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Valorization of Orange Peels as a Source of Pectins †

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Abstract: Pectin is a natural structural polymer that is extensively used in the food industry and in medicinal and pharmaceutical fields. Considering potential applications, in this study, microwave-assisted and conventional extraction were evaluated for the extraction of pectin from orange peel by acid hydrolysis using citric acid as an extractant. For conventional extraction, temperatures higher than 60 °C and long extraction times were necessary to obtained pectin yields of 9.0%. Under conventional conditions of extraction, the degree of esterification of pectin was 55.0%. The extraction procedure assisted by microwave was optimized using an experimental design of 3 factors and 2 levels, and the effect of the operational variables' influence on the pectin yield was analyzed. The optimization of the pectin extraction conditions showed that a temperature of 55 °C, an extraction time of 6 min, and a solid/liquid ratio of 0.02 mg/mL, were necessary to obtain pectin yields of 25.0%. Under the optimal extraction conditions, the degree of esterification of pectin was about 75%. According to the ANOVA analysis, time was the factor that had the greatest influence on the yields of pectin. These results showed that the microwave-assisted procedure to be obtained enabled pectin from the orange peel over mild operation conditions.

Keywords: pectin; valorization; extraction

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1. Introduction

In Argentina, citriculture is one of the most important economic activities. A considerable percentage, around 35% of final citrus production, is represented by the orange sector [1]. Consequently, significant amounts of orange peels are available as a by-product, equating to around 45% of the total bulk [2]. Taking into account the volume of by-products generated, and the fact that most citrus fruit peel is recognized as a good source of pectin [3], such agricultural residues can be considered for use as additives, gelatinizing agents, thickeners, and emulsifiers in the food and flavor industries [4], while in pharmaceutical fields, pectin can be used for delivering drugs [5]. In this way, the conversion of orange peel into a valuable product, such as pectin, offers great scope for utilization and can also reduce environmental pollution [6].

In terms of structure, pectin is an essentially linear polysaccharide present in the cell wall and middle lamellae of several land-growing plants, especially fruit and vegetable crops. The pectin molecule is comprised of about 70% galacturonic acid monomers, which can be acetylated or methyl esterified [7]. Its composition varies with the source and the conditions applied during isolation [8].

Regarding the extraction of pectins from natural sources, tremendous effort is being applied based on the principles of "green" chemistry and technology. Hot conventional extraction requires a prolonged extraction time, high energy input, and the use of strong

acids (such as sulphuric, hydrochloric, and nitric acid), which contradict "green" chemistry and "green" technology principles [7]. In this sense, the use of a suitable method of extraction is of importance during pectin production so that a good yield of pectin is obtained and its properties are preserved [4].

In this research, the extraction of pectin from orange peel using microwave-assisted and conventional procedures was performed. The aim of this study was to develop an acid hydrolysis by microwave-assisted extraction (AH-MAE) method to obtain pectins from orange peel residues and to investigate the effect of process variables (e.g., time, temperature, solid-liquid ratio) on the outcome (pectin yield). To optimize the pectin extraction conditions, ANOVA analysis was used.

2. Materials and Methods

2.1. Materials

The orange peels were obtained from industrial waste to ensure the same origin. The peels were dried (48 h, 60 °C), ground (Delver MPD 1011 A), and stored at 4 °C. The moisture content of the powder sample was determined by gravimetry.

2.2. Extraction of Pectin

2.2.1. Acid Hydrolysis by Conventional Method (AH-CM)

Pectin extraction was performed by modification of the method provided by [9]). A citric acid solution (0.05 M, 240 mL) was mixed with 10 g of peels, and extraction was carried out (90 °C, 60 min) in a shaking water bath. The pH of the extracting agent was adjusted to 1.0 with 0.1 M HCl. After extraction, the resulting sediment was filtered. To separate the remaining insoluble material, the solution was centrifuged at 2000 rpm for 15 min. The clear pectin solution was used for further purification. Subsequently, pectin was precipitated with the addition of 96% ethanol (1:2, v/v), stirred for 10 min, and kept for 2 h without stirring at room temperature. The coagulated pectin was separated by centrifugation at 2000 rpm for 15 min and washed three times with 50% (v/v) ethanol. The orange pectin was dried at 40 °C in a laboratory dryer and then ground using a mortar.

2.2.2. Acid Hydrolysis by Microwave-Assisted Extraction (AH-MAE)

Microwave extraction was carried out on an Anton Paar 300 Microwave Lab using a solution of citric acid as the solvent, at 600 rpm and 850 W of power. The choice of using an organic acid rather than a mineral acid was because mineral acid causes the loss of volatile compounds and some have a negative environmental impact [3]. According to the experimental design (Table 1), the extraction was performed under different AH-MAE conditions. After microwave heating, the mixture was allowed to cool down to room temperature and filtered. The filtered extract was centrifuged and the supernatant was precipitated with an equal volume of 95% (v/v) ethanol. The coagulated pectin mass was washed with 95% (v/v) ethanol three times to remove the mono and disaccharides [6].

Table 1. Experimental design and yield of pectin.

Sample Name	Extraction Conditions			Pectin Yield/%
	Time/min	Temperature/°C	Relation Solid:Liquid/g/mL	
1	6	65	0.02	14.99
2	3	65	0.02	9.11
3	3	55	0.04	19.16
4	6	55	0.04	15.42

Table 1. *Cont.*

Sample Name	Extraction Conditions			Pectin Yield/%
	Time/min	Temperature/°C	Relation Solid:Liquid/g/mL	
5	6	65	0.04	17.65
6	3	65	0.04	15.66
7	6	55	0.02	22.05
8	3	55	0.02	23.92
9	6	65	0.02	16.14
10	3	65	0.04	11.76
11	3	55	0.02	24.03
12	3	65	0.02	10.35
13	3	55	0.04	18.37
14	6	55	0.02	25.09
15	6	65	0.04	15.19
16	6	55	0.04	11.05

2.3. Experimental Design and Statistical Analysis

An ANOVA analysis was used to determine the optimal conditions for pectin extraction from the orange peels. As factors to study, the following were selected: time, temperature, and solid: liquid ratio. The temperatures used were 55 °C and 65 °C. The microwave sample vessel could hold up to a minimum of 6 mL and a maximum of 20 mL of solution, so the chosen solid:liquid ratios were 0.02 g/mL and 0.04 g/mL. The extraction periods for microwave extraction were chosen based on the extraction periods reported by [10]. A factorial design to study the effect of the process variables on the pectin yield was proposed with three factors, two levels, randomized, without blocks, without including central points, with a significance level of 0.05 and two replications. The proposed experimental design is shown in Table 1.

2.4. Determination of Pectin Yield

The pectin obtained was dried at 50 °C in a hot air oven until its weight was constant. The pectin yield (*PY*) was calculated from the following equation:

$$PY\ (\%) = \left(\frac{m_0}{m}\right) \cdot 100 \quad (1)$$

where m_0 (g) is the weight of dried pectin and m (g) is the weight of dried orange peel powder.

2.5. Determination of the Degree of Esterification

The degree of esterification of the pectin samples was determined for the sample that presented the highest pectin yield using a volumetric technique [11]. The pectins (0.15 g) were mixed with 60% ethyl alcohol. Distilled water (30 mL) was added to the mixture and stirred until the sample was completely hydrated. The mixture was titrated against 0.1 N NaOH. The spent volume of the titration was recorded as V1. NaOH (0.1 N, 2 mL) and HCl (0.5 N, 2 mL) were added to the solution and the mixture was titrated against 0.1 N NaOH. The spent volume of the titration was recorded as V2. The degree of esterification was calculated according to Equation (2):

$$DE(\%) = \left(\frac{V_2}{V_2 + V_1}\right) \cdot 100 \quad (2)$$

3. Results and Discussion

The extraction of pectin was carried out by acid hydrolysis. The conventional method requires heating to 90 °C for a period of time to 60 min, which involves significant energy consumption, in contrast to the current trend of using increasingly energy-efficient production methods. The energy in the process can be substantially reduced by applying homogeneous radiation heating, using a microwave-assisted method [10]. This was observed in the results obtained for the AH-MAE method (Table 1). As can be seen, the optimal conditions to achieve the highest pectin yield by AH-MAE were obtained in sample number 14, with a time of 6 min, a temperature of 55 °C, and a solid: liquid ratio of 0.02 mg/mL, with a pectin yield of 25.09%, a value higher than that obtained with the conventional method, which was 9.92%. The efficiency of the extraction by AH-MAE increased concerning the AH-CM would be a consequence of the electromagnetic radiation emitted by the microwave in the sample that increases the thermal energy of the solvent. In this way, the energy induced the vibration of the polar molecules with a rapid increase in temperature increasing the efficiency of the extraction process [3]. It was observed that the pectin obtained by the AH-CM suffered a certain degree of degradation, probably as a consequence of the high temperatures and the long period of heating. This observation is consistent with observations previously reported by other authors [3].

ANOVA was used to estimate the experimental result for the determination of the relative significance of each factor in the AH-MAE method. The percentage involvement of every factor or parameter was evaluated. The method examines and models the correlation among the response and free variables [12]. Two hypotheses were formulated to analyze the experimental data in order to examine the statistical significance of the model terms which are listed in Table 2:

- Null hypothesis (H_0): the experimental factor does not influence the response variable.
- Alternative hypothesis (H_i): the experimental factor influences the response variable.

Table 2. Hypothesis testing to determine the optimal parameters.

Experimental Factor	*p* Value	Criteria for Acceptance/Rejection
Time	0.026	Is rejected
Temperature	0.493	Not rejected
Relation solid:liquid	0.456	Not rejected
Time/Temperature	0.275	Not rejected
Time/Relation solid:liquid	0.624	Not rejected
Temperature/Relation solid:liquid	0.028	Is rejected

Based on the results obtained, the acceptance or not of the null hypothesis for each factor with respect to the response variable was determined applying a confidence level of 95%.

According to the ANOVA analysis, the temperature and the solid:liquid ratio were not associated with a significant increase in the pectin yield for the range of variation established; however, time had a significant influence. The *p* values for time/temperature, time/solid:liquid ratio, and temperature/solid:liquid ratio showed that the last was associated with a significant increase in pectin yield.

The gelling properties of pectin obtained were evaluated by the degree of esterification. The degree of esterification for the run with which the best pectin yield was obtained by AH-MAE was compared with the pectin obtained by the AH-CM. The DE for sample number 14 was 75.16%, compared to the DE of pectin obtained by the conventional method, which was 54.58%. Thus, the pectin extracted using citric acid in this study can be categorized as high methoxyl pectin because it had a %DE that was higher than 50% [13].

4. Conclusions

In this study, the potential of citrus peel for use as a source of pectin was studied. Microwave-assisted extraction was employed to extract pectin from orange peel and compared to the usual extraction method by conventional heating. The experimental results of PY from orange peel by AH-MAE were superior to the results obtained by AH-CM.

The optimization of the pectin extraction conditions by AH-MAE showed that the optimal condition was a time of 6 min, a temperature of 55 °C, and a solid/liquid ratio of 0.02 g/mL. Under the optimal extraction conditions, the degree of esterification of the pectin was about 75%, which can be categorized as high methoxyl pectin.

The acid hydrolysis by microwave-assisted extraction promoted higher pectin recovery in a shorter time compared to acid hydrolysis by the conventional method, demonstrating that it is a promising alternative to increase extraction efficiency. However, additional studies are required to evaluate the economic viability of these processes and the properties of the pectin obtained.

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