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VALORIZATION OF APPLE PROCESSING BY-PRODUCTS

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Abstract

Apple products are considered to be one of the major fruit products consumed globally. In apple processing industries, the remaining mixture of seeds, peels and pulp are collectively referred to as "apple pomace". Although this waste has a lot of potential for biodegradation, its disposal lead to concerns regarding the impact on the environment. This study is focused on valorization of apple pomace, by using it as a substrate for pectin extraction. Extraction was optimized by varying several factors such as: extraction solvent (HCl, HNO_3, acetic acid or citric acid), temperature (60 or 75°C) or extraction period (1 or 2 hours). The best extraction was registered with citric acid, at 60°C for 2 hours. These results are significant for further studies on pectin extraction from apple pomace.

Key words*: apple, pectin, pomace.*

INTRODUCTION

According to FAO, a third of the food directed for human consumption is lost during earlier stages of production or wasted, which amounts to almost 1.3 billion tons annually (http://www.fao.org/food-loss-and-food-waste/en/). While loss of food happens in low-income countries, waste of food is more encountered in industrialized countries due to bad habits of both consumer and producer.

One of the most consumed fruits are apples, the production rate annually being 70 million tons worldwide (Catană et al., 2018).

Apple processing generates sometimes almost 50% solid waste of raw material such as pomace, core, peel, unripe or damaged fruits etc. (Virk & Sogi, 2004). This mixture, generally known as apple pomace or apple cake is a valuable by-product that can be use as a substrate for different applications such as food, feed, fuel etc. (Toma et al., 2019).

One of the main products recovered primarily from apple wastes is a complex macromolecule known as pectin.

In 1790, Vauquelin was the first who designed the chemical structure of pectin, a complex heteropolysaccharide consisting of D-α-(1-4) anhydro-galacturonic acid (Ziari et al., 2011).

Pectin was first isolated and named by Braconnot in 1824. Pectin is found in higher plants in the primary cell walls and in the middle lamella between plant cells (Sundarraj & Ranganathan, 2017) and acts as a hydration and binding agent for cellulose (Loyola et al., 2011).

Pectin has a very complex structure in higher plants, which gives shape to the soft non-woody parts of the plant (Ziari et al., 2011).

Pectin is widely used in various industrial applications (food, pharmaceutical, cosmetic, biomedical etc.), due to its stabilizing or gelating properties (Venkatanagaraju et al., 2019). Its role includes: thickener, emulsifier, gelling and glazing agent and stabilizer (Ziari et al., 2011; Tiwari et al., 2017). In food industry, pectin is considered to be a safe additive with no specified limit on accepted daily intake (Tiwari et al., 2017).

Pectin can be isolated from various sources (carrots, sugarbeet, sunflower, mango, pomegranate, sweet potatoes etc.) with different extraction protocols such as: hot acidic solution, cold diluted sodium hydroxide, cold and/or hot solutions of chelating agents (EDTA, CDTA, ammonium oxylate, sodium hexa meta phosphate) (Toma et al., 2019; Srivastava & Malviya, 2011; Pereira et al., 2016; Zaidel et al., 2015; Renard & Thibault, 1993; Albu et al., 2019).

An improved extraction can be achieved by optimising several parameters such as: extraction solvent, temperature, pH or extraction time. Due to pectin solubility in

water and insolubility in organic solvents, its extraction requires aqueous solvent followed by precipitation and recovery (Perussello et al., 2017). The solvent should have a low pH (1-3) in order to break protopectin, but not too low in order to obtain a higher quality pectin (Perussello et al., 2017).

For economic reasons, the sources used for extracting pectin commercially are represented by wastes from food industry, such as: peels, pulp, pomaces, rinds, husks etc. (Ziari et al., 2011; Sundarraj and Ranganathan, 2017). Usually, the extraction method used is conducted with acidic solution at elevated temperature (Ziari et al., 2011). The most used pectin sources are citrus peels (25-35% dry basis pectin content) and apple pomace (10-15% dry basis pectin content) (Sundarraj & Ranganathan, 2017).

Pectin composition and properties are conditioned by the source from which is extracted. Therefore, several studies suggested that pectin from apple pomace has superior gelling properties in comparison with pectin from citrus peels (Ziari et al., 2011).

The annually production of pectin worldwide is around 40.000 metric tons (Sundarraj & Ranganathan, 2017) and specialists suggest that it may increase, therefore deriving the importance of establishing an optimized protocol for pectin extraction.

This study is focused on valorization of apple pomace as a substrate for pectin extraction. In order to achieve an improved protocol, several factors were considered such as: temperature, extraction period or optimal aqueous solvent.

MATERIALS AND METHODS

Sample preparation

The materials used were green apples (Golden delicious variety), considered to have a higher pectin content than other varieties (Rascón-Chu et al., 2009).

The apples were washed, cut and pressed for juice extraction, resulting an apple pomace that contained peels, seeds, cores and pulp residues.

Pectin extraction

The fresh apple pomace was subjected to pectin extraction with different aqueous solvents (Figure 1) in fresh sample:solvent ratio of 1:25 (w/v). The extraction solvents used in this study were selected as optimal after reviewing the literature (Perussello et al., 2017; Ziari et al., 2011; Sandarani, 2017; Sayah et al., 2014; Canteri-Schemin et al., 2005; Tiwari et al., 2017): 0.1 N hydrochloric acid, 0.5% nitric acid, 10% acetic acid and 5% citric acid.

After the extraction, the samples were cooled and precipitated with 96% ethanol (Figure 1). After filtration, the precipitates were washed with 60% ethanol and pressed down to remove excess alcohol.

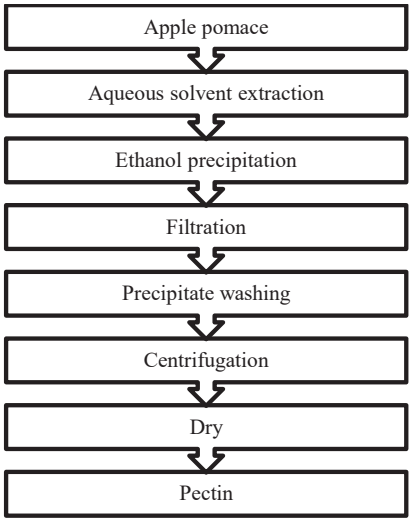

Figure 1. Extraction protocol

The extraction protocol was conducted at different temperatures (60°C and 75°C) for different extraction time: 1 or 2 hours.

Determination of pectin yield

The pectin yield of the samples was assessed gravimetrically after the extraction protocol, by oven drying the washed precipitates (Figure 1) at 40°C until constant weight was obtained.

Pectin yield was calculated after the following formula:

$$\text{Pectin yield (\%)} = \frac{\text{Pectin (g)}}{\text{Dry matter of apple pomace (g)}} * 100$$

The dry matter content was necessary for the assessment of pectin yield. The method involved drying the weighed samples in an oven at 105°C until it reaches constant weight.

The dry matter content was calculated by the next equation:

$$\text{Dry matter (\%)} = \frac{\text{Dried sample (g)}}{\text{Fresh sample (g)}} * 100$$

RESULTS AND DISCUSSIONS

Due to its biodegradability, apple pomace is often discarded near the processing units, which lead to environmental and economic concerns (Sharma et al., 2014). Therefore, an important application for this waste could be pectin extraction.

The dry matter content of the apple pomace was necessary for the comparison of the results of the extraction protocols with different design. For this purpose, 4 samples were weighed and subjected to oven dry at 105°C for several hours until they reached constant weight, as seen in Table 1.

Table 1. Dry matter content of apple pomace

Sample	Fresh apple pomace (g)	Dried apple pomace (g)	Dry matter (%)
1.	6.87	2.579	37.54
2.	6.87	2.577	37.51
3.	6.87	2.578	37.53
4.	6.87	2.579	37.54

Therefore, the average dry matter content was calculated to be 37.53%, similar to the results of other studies (Gullón et al., 2007).

The first design for the extraction of pectin involved selecting the best aqueous solvent between 2 mineral acids (0.1 N hydrochloric acid and 0.5% nitric acid) and 2 organic acids (10% acetic acid and 5% citric acid). Different acid concentrations were selected because of their different acidity constants - pKa (-6 for HCl, -1.32 for HNO_3, 4.75 for acetic acid and 2.92, 4.28 and 5.21 for citric acid).

The solvent + apple pomace mixtures were left to extract for 1 hour, at 60°C in a shaker at 150 rpm, and the results obtained were presented in Table 2.

Following the extraction with the 4 aqueous solvents, it was found that by using mineral acids (HCl and HNO_3) were obtained similar concentrations of pectin 1.57-2.16% pectin of fresh matter (Table 2). Comparable value was also recorded with acetic acid, being even lower than those recorded with nitric acid extraction, as seen in Table 2.

Table 2. Pectin content of apple pomace extracted at 60°C for 1 hour and 150 rpm

Sample	Extraction solvent	Pectin content (% of fresh matter)	Pectin content (% of dry matter)
1.	HCl	1.57	4.19
2.	HNO_3	2.16	5.75
3.	Acetic acid	1.65	4.40
4.	Citric acid	**13.49**	**35.96**

Unexpectedly, citric acid extraction resulted in considerably better results (13.49% pectin of fresh matter and 35.96% pectin of dry matter), about 6-7 times compared to other extractions (Table 2). Developing an efficient extraction using citric acid has a great importance for obtaining pectin intended as a food additive.

The second step in optimising this protocol implied selecting the best temperature for pectin extraction, by conducting a similar experiment but at 75°C. The other parameters remained constant: 1 hour and 150 rpm (Table 3).

Table 3. Pectin content of apple pomace extracted at 75°C for 1 hour and 150 rpm

Sample	Extraction solvent	Pectin content (% of fresh matter)	Pectin content (% of dry matter)
5.	HCl	2.42	6.46
6.	HNO_3	3.47	9.26
7.	Acetic acid	1.58	4.21
8.	Citric acid	**10.69**	**28.50**

The extractions conducted with HCl, HNO_3 and acetic acid resulted in low pectin content related to total dry matter of apple pomace (Table 3).

Similar to the first protocol, citric acid extraction resulted in a higher pectin content, but this time it was 3-4 times higher than the other extractions, reaching 10.69% pectin content of fresh apple pomace (Table 3).

The temperature change from 60°C to 75°C lead to slightly higher pectin content for mineral acid extractions, but for acetic acid

extraction there were no significant differences in pectin content (Tables 2 and 3).
However, by increasing the temperature for citric acid extraction, it was concluded that pectin content decreased by almost 20.74% (Tables 2 and 3). These results indicated that increasing the temperature was not beneficially for all the aqueous solvents, the optimal temperature for citric acid extraction being 60°C.
The final step required for optimizing pectin extraction involved selecting the best extraction period, by using the same solvents at 60°C and 75°C but for 2 hours (Table 4). The experiment was conducted at both 60°C and 75°C, because it was not determined the best temperature optimal for all the aqueous solvents. The results were compared with those recorded in the previous experiments, where the extractions were performed for 1 h (Tables 2 and 3).
The extractions with HCl, HNO_3 and acetic acid at 60ºC for 2 hours lead to lower pectin content in comparison with citric acid extraction (Table 4), which recorded the highest content of 23.06% of fresh matter.
By conducting the experiment at 75ºC for 2 hours, the pectin content was also lower for the first 3 acids but higher for citric acid with a value of 14.38% (Table 4).

Table 4. Pectin content of apple pomace extracted at 60°C and 75°C for 2 hours and 150 rpm

Sample	Extraction solvent	Extraction temperature	Pectin content (% of fresh matter)	Pectin content (% of dry matter)
9.	HCl	60ºC	1.66	4.44
10.	HNO_3	60ºC	3.48	9.29
11.	Acetic acid	60ºC	1.93	5.14
12.	Citric acid	60ºC	**23.06**	**61.45**
13.	HCl	75ºC	2.46	6.55
14.	HNO_3	75ºC	4.80	12.81
15.	Acetic acid	75ºC	2.38	6.35
16.	Citric acid	75ºC	**14.38**	**38.32**

Therefore, it was concluded that pectin extraction with hydrochloric acid was improved significantly by increasing the temperature from 60ºC to 75ºC and it was noted that by increasing the extraction period the results were comparable (Tables 2, 3 and 4). Pectin content of dry matter was variable between 4.19-6.55%, the results being comparable with other studies (Canteri-Schemin et al., 2005).
Pectin extraction with HNO_3 was improved both by increasing the temperature to 75ºC as well as by increasing the extraction period from 1 hour to 2 hours (Tables 2, 3 and 4). Pectin content was registered between 5.75-12.81% of dry matter, higher than the values obtained HCl extraction, but comparable with other studies (Sandarani, 2017).
Organic acid extractions were not significantly improved by increasing the temperature and the extraction period, as noted for the mineral acid extractions (Tables 2, 3 and 4).
Acetic acid extraction lead to low pectin content (4.21-6.35% of dry matter), comparable with citric acid extraction, with the mention that it was observed a slightly higher pectin content by increasing the temperature to 75ºC (Table 4).
The best results in all of the experiments were registered with 5% citric acid extraction, pectin content ranging from 28.5-61.45% of dry matter (Tables 2, 3 and 4), higher than the results of other studies (Canteri-Schemin et al., 2005). Also, it was concluded that increasing the extraction time from 1 hour to 2 hours lead to higher contents of pectin by 34.45-70.88%.
The higher temperature affected pectin extraction, resulting in lower values in all of the experiments. This may be linked with thermal degradation of pectin, as suggested by other researchers (Fraeye et al., 2007; Woo et al., 2010).

CONCLUSIONS

Apple pomace is an important by-product in apple processing, one main application being extraction of valuable compounds such as pectin.
This paper was centred on optimizing pectin extraction protocol from apple pomace derived from pressing fruits for juice.

The experiments lead to selecting the best aqueous solvent for extraction (5% citric acid), its high extraction efficiency being of great interest for food industry. The others factors that positively influenced extraction were temperature (60ºC - optimal for citric acid and 75ºC for the other solvents extractions) and extraction period (2 hours for all the protocols). The results of the research are valuable because they allow for milder extraction conditions, but also that they have a reduced impact on the environment, by using organic acids instead of mineral ones.

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