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ORIGINAL PAPER

Optimization of pectin extraction from crab apple peel and usage in a model meat emulsion system

Hazal Aldemir[1] · Aybike Kamiloğlu[1] · Özlem Çakır[1]

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Abstract
The aim of this study was to optimize conditions of microwave-assisted pectin extraction from crab apple peels using the Box–Behnken experimental design. For this purpose, microwave-assisted pectin extraction was performed at different extraction time (3, 6, and 9 min), liquid/solid ratio (75, 100, and 125), and pH (1.5, 2.0, 2.5). The optimum conditions were selected as extraction time (7.77 min), liquid/solid ratio (77.53 mL/g), and pH/1.79). The response, obtained under optimum conditions was determined as 0.1128 ± 0.0137 g pectin/g crab apple peel. In addition, it was determined that the obtained pectin sample had an esterification degree of 79.14% and oil and water binding capacities of 8.5 ± 0.7 g oil/g pectin and 8.1 ± 1.5 g water/g pectin, respectively. It was determined that pectin emulsions showed higher stability at 1% pectin level. The possibilities of using pectin obtained under optimized conditions as a fat replacer in a model sausage system were investigated. Pectin was evaluated in the model sausage system at two different concentrations. With the increasing pectin concentration, the cooking loss value increased from 14 to 18%, while leakage decreased from 0.31% to 0.18%, showing a negative effect on cooking loss and a positive impact on the amount of leakage into the packaging. Pectin obtained from crab apple peel has the potential to be used for reducing fat content in sausage environment.

Keywords Pectin · Response surface method · Microwave extraction · Model sausage system

Introduction

Pectin is found in the intercellular spaces and cell walls of plant tissues. It provides plants with resistance and plays a role in their growth and development. Pectins, found in different amounts in fruits and vegetables, are plant-derived stabilizers [1]. The main structure of pectin is the galacturonic acid chain. This heteropolysaccharide is mostly composed of α-galacturonic acid polymers linked by α-1.4-glycosidic bonds [2]. Some of the carboxyl groups of galacturonic acid can be esterified with methanol. Pectins with esterification degree more than 50% high methoxylated (HM) pectins, while pectins with esterification degree less than 50 pectins (ED < 50%) are referred to as low methoxylated (DM) pectins. The differences in the pectin molecule are due to the degree of esterification, the distribution of methyl ester groups along the polygalacturonic acid chain, the degree of polymerization (molecular weight) and the type and amount of neutral sugars bound to the pectin molecule [1].

Pectin is a food additive commercially known as code E440 and is generally obtained from food waste by various methods. The interaction of pectin with other ingredients in a food is significant. The food's appearance, texture and emulsion stability can be improved by using pectin, which means it can be used in the confectionery of varying hardness, acidic milk, reduced fat intake foods, drinks, etc. [3]. Additionally, pectin has good water and oil-binding properties. Therefore, it can be used as a gelling agent, film/coating, emulsifier, and fat and sugar replacer (dietary fiber) in low-calorie meat products [4]. The use of pectin as a food additive is permitted in all countries and there are no restrictions on daily consumption [5, 6].

The main pectin extraction methods are as follows: traditional method (acid solution), enzymatic assisted extraction, supercritical water extraction, microwave-assisted extraction, ultrasound-assisted extraction, electric field assisted extraction. According to studying conditions, various chemical methods can be preferred to recover pectin from plants because pectin extraction consists of multiple

✉ Aybike Kamiloğlu
abereketoglu@bayburt.edu.tr

[1] Food Engineering Department, Faculty of Engineering, Bayburt University, 69000 Bayburt, Turkey

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processes. The separation of pectin macromolecules from plant tissue (hydrolysis, extraction and dissolution, respectively) occurs under different factors. Therefore, it is a multi-stage process [4]. Pectins can be easily extracted in an acidic and hot solution, but this process may cause environmental pollution and produce large amounts of waste. The points to be considered in pectin extraction methods are as follows: achieving high efficiency, achieving high-quality products, completing in a shorter time and saving energy [2, 7]. New technologies such as microwave heating, ultrasound, subcritical water and enzyme-assisted extraction are powerful tools to ensure high production and good products. Combinations of these techniques are also being investigated. One of the most preferred and advantageous methods is microwave-assisted extraction.

Microwave-assisted extraction is a practical, high-quality pectin extraction method compared to conventional heating methods. Additionally, it presents some advantages, such as short extraction time and less solvent usage [8–10]. There are several sources to recover the pectin using different plants, especially fruits. For instance, citrus peels contain 20–30% pectin, while apple pulp includes 10–15% [11]. However, commercial pectin is generally produced using citrus peels and apples in the food industry, and new scientific investigations have been carried out for alternative pectin sources [12]. Additionally, it is thought there are a lot of potential pectin sources in nature, but they have not been investigated yet. Studies on obtaining pectin from different sources by various methods and using pectin as an additional additive atract attention. In a study, Syeitkhajy [13] compared the traditional method with microwave-assisted extraction and ultrasound-assisted extraction using waste citrus peel. He reported that the new methods of obtaining pectin take less time and that the microwave method is more advantageous regarding energy costs. In another study, Keleş [14] compared the pectin obtained from pomegranate peel by traditional and enzymatic extraction methods. The structures of the two pectins were similar due to FTIR analysis, while the yield and degree of esterification were higher in the enzymatic extraction method [14]. And also, Taşan [15], reported the pectin showed similar structures obtained from dried grapefruit peel by applying microwave-assisted and traditional extraction methods. Apricot marmalade was made with the pectin obtained was found to be sensory superior in the microwave-assisted extraction method. Apart from the fruits mentioned here, pectin potential studies have also been conducted for different fruits such as pomelo peels [16], *Carcia papaya* L. peel [7] and sweet lemon peel [17].

One alternative pectin source is *Malus sylvestris* Miller; also known as Bayburt wild apple by locals, is a yellow-colored, white-fleshed fruit that grows naturally in rural areas and on mountain slopes. It is suitable for the harsh conditions of the region's climate [18, 19].

In recent years, applications on pectin in meat and meat products have become widespread. For example, in a study conducted on substituting 5% pectin for fat content in Chinese sausage. It has been reported that the application of pectin increases the color and preserves the sensory properties as well as the physical qualities. It has been determined that pectin can be used as a new fat substitute in low-fat Chinese sausage [10]. Pectin can improve color parameters associated with consumer acceptance; meat products can be reformulated with fibres, preserving protein content and water retention capacity, and ultimately can be used as fat replacers in sausages and also as a source of prebiotic ingredients [20].

This study consists of three points. In this context, the three main pillars of pectin are unified, source, producing/recovering method and purpose usage. First, the Bayburt apple's potential as a pectin source is assessed. Currently, it is grown in abundance and not consumed except for traditional purposes (added to the tea) by locals. Besides, much of it is wasted and cannot be evaluated economically. The aims of this study are to reach an economical and organic source of pectin and to introduce wild apple to the food industry. This study focuses on the microwave-assisted pectin extraction method on the second pillar. In this context, it was aimed to optimize the mentioned method with the help of the response surface method and Box-Behnken experimental design. Additionally, the general structure of the extracted pectin is characterized to compare existing commercial pectin types. The third point of this study is to expose the possibilities of using pectin as a fat replacer in the model sausage emulsion. In this context, the effect of fat substitution on the chemical composition, and textural and sensory properties of emulsion-type sausages were investigated.

Materials and methods

Material

Crab apples were purchased from local producers in Örence village of Bayburt. It was packaged and stored at − 18 °C. Then, after the apples were sorted and washed, the peels were removed, cleaned with distilled water, and dried in a drying oven. The drying process was carried out in an oven at 45 °C for 2–3 days. Dried peels were pulverized before being used.

Microwave assisted pectin extraction

Extraction was performed at different times, liquid/solid ratio, and pH ranges using a Box–Behnken experimental design for the extraction procedure. Microwave oven (Beko,

MD 1510) with a frequency of 2450 MHz was used as the microwave source for the extraction. The apple peel powder were weighed 1 g, mixed with acidic water of different volumes (75–100–125 mL, acidified with HCl) and pH (1.5–2–2.5) into the Erlenmeyers, and left at room temperature for 20 min. The samples were kept in the microwave oven at 833 Watts for different times (3–6–9 min), and the extraction was carried out. After the microwave process, the liquid was centrifuged at 5000 rpm 4 °C for 20 min. After the centrifugation process, the liquid part remaining on the tubes was poured into the measuring tubes, and the precipitation process was carried out by adding 95% ethanol, two times the amount of liquid. The precipitated pectins were collected on the paper by filtration of the liquid part from the simple apparatus set up with the help of a funnel and filter paper. At the end of the period, the pectin yield for the samples was calculated according to Eq. (1) as follows after drying at 50 °C for 24 h. The dried pectins were kept in tubes at 4 °C.

$$\text{Pectin yield}(g/g) = (\text{dry pectin}(g)/\text{dry peel}(g)) \quad (1)$$

Experimental design

The study aimed to shorten the experimental time and reduce the number of tests determining the parameters in optimizing the microwave-assisted pectin extraction from dried apple samples using the Response Surface Method (RSM). For this purpose, the statistical formula that gives the relationship of experimental conditions in microwave-assisted pectin extraction has been determined. Experimental design and statistical analysis were performed using Minitab.19 program. The Box–Behnken method was used to determine the effects of extraction time (minutes), liquid/solid ratio (mL/g), and pH as independent variables on pectin yield (g/g). The polynomial quadratic model and regression coefficients given in Eq. 2 below were used in Multiple Regression analyses. In this equation, "Y" represents the amount of pectin in response, "X" values represent independent variables (X_1 (extraction time), X_2 (liquid/solid ratio), X_3 (pH)) and β_0, β_i, β_{ii}, β_{ij} values are regression values.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_i^2 \quad (2)$$

The lower and upper limit values of the independent variables used in the optimization of the microwave-assisted pectin extraction process are given in Table 1.

The experimental design used in the study is given in Table 2.

In this study, the model was improved by applying backward analysis ($\alpha = 0.1$) for response (pectin yield) and removing insignificant parameters ($p < 0.1$).

Table 1 Lower and upper limit values of independent variables for RSM

Independent variables	Extraction time	Liquid/solid ratio	pH
Unit	min	mL/g	
Symbol	X_1	X_2	X_3
Coded	Real		
Factor level			
− 1	3	75	1.5
0	6	100	2.0
+ 1	9	125	2.5

Table 2 Box–Behnken experiment design

Run	Independent variables			Response
	X_1	X_2	X_3	Y_1
1	3	100	1.5	0.0417
2	3	75	2.0	0.0689
3	3	125	2.0	0.0242
4	6	75	2.5	0.0979
5	9	100	2.5	0.1046
6	9	75	2.0	0.1181
7	6	75	1.5	0.1011
8	6	125	2.5	0.0562
9	9	125	2.0	0.0586
10	6	125	1.5	0.0547
11	6	100	2.0	0.0953
12	3	100	2.5	0.0222
13	6	100	2.0	0.1307
14	9	100	1.5	0.0919
15	6	100	2.0	0.1307

X_1—Extraction time (min), X_2—liquid/solid ratio (mL/g), X_3—pH, Y—pectin yield (g/g)

Pectin characterization

Degree of esterification (DE)

The degree of esterification, one of the most critical parameters of the pectin obtained, is measured in various ways; it is generally an analysis method performed by titration. Dried pectin (0.1 g) was placed in a weighing bottle for titration, dissolved in 20 mL of water, and soaked in 2 mL of 96% ethanol. Deionized water at 40 °C (20 mL) was added with stirring. After completely dissolving the pectin, three drops of phenolphthalein were added to start titration with 0.1 M sodium hydroxide (V_1 spent with the initial titer). Then, 10 mL of 0.1 M sodium hydroxide was added, and stirred for 20 min for hydrolysis.

In the next step, 10 mLof 0.1 M hydrochloric acid was added, and stirred until the pink color of the solution disappeared. Excess hydrochloric acid was titrated with 0.1 M sodium hydroxide (V_2 spent by the second titer) [21].

$$\mathrm{DE}(\%) = \frac{V_1}{V_2 + V_1} \times 100 \tag{3}$$

Methoxyl and galacturonic acid content

Methoxyl contents (MC) of pectins obtained from crab apple peel was determined esterification by the method suggested by Bochek et al. [22].

$$MC = \frac{100 * DE \times 31}{176 + DE * 14} \tag{4}$$

The galacturonic acid content of the pectin sample was determined based on a Spectrophotometric method [23]. In determining the galacturonic acid content, 1 mL sample solution (100 µg/mL) was taken into a glass tube, then 6 mL 98% H_2SO_4 was added and left for 25 min. 200 µL of carbazole (0.1% w/v) was added to the cooled samples, the color change was waited for 20 min, and the absorbance was measured at 520 nm. The curve prepared using standard galacturonic acid (0–200 µg/mL) solution was used to determine the galacturonic acid content.

Water/oil uptake capacity

0.1 g of the obtained pectin was taken and transferred to the test tube, and 1 mLof distilled water was added and mixed. After the process, it was shaken for 30 min and centrifuged at 3200 rpm for 20 min at room temperature. After centrifugation, the supernatant was removed, and the precipitate was weighed. The determination of the oil absorption capacity was carried out by using oil instead of water [24]. Water and oil binding capacities were expressed as g water retained per g sample and g oil per g sample, respectively.

Emulsifying properties

Preparation of pectin emulsions: 25 g of minced meat is taken into a beaker with 100 mL of cold NaCl solution (0.4 M, pH 6.6). It is homogenized with ultraturrax at 13,000 rpm for 2 min. 12.5 g suspension and 37.5 mL of 0.4 M NaCl mixed for 10 s. 50 mL of sunflower oil was added and mixed slowly at low speed. The process was continued until the emulsion absorbed the oil, and the spent oil was noted. After adding the oil, it was mixed for another 5 s. The temperature should not exceed 15 °C. The control sample was taken only from the emulsion prepared with minced meat. Pectin was added to the emulsion as 0.5%, 1%, and 2% by calculating the final suspension.

Table 3 Ingredients of model sausage emulsions

Ingredients	Control	A	B
Meat	60	60	60
Fat	10	5	5
Water	35	35	35
Crab apple pectin	–	0.2	0.4
Sodium caseinate	3	3	3
Wheat starch	4	4	4
Sodium nitrite	0.015	0.015	0.015
NaCl	1.5	1.5	1.5
Black pepper	0.75	0.75	0.75
Red pepper	0.75	0.75	0.75

*Control: Model emulsion sample without pectin, A: with 0.2 g pectin, B: with 0.4 g pectin

Emulsion stability (ES) was determined according to Hosseini et al. [21]. Oil-in-water (O/W) emulsions were prepared by adding 5 mL of sunflower oil to 5 mL of pectin solution (0.5, 1 and 2%; w/w). Emulsions were transferred to centrifuge tubes and centrifuged at 3000×*g* for 5 min. The remaining volume is expressed as a percentage of the initial volume.

Emulsion viscosity (EV) emulsion samples prepared according to [25] were used to determine stability. 25 g samples of these emulsions were taken into a glass beaker and given in Pa.s using spindle no-7 of the viscometer.

Differential scanning calorimeter (DSC)

The thermal properties of pectin obtained from crab apple peel were determined by Differential scanning calorimetry (Perkin–Elmer DSC 4000, Boston, USA). Approximately 3 mg of the sample was weighed into aluminum cups, and the cups were hermetically sealed. It was conducted between 0 and 500 °C with a temperature scan of 10 °C*min^{-1} under nitrogen gas [26].

Fourier-transform infrared spectroscopy (FTIR)

In the structural characterization of pectin obtained from crab apple peel, its absorption spectrum was determined by an FTIR (Perkin Elmer Spectrum) device. In determining these components, spectra with a wavelength of 4000–450 cm^{-1}, the mid-length infrared range, were used [27].

Model sausage system

The amounts of the ingredients eused in providing the model sausage media are given in Table 3.

The meat was minced again for 2–3 s at low speed in the mixer. At the end of the period, a mixture of sodium nitrite and NaCl was added, and mixing was continued at high speed for 20–30 s. The spice mixture was then added to the wheat starch, sodium caseinate, pectin, and remaining water as ice, and stirring was continued until the temperature reached 8 °C. Finally, the used oil was added, and the emulsification process was continued until the mixing temperature was 12 °C. Sausage batter filled into centrifuge tubes was heat treated in a water bath at 90 ± 2 °C for 30 min. After cooking, the sausage temperature was cooled to 5 ± 1 °C with cold water. Sausages stored at 4 °C overnight were removed from the tubes and stored in the refrigerator.

Model sausage system product analysis

Color analysis The color values of the samples (TES 135 A, China) were measured with a colorimeter (Fig. 3). L*, a*, and b* values were determined according to the International Commission on Illumination (CIE) standards based on three-dimensional color measurements. Here, L* values ranging from 0 to 100 for dark to light, negative a* values for green, positive a* values for red, negative b* values for blue and positive b* values for yellow.

The amount of leakage into the packaging Leakage measurements of sausage samples in centrifuge tubes were performed with some modifications of the method of Bloukas et al. [28]. The weight of the sausage before and after drying was recorded by weighing the weight of the paper towel before and after soaking [28]. The amount of leakage in the package was calculated using the following formula:

$$\text{The amount of leakage into the packaging}(\%) = \left(\frac{x}{m_1}\right) \times 100 \quad (5)$$

$$x = \frac{(k_2 - k_1) + (m_1 - m_2)}{2} \quad (6)$$

k_1: Initial weight of the paper towel, g
k_2: The weight of the paper towel after moistening, g
m_1: Weight of the sausage sample before drying, g
m_2: The weight of the sausage sample after drying, g

Cooking loss The weights of the sausage slice samples cut to 1 cm were recorded. Sausage slices were cooked in an oven at 150 °C for 5 min on both sides. After the sausages were cooked, the samples were cooled to room temperature and weighed, and the cooking loss value was calculated as follows.

$$\text{Cooking loss}(\%) = \left(\frac{m_1 - m_2}{m_1}\right) \times 100 \quad (7)$$

m_1: Weight of the sausage sample before cooking, g
m_2: The weight of the sausage sample after cooking, g

pH measurement 10 g sausage batter was weighed and mixed with 100 mL distilled water. After homogenizing with Ultraturrax (IKA T25) for 1 min and the pH value was determined with pH meter (Mettler Toledo S210K).

Water activity measurement The water activity of the batter was measured at room temperature using a water activity meter (Novasina, LabMaster). When the device was ready for measurement, the sample was placed in the sample cup, and the analytical result was read from the device screen.

Statistical analysis

Analysis data were evaluated using the SPSS 16.0 package program. Sausage emulsion production was carried out in two replicates. The analysis data were provided in three replicates. The data were subjected to analysis of variance. As a result of the analysis of variance, the data of the variables that were significantly effective were compared with the Duncan test.

Results and discussion

Statistical analyses were performed using the responses provided by the Box–Behnken experimental matrix given in Table 2. In the modeling phase, the response surface method statistics and ANOVA results are shown in Table 4.

Table 2 shows the experimental design scheme for the test conditions in which the pectin yield was determined. The highest pectin yield was obtained with 6 min of microwave application, a liquid/solid ratio of 100, and a pH of 2. Table 4 shows the ANOVA and RSM model statistics of the experimental design. With the evaluation of statistical data, a high regression coefficient was obtained with the quadratic model (R^2, 93.02%). At this stage, the "backward analysis" of the parameters in the model was used to differentiate the unimportant ones at the $p > 0.1$, $p > 0.01$ and $p > 0.05$ levels. The equation containing the coded factors obtained for pectin yield using the reduced quadratic model is given in Eq. 7

Table 4 RSM model statistics and ANOVA analysis

Source	Coefficient	Sum of squares	DF	F value	P value	
Model (backward)	0.1059	0.0139	6	17.78	0.0003	Significant
X_1	0.0270	0.0058	1	44.80	0.0002	
X_2	− 0.024	0.0046	1	35.44	0.0003	
X_3	− 0.0011	0.000009	1	0.0692	0.7991	
X_1^2	− 0.0254	0.0024	1	18.28	0.0027	
X_2^2	− 0.0130	0.0006	1	4.81	0.0596	
X_3^2	− 0.0154	0.0009	1	6.70	0.0322	
Lack of fit		0.0007	6	0.5627	0.7523	Insignificant
Pure terror		0.0004	2			
Cor total		0.0150	14			
R^2	93.02%					
Adjusted R^2	87.79%					
Predicted R^2	76.63%					

X_1—Extraction time (min), X_2—liquid/solid ratio (mL/g), X_3—pH

$$Y = 0.1059 + 0.0270X_1 - 0.0240X_2 - 0.0011X_3 - 0.0254X_1^2 - 0.0130X_2^2 - 0.0154X_3^2 \quad (8)$$

Likewise, Wang et al. [29] explained the extraction of pectin from apple pomace with a quadratic equation in their optimization study. When the model was evaluated, the ANOVA values given in Table 4 showed that the model was important ($p < 0.01$), while the lack of fit ($p = 0.942$) was determined to be insignificant. Linear parameters X_1, X_2, and quadratic terms X_1^2 and X_3^2 were found to be significant ($p < 0.05$).

The contour plots in Fig. 1 show the effects of independent variables on pectin yield. As seen in Fig. 1, the pectin production is maximum at conditions where the extraction time is between 6 and 8 min and the liquid/solid ratio is about 80–100. Pectin yield tends to increase in conditions where the liquid/solid ratio is above 75, while it tends to decrease above 100. The increase in the contact surface of the cells with the solvent in the dried crab apple samples with the increase in the liquid/solid ratio supports pectin extraction. In addition, the formation of cell deformations due to increased fluid concentration also supports the extraction [30]. It is observed that the pectin yield decreases as the extraction time exceeds 8 min. Similarly, Maran et al. [31] reported that the pectin yield decreased over a specific processing time in their study, where they performed microwave-assisted pectin extraction from orange peel. Due to the effect of the microwave energy provided during the extraction, the thermal accumulation in the solution, and the pectin structure may deteriorate with the increasing temperature.

Maximum pectin yield is obtained in conditions where pH at 2 and extraction time is approximately 6–7 min. In addition, it is seen that maximum pectin yield is obtained in conditions where the pH at 2 and the liquid/solid ratio is between 90 and 100. While the linear pH variable does not affect pectin yield ($p > 0.5$), the pH*pH interaction has a significant effect ($p < 0.01$). In the study, extraction processes were applied between pH 1.5 and 2.5. While pectin is generally soluble in weakly acidic conditions, this effect may vary depending on the structure. It may be because the pectin molecule is primarily attached to other structures, such as hemicellulose. Therefore, acidic environments may be needed [32]. However, in cases where the acidity is high, the surface properties may be affected due to the reduction of the molecular weight of the pectin molecule [33]. For this reason, the decrease in the pH value below 2 is likely due to the reduction in the tendency of pectin to precipitate.

Determination and validation of the optimum point

As a result of the optimization study, pectin extraction was carried out in 4 repetitions under conditions where the desired degree of extraction was 1, the extraction time was 7.77 min, the liquid/solid ratio was 77.53 mL/g and the pH was 1.79. As a result of the production carried out under these conditions, the model estimated 0.1218 ± 0.0114 g pectin/g crab apple peel production. In contrast, the average pectin yield was determined as 0.1128 ± 0.0137 g pectin/g crab apple peel. Experimental and predicted values were in agreement. Compared to the literature, approximately 6% pectin yield is obtained from apple peel [34], while it can be said that higher pectin yield is achieved with the effect of the raw material used in this study and the ultrasonic extraction method.

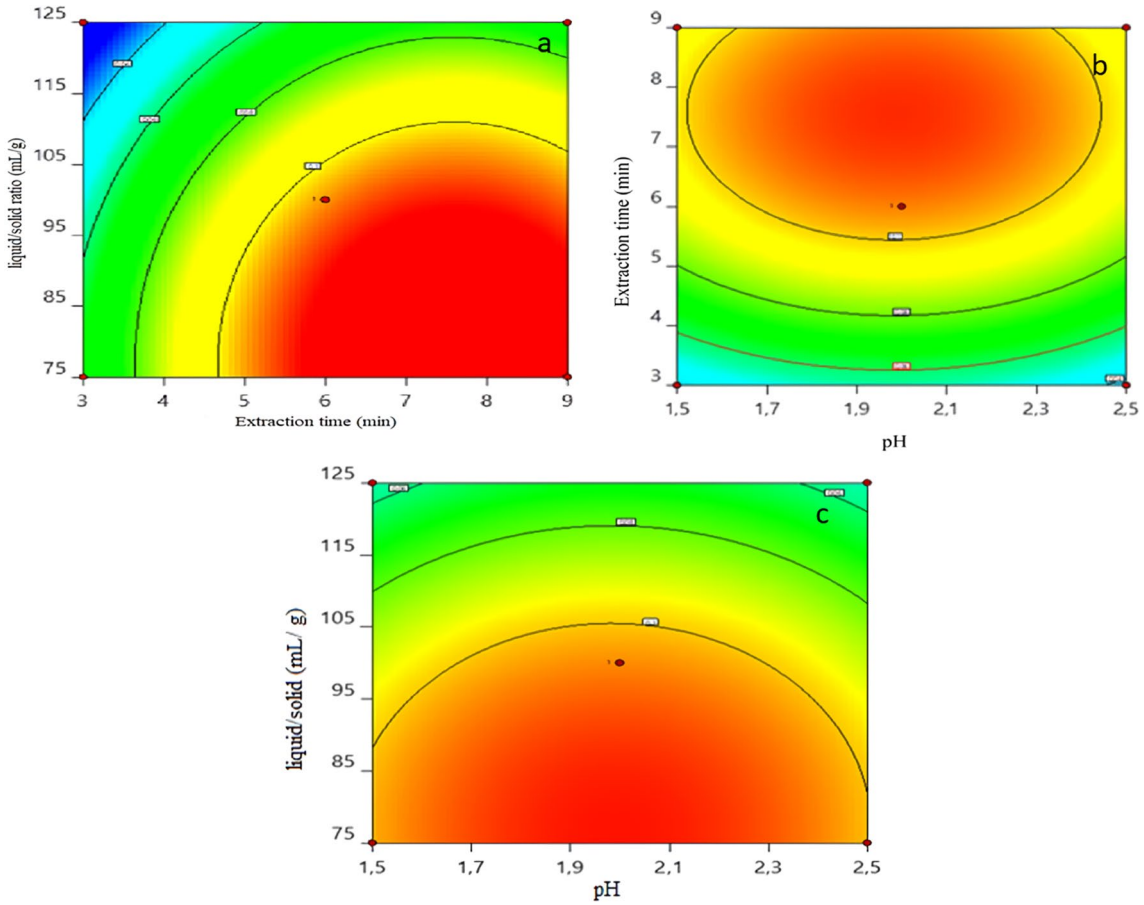

Fig. 1 Contour graphs of the effect of extraction time, liquid/solid ratio and pH on pectin yield

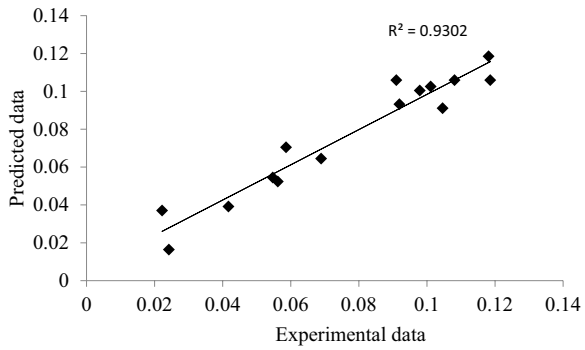

Fig. 2 The model compatibility of experimental data *predicted data

Model validation

Figure 2 shows the effect of extraction time, liquid/solid ratio, and pH on pectin yield in microwave-assisted pectin extraction from crab apple peels. The R^2 value (0.9169) of the curve formed by the experimental and estimated data is close to 1.

Pectin characterization

Fourier transform ınfrared spectroscopy (FTIR)

FTIR results are given in Fig. 3. The peaks between 3000 and 3780 cm^{-1} in the FTIR spectra of commercial pectin and crab apple pectin samples indicate O–H stretching. The peaks between 2980 and 2800 cm^{-1} reflect the C-H stretching of alkyl groups (CH, CH_2, and CH_3) in the galacturonic acid structure [35]. Crab apple peel pectin shows more peaks than commercial pectin. Absorption bands detected at 1730 and 1650 cm^{-1} are in both pectin samples. The presence of these bands indicates free and esterified carbonyl C=O bonds and the intensity and area of the bands provide information about the degree of esterification [36]. The crab apple peel pectin obtained in the study has a higher degree of esterification than the commercial pectin sample. This absorption band, which may result from hydrogen bonding of carboxylic acid (-COOH) and hydroxyl groups in polysaccharide molecules, is observed in the pectin FTIR spectra.

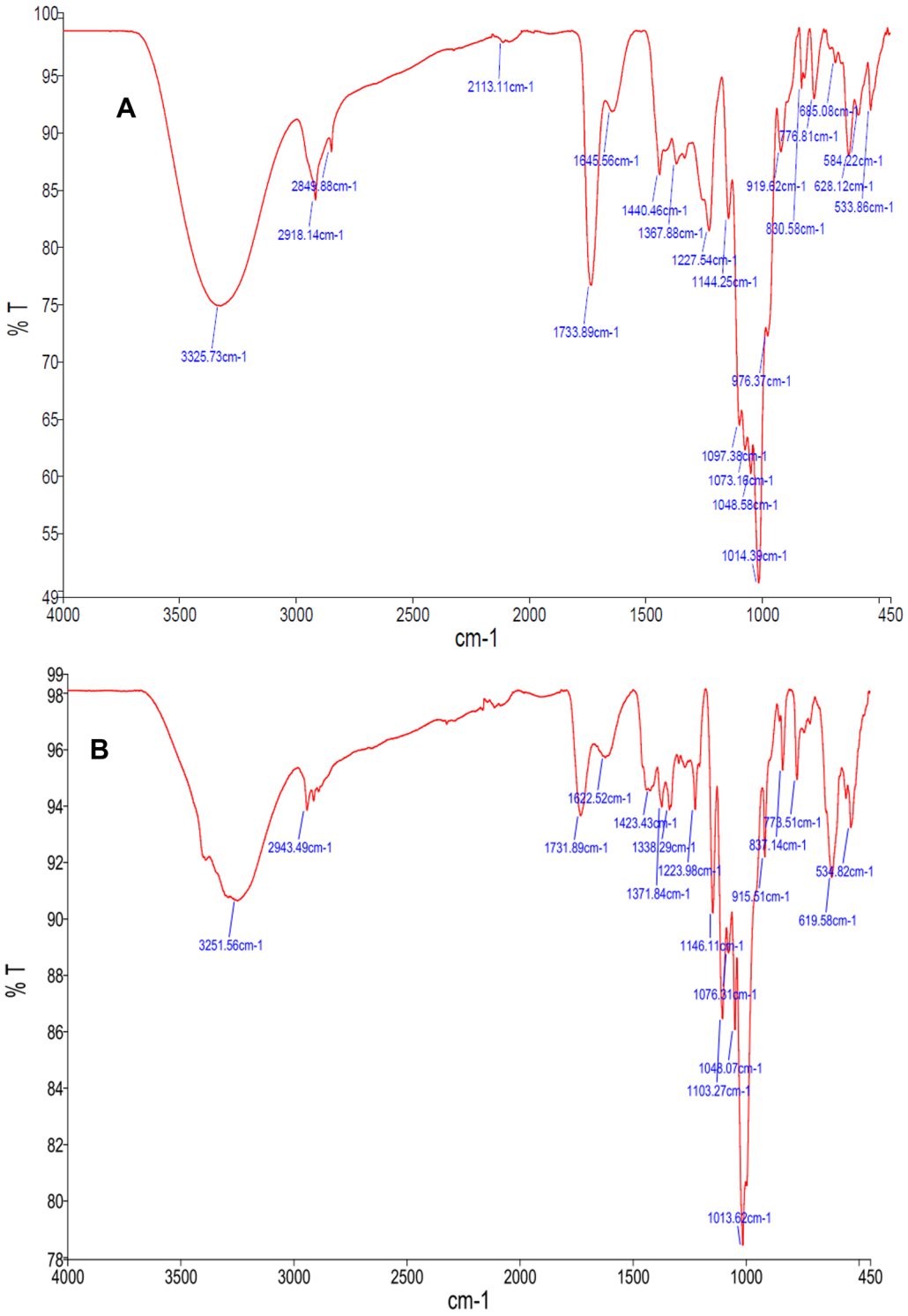

Fig. 3 FTIR spectra of crab apple peel pectin (**A**) and commercial pectin (**B**) (450–4000 cm^{-1})

Cerna and Coimbra [37] reported that the 1200–800cm^{-1} region is effective in the separation of carbohydrates. Pectin and commercial pectin obtained from crab apples give consistent peaks in this range.

Thermal properties

The thermodynamic properties of the obtained pectin between 0 and 500 °C were investigated by DSC. As

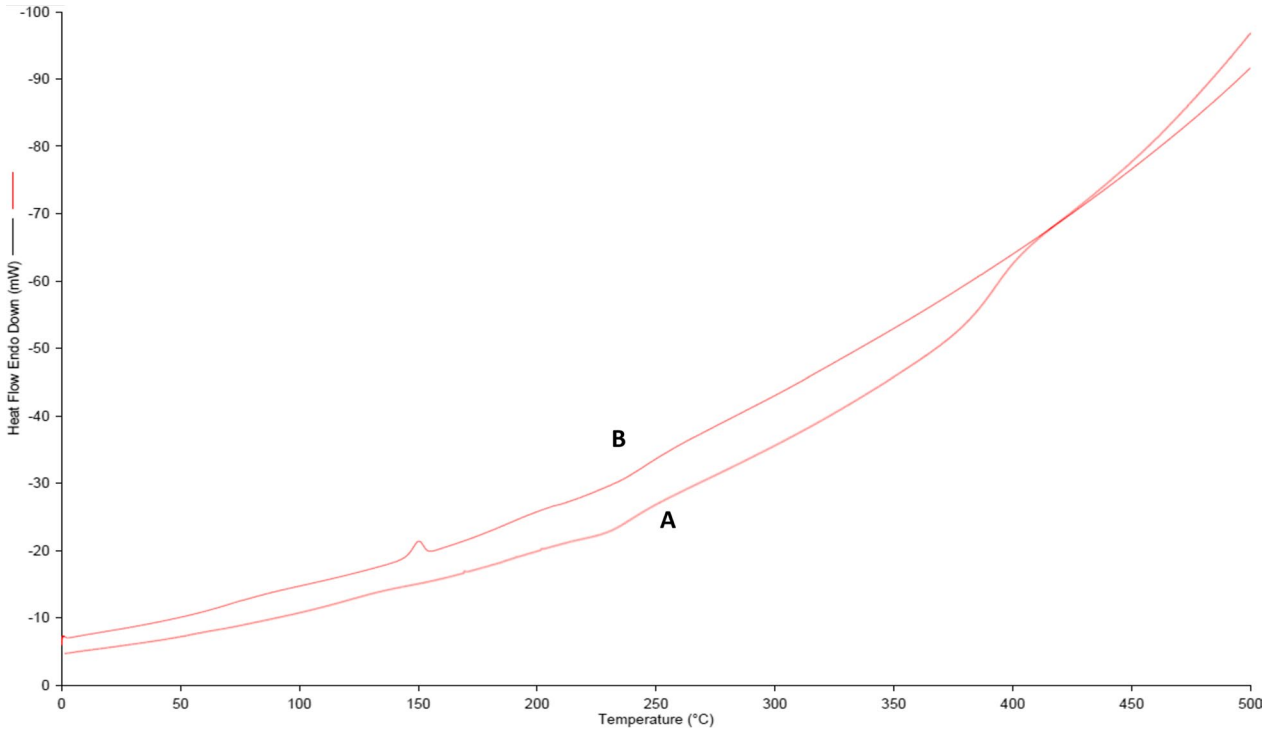

Fig. 4 DSC diagrams of crab apple peel pectin (A) and commercial pectin (B)

shown in Fig. 4, an endothermic and exothermic peaks were observed in the DSC diagrams of pectin from crab apple peel and commercial pectin. The melting temperature, determined as about 148 °C in the crab apple peel pectin sample, was defined as 156 °C in the commercial pectin sample. The high melting temperature and melting enthalpy values are generally directly proportional to the degree of esterification. The increase in the degree of esterification indicates that the crystallinity also increases [38]. While it can be said that the bound and free water in the pectin molecule is removed at the melting point, the second peak is accepted as the degradation peak of the pectin [39]. The decomposition temperature of commercial pectin and pectin obtained from crab apple peel was determined as 250 °C.

Physicochemical properties

The degree of methyl esterification provides information on the ability of pectins to form gels with a high content of soluble solids while providing an effect on the texture of pectin. In line with this feature, it manages the content used in the structure of various foods such as dairy products, fruit juices, sauces, and meat products [40]. For this reason, the degree of esterification of the pectin obtained from the crab apple peel was determined as 79.14%, as given in Table 5.

The galacturonic acid content of the pectin sample was determined as 448.48 mg/g powder pectin. Similar results were obtained for apple peel pectins used in another study. [34]. Structurally, pectin is mainly composed of parts of homogalacturonan (HG), rhamnogalacturonan I (RG-I), rhamnogalacturonan II (RG-II), xylogalacturonan (XGA), and apiogalacturonan (AP). As is known, according to the degree of esterification in the structure of the pectin molecule, if the DE value is below 50%, it is defined as low methoxylated pectin and above it as high methoxylated pectin. Both groups of pectin show gelling properties. However, the gelation mechanisms vary. While low methoxyl pectin needs divalent ions in its structure, high methoxyl pectin needs low pH in the presence of auxiliary additives such

Table 5 Some physicochemical properties of pectin

	GA (mg/g)	MC (%)	DE (%)	OUC (g oil/g pectin)	WUC(g water/ g pectin)
Crab apple pectin	448.48 ± 4.29	14.11 ± 0.02	79.14 ± 0.11	8.5 ± 0.7	8.1 ± 1.5

GA Galacturonic acid content, *MC* Methoxyl content, *DE* Degree of esterification, *OUC* Oil uptake capacity, *WUC* Water holding capacity

Table 6 Emulsion properties of crab apple peel pectin

Emulsion properties	Control	0.5% pectin	1% pectin	2% pectin
Emulsion stability (%)	50 ± 14.14	80 ± 0	100 ± 0	90 ± 14.14
Emulsion viscosity (Pa.s)	1.22	2.10	2.34	2.94

as sugar [41]. It can be said that the obtained crab apple peel is high in methoxyl pectin (14.11%). Galindo and Piagetini [42] reported a degree of esterification of up to 60% in 'Grannt Smith's apple peels, while Cho et al. [34] obtained pectin of up to 67% esterification degree in apple peel as a result of extraction using different organic acids.

Water binding capacity is an essential property of pectin. It can effectively increase the volume of food and change its viscosity and texture. In addition, this property of pectin can be used to produce low-calorie products [43]. The obtained crab apple peel pectin has been determined to bind water at 8.1 g water/g pectin. As stated before, the high degree of esterification of the obtained pectin can provide an excellent water-holding capacity. The high water holding capacity obtained also shows this. High methoxyl pectins are less resistant to swelling of the structure by absorbing water due to the low crystallinity in their structure [44]. Similarly, when the oil binding property was examined, it was determined that crab apple peel pectin could bind at 8.5 g oil/g pectin. The combination of high water holding capacity and oil binding capacity indicates that it has the potential to be a good emulsifier [45].

Emulsion properties of emulsions containing crab apple peel pectin at different concentrations are given in Table 6. The addition of pectin increases emulsion stability. However, a decrease in emulsion stability was detected under conditions of 2% pectin content. Yang et al. [46] investigated the emulsion properties of pomegranate peel pectin. They also observed increased emulsion stability by adding pomegranate peel pectin in increasing concentrations from 0 to 2%. High emulsion stability in crab apple peel pectin was achieved at 1% pectin concentration. The influential factor in ensuring the stability of the emulsion is the small size of the droplets forming the emulsion at the beginning. Studies have shown that small droplet sizes in oil/water emulsions can be achieved with 1% pectin concentration [33, 46, 47].

In emulsification, the charged polysaccharide units in the pectin structure disperse into the aqueous solution. At the same time, the complex is tightly adsorbed at the oil/water interface, thus providing a steric barrier against (instant) droplet aggregation, aggregation, and further instability during storage [48]. However, the emulsifying activity of pectin can be caused by many factors, such as acetyl content, protein fraction, molecular weight, degree of methylation, and internal charge distribution [49].

When the emulsion viscosities given in Table 6 were evaluated, increasing pectin concentration also increased the viscosity. Yang et al. [46] mentioned a similar increase in emulsions using pomegranate peel pectin.

Table 7 Some physicochemical properties of model emulsion samples

	pH	Cooking loss (%)	Water activity	Leakage (%)
Control	6.23 ± 0.02^{a}	14.24 ± 0.37^{c}	0.926 ± 0.004	0.31 ± 0.08^{ab}
A	6.16 ± 0.01^{b}	16.69 ± 0.47^{b}	0.927 ± 0.001	0.35 ± 0.12^{a}
B	6.14 ± 0.01^{c}	18.28 ± 1.28^{a}	0.927 ± 0.002	0.18 ± 0.09^{b}

*a–c: No significant difference exists between two averages with the same letters in the same column ($p < 0.05$). Control: Without pectin A: Containing 0.2 g of pectin, B: Containing 0.4 g of pectin

Table 8 Color characteristics (L*, a, and b* values) of batter and post-baking stages in model emulsion samples

	Control	A	B
Batter			
L*	38 ± 7.84^{b}	40.05 ± 4.52^{ab}	47.3 ± 3.19^{a}
a*	17.98 ± 4.91	19.84 ± 7.60	19.65 ± 7.20
b*	10.52 ± 3.88	13.73 ± 2.08	17.17 ± 5.53
Product			
L*	58.45 ± 16.75	40.3 ± 9.3	50.23 ± 13.98
a*	29.57 ± 6.6	21.53 ± 7	26.42 ± 3.55
b*	12.83 ± 4.67	12.2 ± 4.08	15.82 ± 4.33

*a–c: No significant difference exists between two averages with the same letters in the same line ($p < 0.05$). Control: Without pectin, A: Containing 0.2 g of pectin, B: Containing 0.4 g of peçtin

Analysis of model sausage system containing pectin

The data of the emulsion samples prepared in the model system are given in Tables 7 and 8. Different concentrations of pectin were added to the meat emulsion medium to determine the effect of crab apple pectin obtained in the meat emulsion medium as a fat replacer. It was determined that the water activity values of the samples containing 0.2 g and 0.4 g pectin with low oil content were not different $p > 0.05$). The pH was lower compared to the control group with the increase in pectin content. As a result of the interaction of polysaccharides in foods with proteins, pH changes can be observed due to the electrostatic interaction between polar and nonpolar groups [20]. In addition, it is seen that cooking losses increase with the increase in pectin content. Similarly, Yadegari [50] reported higher cooking losses in samples using pectin compared to the control group in his study. He

examined the effects of hydrocolloids containing pectin as a fat replacer in sausage *batter*. One of the parameters that affect the gelation properties of proteins and ensure protein functionality is pH. It collects and unfolds proteins during heat application [51]. Considering the change in pH with the increase of pectin presence, it is seen that the rise in cooking loss is proportional to pH. Similarly, it was reported in a study by Hughes et al. [52] that cooking loss could increase with a decrease in fat content. In contrast to cooking loss, the presence of pectin reduced the amount of leakage into the packaging. The amount of leakage to the packaging is less in the samples with 0.4 g pectin, which may be because the pectin gel is more stable at low temperatures.

The color properties of the model emulsion samples are given in Table 8, pectin-added groups showed similar characteristics to the control group. While it was observed that the L value in the color properties determined before cooking was higher in the group with higher pectin added, this difference disappeared in the baked product. Similarly, Yadegari [50] reported that adding hydrocolloids to the sausage did not change the color properties. When the groups with reduced fat content and the control groups were evaluated, no statistical difference was detected in the L* values. The color would allow the reduction of the fat ratio so that the control group remained similar.

It was observed that adding pectin as a fat replacer increased the cooking loss. The applied cooking process was carried out at 150 °C. Considering the thermal properties of crab apple peel pectin, it can be said that cooking loss has increased due to this process, which takes place at approximately the melting temperature of pectin. It is thought that this effect may decrease if the cooking at low temperatures (< 150 °C).

Conclusion

The optimization and modeling of microwave-assisted pectin extraction of crab-apple were examined using RSM. This study demonstrates that microwave-assisted pectin extraction enhances the pectin yield. Furthermore, with optimization maximum 0.1218 ± 0.0114 g pectin was estimated per g crab apple peel and according optimal conditions experimental pectin yield was achieved with 0.1128 ± 0.0137 g pectin. The pectins also exhibited emulsifying properties indicating they could be used for stabilizing emulsions. Model sausage medium was prepared using pectin. When some physicochemical and color characteristics of the produced sausage samples are determined, it can be said that adding pectin effects the cooking loss for the consumer. In contrast, the presence of pectin positively impacts the amount of leakage into the package. Consistent with the characterization, it can be said that pectin obtained from crab apple peel has the potential to be used as a fat replacer for low fat meat emulsions. As a result, in this study, microwave-assisted pectin was obtained from crab apple peel, and some of its properties were determined. Pectin production optimization was made under suitable conditions, and high-efficiency production was realized under these conditions.

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Data availability The data underlying this article will be shared on reasonable request to the corresponding author.

Declarations

Conflict of interest This work was produced from the first author's master's thesis. All authors declare that no financial or otherwise support has been received from any organization that may have an interest in the submitted work.

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