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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, medicinal and pharmaceutical fields. Considering their potential applications, in this work, microwave-assisted and conventional extraction were evaluated to extract 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 convention 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, analyzing the effect of operational variables' influence in the pectin yield. The optimization of pectin extraction condition showed that temperature of 55 °C, extraction time of 6 min, and solid/liquid ratio of 0.02 mg/mL, are necessary to obtained pectin yields of 25.0%. Under the optimal extraction condition, the degree of esterification of pectin was about 75%. According to the ANOVA analysis, time was the factor that more influence had on yields of pectin. These results showed that microwave-assisted procedure allows obtaining pectin with suitable properties from 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 the final citrus production, represents the orange sector (Larocca, 1995). Consequently, significant amounts of orange peels are available as a by-product, around 45% of the total bulk (Yeoh et al., 2008). 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 (Rodsamran & Sothornvit, 2019), it is interesting to use such agricultural residues as additives gelatinizing agents, thickeners, and emulsifiers in the food and flavor industries (Kratchanova et al., 2004) and in pharmaceutical fields pectin can be used for delivering drugs (Kumar et al., 2018). In this way, the conversion of orange peel into a valuable product such as pectin offers great scope for utilization and also reduces environmental pollution (Prakash Maran et al., 2013).

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 (Picot-Allain et al., 2020). Its composition varies with the source and the conditions applied during isolation (Srivastava & Malviya, 2011).

Regarding the extraction of pectins from natural sources, tremendous effort is being made on the principle of "green" chemistry and technology. Hot conventional extraction

requires prolonged extraction time, high energy input, and the use of strong acids (such as sulphuric, hydrochloric, and nitric acid), as against "green" chemistry and "green" technology principles (Picot-Allain et al., 2020). 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 (Kratchanova et al., 2004).

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) to obtain pectins from orange peel residues and investigate the effect of process variables (time, temperature, solid-liquid ratio) and the response (pectin yield). To optimize such 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 with the modification of the method provided by (Güzel & Akpınar, 2019). Citric acid solution (0.05 M, 240 mL) was mixed with 10 g of peels, and extractions were 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 Anton Paar 300 Microwave Lab using a solution of citric acid as solvent, at 600 rpm and 850 W of power. The choice of using an organic acid rather than a mineral acid was based on the mineral acid causes the loss of volatile compounds and some have a negative environmental impact (Rodsamran & Sothornvit, 2019). 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 (Prakash Maran et al., 2013).

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
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 orange peels. As factors to study, the following were selected: time, temperature, and solid: liquid ratio. The temperatures studies were 55 °C and 65 °C. The microwave sample vessel could hold up a minimum of 6 mL and a maximum of 20 mL of solution, so the chosen solid:liquid ratio 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 (Franco Zegada, 2015). In this way, the factorial design to study the effect of process variables on the pectin yield was proposed for 3 factors, 2 levels, randomized, without blocks, without including central points, with a significance level of 0.05 and 2 replications. In this way, the experimental design proposed is shown in Table 1.

2.4. Determination of Pectin Yield

The pectin obtained was dried at 50°C in the hot air oven until its weight was constant.

The pectin yield (PY) was calculated from the following equation:

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

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 pectin samples was determined for the sample that presented the highest pectin yield using a volumetric technique (Chittasupho et al., 2013). 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 by equation 2:

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

3. Results and Discussion

Extraction of pectin was carried out by acid hydrolysis. The conventional method required heating to 90 °C for a period of time to 60 min, which represents a significant energy consumption, in contrast to the current trend of using increasingly energy-efficient production methods. So, the energy in the process can be substantially reduced by applying homogeneous radiation heating, by the microwave-assisted method (Franco Zegada,

2015). In fact, this is observed in the results obtained in the AH-MAE method (Table 1). As we can see, the optimal conditions to achieve the highest pectin yield by AH-MAE were obtained in sample name 14, with a time of 6 min, a temperature of 55 °C, and a solid: liquid ratio of 0.02 mg/mL, doing the pectin yield of 25.09% a value higher than that obtained with the conventional method which was 9.92%. In this sense, the efficiency of the extraction by AH-MAE increased with respect to the AH-CM probably as a consequence of the electromagnetic radiation emitted by the microwave in the sample manages to rotate and produce thermal energy in the solvent. In this way, the energy induces the vibration of the polar molecules with a rapid increase in temperature increasing the efficiency of the extraction process (Rodsamran & Sothornvit, 2019). Besides, it was observed that the pectin obtained by the AH-CM suffered a certain degradation, probably as a consequence of high temperatures and long periods of heating. This observation coincides with the previously reported by other authors (Rodsamran & Sothornvit, 2019).

On the other hand, ANOVA was used to estimate the experimental result for the determination of the relative significance of each factor in the AH-MAE method. Percentage involvement of every factor or parameter was evaluated. It examines and models the correlation among the response and free variables (Kohli et al., 2018). 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.

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

Table 2. Hypothesis test 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

According to ANOVA analysis, the temperature and the solid:liquid ratio do not generate a significant increase in the pectin yield in the ranges of variation established, while time has a significant influence. Results of the *p* values for time/temperature, time/solid:liquid ratio, temperature/solid:liquid ratio shown that the last generate a significant increase in the pectin yield.

The gelling properties of pectin obtained were evaluated by the degree of esterification. The degree of esterification of the run with which the best pectin yield was obtained by AH-MAE was compared with the pectin obtained by the AH-CM. So, the DE for sample name 14 was 75.16% besides the DE of pectin obtained by the conventional method was 54.58%. Thus, the pectin extracted using citric acid produced in this study can be categorized as high methoxyl pectin because it has a %DE that is higher than 50% (Wahengbam et al., 2014)

4. Conclusions

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

The optimization of pectin extraction condition 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. Also, under the optimal extraction condition, the degree of esterification of pectin was about 75% which can be categorized as high methoxyl pectin.

In this way, acid hydrolysis by microwave-assisted extraction promoted higher pectin recovery in a shorter time, as compared to acid hydrolysis by the conventional method, proving to be promising alternatives for increase the extraction efficiency. However, some additional studies must be done to evaluate the economic viability of these processes and the properties of the pectin obtained.

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