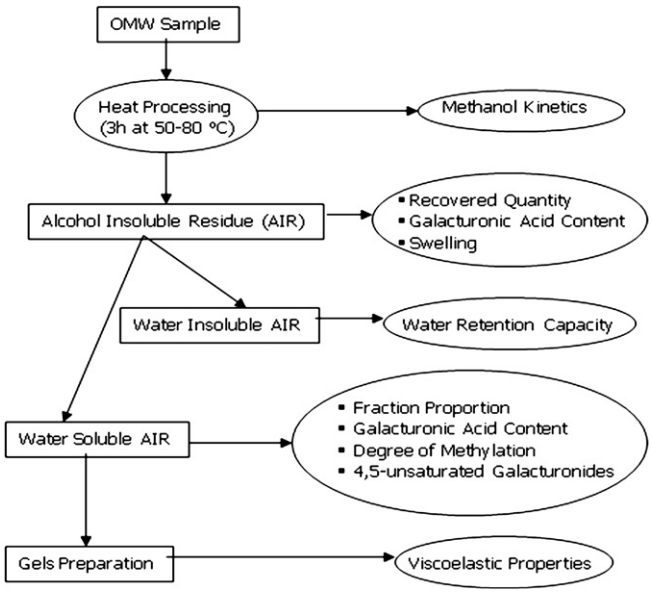

Fig. 1. A schematic overview of the research strategy. "OMW" for "olive mill wastewater".

2.3. Recovery of the alcohol insoluble residue and separation to different fractions

Aliquots (200 mL) of OMW heat treated samples were dispersed in 95 mL ethanol/100 mL to give a final ethanol concentration of 85 mL ethanol/100 mL. Each mixture was stirred at 4 °C for 60 min and filtered through a G3 glass filter. The residue was then washed twice with chloroform/methanol (2:1 v/v, 3-fold initial fresh weight) for 30 min under continuous stirring with a spoon in order to remove any residual oil. The resulting residue was then further washed with acetone and dried overnight at 40 °C in a vacuum oven. The powdered residue was named Alcohol Insoluble Residue (AIR).

Aliquots (2 g) of AIR samples were dispersed in 100 mL distilled water with a magnetic stirrer overnight at 10 °C and the resulting mixtures were centrifuged with 3000 g at 20 °C for 20 min. The pellet was separated from the supernatant and to ensure that the supernatant is free of particles it was filtered through a G3 glass filter with water suction. The amount of soluble and insoluble fractions was determined by freeze drying, grinding and weighing the supernatant and the pellet, respectively. The resulting powder residues were named Water Soluble Alcohol Insoluble Residue (WSAIR) and Water Insoluble Alcohol Insoluble Residue (WIAIR), respectively. The solubility percentage of the AIR material was defined as the ratio of the WSAIR weight per the sum of the WSAIR and the WIAIR weights:

$$\text{Solubility (g/100g)} = \frac{\text{weight}_{\text{WSAIR}}}{\text{weight}_{\text{WSAIR}} + \text{weight}_{\text{WIAIR}}} \times 100\%$$

2.4. Preparation of the gels and rheological assays

Gels were prepared by solubilizing an amount of WSAIR sample in distilled water up to a final volume of 20 mL and then loaded immediately into the pre-heated (20 °C) vessel of the rheometer. An equilibrium time of 120 min was kept for all the gels prior to the rheological assays. Two series of gels were prepared: (i) gels prepared with the same GalA content (1.5 g/100 mL): (ii) gels