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ORIGINAL PAPER

Microwave-assisted extraction of pectin from onion and garlic waste under organic, inorganic and dual acid mixtures

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Abstract

This study aims to investigate pectin extraction from garlic (GW) and onion waste (OW) by microwave-assisted (MAE) and sequential microwave assisted-hot acid extraction (MAHE) methods. All extractions were performed under three different media including organic acids [citric (CA) and acetic (AA)], inorganic acids [sulfuric (H_2SO_4) and hydrochloric (HCl)] and their mixtures. GW provided more pectin yields compared with OW. While the highest pectin yields from GW and OW by MAE in H_2SO_4 were respectively 24.62 ± 0.65 and 24.93 ± 0.59%, these yields under MAHE were 27.99 ± 0.36 and 28.43 ± 0.42%, respectively. Higher pectin yields and galacturonic acid (Gal-A) contents were mostly achieved in inorganic acids. However, degree of esterification (DE), methoxyl content (MeO) and equivalent weight (EW) values were higher for the pectins extracted under organic acids. Extraction of pectin from GW and OW was also accomplished in dual acidic media by MAE. Addition of inorganic acids to the organic acid solutions resulted in increasing pectin yields. The highest pectin yields from GW and OW under dual acid solutions were respectively 23.36 ± 0.66 and 21.88 ± 0.52%, and achieved in 1/3 HCl-H_2SO_4 and 1/3 CA-H_2SO_4 mixtures by MAE. While increasing inorganic acid contents in dual acid solutions resulted in enhanced Gal-A contents, increasing organic acid volume also generated higher DE and MeO values of the pectins. Obtained successful outcomes indicate that MAHE method could be used as an efficient extraction technique for the higher pectin yields, and utilization of organic-inorganic dual acid mixtures during MAE provides enhanced yields and controlled physicochemical properties of pectin.

Keywords Microwave-assisted extraction · Onion waste · Garlic waste · Pectin · Organic and inorganic acids

Introduction

Food waste is one of the serious concerns for food industry since substantial amounts of by-products are directly thrown away without evaluating their nutrient contents [1]. Low cost, abundance and renewability of food by-products made them economically beneficial sources for their valuable bioactive components [2]. Garlic has been consumed for both medicinal and culinary purposes in our daily life either as an important part of our diet or as a flavoring agent [3]. Around 3.7 million tons of GW is annually generated by food industry around the world [4]. GW was reported consist of ash, fat, protein, lignin and fiber [4]. One of the main components of GW was also reported to be pectin carbohydrate, and GW was reported to contain approximately 10% of pectin [5]. A significant amount of GW thrown into landfills causes environmental pollution, and endangers the life of flora and fauna.

Onion is one of the most produced vegetable, and it has large quantities of waste parts consisting of skins, roots and other waste parts [6]. Onion waste has useful and rich substances including dietary fiber, fructooligosaccharides, flavonoids, and alk(en)yl cysteine sulfoxides. Due to the abundance of biologically active phytocompounds in onion waste, its utilization for the production of these kinds of compounds is very beneficial and economically valuable [7]. However, OW is not beneficial for the utilization as a fodder or organic

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fertilizer due to its high sulfur content, specific flavor, or possible toxicity. Destroying OW is also difficult especially by combustion because of its high moisture level [8, 9]. Each year, approximately 450,000 tons of OW are produced in the European Union and thrown away as waste [10].

Pectin is an important heteropolysaccharide component of the cell walls of all plants, especially in fruits and vegetables [11]. Pectin is economically valuable product due to its utilization in a various industrial fields including food and pharmaceutical industries [12]. A variety of pectin extraction methods has been explored to enhance extraction yield, and decrease time and cost of the process. Conventional pectin production is mainly achieved under hot-acid extraction (HAE) conditions [13, 14]. However, this process requires higher amounts of solvents, and consumes more energy compared to innovative techniques such as microwave-assisted (MAE) and ultrasonic-assisted extraction methods [15].

MAE is a simple and efficient heating method for the extraction of some components from plant matrices. MAE method is very effective compared to the traditional techniques, and extraction time of MAE usually ranges from a few seconds to an hour [16]. A variety of biologically active compounds including essential oils, flavonoids, terpenes, phenols, alkaloids, and glucosides can be extracted using MAE technique [17]. Microwaves are not ionizing radiations, and molecular structures of the components do not change by microwave radiations. MAE method provides homogeneous temperature distribution in the extraction media, and therefore, significant increase in the yield and quality of extracted pectin can be obtained [15]. In addition to these advantages, MAE also provides decreased extraction time, utilization of less solvent and reduced cost.

The aim of this study is first to investigate pectin extraction from OW and GW by MAE condition under pure water, different organic-inorganic acids and their mixtures, and second to apply sequential microwave assisted-hot acid extraction (MAHE) method to determine its effect on the pectin yield. Physicochemical properties of pectins extracted from OW and GW by MAE were also demonstrated in detailed. The effects of the types of acids or acid mixtures on the yield and properties of extracted pectin were also investigated for MAE method. MAHE method resulted in higher pectin yields from both GW and OW. Increasing pectin yield by MAHE showed that there was still some amount of pectin existing in the residue of MAE. Therefore, utilization of MAHE conditions could be very beneficial for obtaining higher pectin yields.

Materials and methods

Materials and instrumentation

Citric acid (CA, catalog# 100247), HCl (37%, catalog# 100317) and ethanol were supplied from Merck KgaA. Commercial citrus pectin, NaOH, 3-phenylphenol, D-(+)-galacturonic acid monohydrate and sodium tetraborate were supplied from Sigma Aldrich. Acetic acid (AA, 99–100%, catalog# 27221) and H_2SO_4 (95–98%, catalog# 970.023) were purchased from Riedel-de Haen and Isolab, respectively. All other chemicals were purchased analytical grade from Merck chemicals (Chennai, India), and used without further purification. Macherey-Nagel MN 640w # 41 black ribbon filter paper was used for the experiments. Termal-H11900 shaking water bath (Türkiye) was used during the experimental studies. MAE experiments were accomplished using a microwave oven (Samsung MS23F300EEW, South Korea). NÜVE NF 400 centrifuge (Türkiye) was used during the experimental studies. FT-IR analyses of extracted pectin samples were recorded on a Thermo Fisher Scientific–Nicolet/IS50 (USA) Infrared Spectrophotometer device with diamond ATR probe between 400 and 4000 cm^{-1}. Each experiment was carried out in triplicate, and results were given as mean standard deviation. Statistical analysis was accomplished using single factor analysis of variance (ANOVA) to analyze obtained data. Data was tested at 95% confidence interval for statistical significance.

OW (peels and straw) and GW were obtained from the dining hall of the university. OW and GW were separately dried at 50 ºC in an oven (JSON-100 Natural Convection Oven 100 L, JS Research Inc., South Korea). Then, these wastes were ground by milling device. They were stored in vacuum bags and kept in a dry environment prior to the experiments.

Extraction of pectin under microwave assisted extraction (MAE) condition

Extraction of pectin from ground OW and GW was accomplished under MAE conditions performed in a microwave oven at working frequency of 2450 MHz with adjustable microwave power and time. 1/30 (w/v) solid/liquid ratio (SLR) was used during the extraction procedures. About 6 g of ground waste (GW or OW) was placed into a 250 mL Pyrex beaker, and 180 mL of an extractant (0.1 N of acid solution) was added on it. Pure water, two organic acids (CA and AA), two inorganic acids (H_2SO_4 and HCl) and six different mixtures of these acids (CA-AA, CA-HCl, AA-HCl, CA-H_2SO_4, AA-H_2SO_4, HCl-H_2SO_4) were used as extractants. The obtained mixture was put in the microwave oven, and was exposed to microwave radiation at 600 W power for 4 min. After extraction completed, the mixture was allowed to cool down to room temperature and filtered to separate unreacted residue and supernatant. In order to precipitate pectin in the supernatant, 300 mL of 96% of ethanol was slowly added in it. The mixture

was kept in a refrigerator at 4 ºC for 12 h to complete precipitation of pectin in the gel form. The pectin in the gel form was then filtered, and washed several times with ethanol to remove the residues (mono-disaccharides and other impurities) [18]. Obtained pectin was then dried at RT and stored in vacuum bags in the refrigerator.

Extraction of pectin under sequential microwave-assisted and hot-acid extraction (MAHE) condition

After extraction of pectin from GW and OW by MAE method, the separated residue from the extraction media were subsequently subjected to the HAE method at 90 ºC in 75 min under applied acidic solution. After extraction was completed, the purification steps for the extracted pectin samples were accomplished the same as MAE method mentioned above.

Determination of Gal-A contents of pectins

Gal-A contents of pectins extracted from GW and OW were determined using the colorimetric method reported by Blumenkrantz and Asboe-Hansen [19]. In this method, reaction between galacturonic acid and 3-phenylphenol was first carried out. Gal-A % of the extracted pectin was then spectrophotometrically determined by color change. In order to achieve this method, 0.2 mL of sample containing 0.5–20 µg Gal-A was first prepared. After adding 1.2 mL of sulfuric acid/tetraborate solution to the sample, obtained mixture was cooled in an ice bath. The mixture was continuously stirred, and heated at 100 °C for 5 min. After that, the mixture was cooled again in an ice bath to room temperature. After cooling, 20 µL of 3-phenylphenol was added to the mixture. Then, absorbance measurements were performed at 525 nm on a UV spectrophotometer. Calibration curve was created using standard D-galacturonic acid solution (0-200 µg/mL).

Determination of degree of esterification (DE%) and methoxyl contents (MeO%) of pectins

DE and MeO % of pectins extracted from GW and OW were calculated using titration method reported by Bochek et al. [20]. 0.2 g (W) of the extracted pectin sample was taken into a flask, and ethyl alcohol was added on it. 20 mL of distilled water at 40 ℃ was added to the mixture, and obtained mixture was stirred at room temperature for 2 h to dissolve the pectin. The obtained solution was titrated with 0.1 N NaOH using phenolphthalein indicator, and NaOH consumption volume was recorded as V_1 (mL). After titration, 10 mL of 0.1 N NaOH was added to the solution, and the mixture was stirred at 300 rpm for 2 h at room temperature for saponification of esterified carboxylic acid groups of pectin. Then, 10 mL of 0.1 N HCl was added, and the obtained mixture was titrated again with 0.1 N NaOH. Consumed NaOH volume was recorded as V_2 (mL). DE and MeO% were determined from the following equations, respectively. In the equations; K_f: the number of free carboxylic acid groups, K_e: the number of esterified carboxyl groups, K_t: represents the total number of carboxyl groups.

$$K_f = \frac{N_{\mathrm{NaOH}} \times V_1 \times 0.045}{W} \times 100 \tag{1}$$

$$K_e = \frac{N_{\mathrm{NaOH}} \times V_2 \times 0.045}{W} \times 100 \tag{2}$$

$$K_t = K_f + K_e \tag{3}$$

$$DE\% = \frac{K_e}{K_t} \times 100 \tag{4}$$

$$MeO\% = \frac{DE \times 31}{176 + (DE \times 14)} \tag{5}$$

Determination of equivalent weights (EW) of pectins

EW values of the pectins were also determined using titrimetric method reported by Ranganna [21]. 0.5 g of pectin (W) sample in ethyl alcohol was added to a solution contained 1 g of NaCl in 100 mL of pure water. The mixture was stirred at room temperature for a while. The solution was titrated against 0.1 N NaOH using phenol red indicator, and consumed NaOH volume was noted as V (mL). EW values of the pectins were calculated using the following Eq.

$$EW = \frac{W \times 1000}{V \times N_{\mathrm{NaOH}}} \tag{6}$$

Results and discussion

Conventional pectin production is accomplished using hot-acid extraction method (HAE) from different plant resources. Microwave assisted extraction (MAE) technique is one of the advance methods for the efficient extraction of pectin in terms of obtaining higher yields and better physicochemical properties.

This study reveals the influences of MAE method on the extraction of pectin from OW and GW, and shows the effects of different extraction media on the yield and physicochemical properties of extracted pectins (Tables 1 and 2). Both OW and GW were first separately dried and

ground before the extraction processes. SLR for all extraction conditions was used as 1/30 g waste (solid) per mL acid solution as reported to be the most efficient ratio for observing better pectin yields [22]. CA and AA organic acids, and H_2SO_4 and HCl inorganic acids were used during the extractions. The mixtures from these acids were

Table 1 Extraction of pectin from GW and OW under MAE, HAE (after MAE) and MAHE techniques

Entry*	Extractant	pH			Yields (%)			Gal-A (%)	
		Initial pH	Final pH after MAE	Final pH of HAE (after MAE)	MAE	HAE (after MAE)	MAHE	MAE	HAE (after MAE)
Commercial Pectin (CP)								80.10 ± 0.44^{a}	
Pectin from GW									
1	H_2O	5.44	5.94	6.43	8.00 ± 0.67^{dB}	3.27 ± 0.58^{bC}	11.27 ± 0.47^{dA}	30.79 ± 0.57^{fB}	44.65 ± 0.52^{fA}
2	CA	2.25	3.21	2.63	9.55 ± 0.44^{cB}	5.57 ± 0.41^{aC}	15.12 ± 0.33^{cA}	49.96 ± 0.59^{dB}	63.60 ± 0.59^{cA}
3	AA	2.98	4.09	3.71	7.22 ± 0.55^{dB}	1.78 ± 0.42^{cC}	9.00 ± 0.42^{eA}	44.85 ± 0.57^{eB}	46.94 ± 0.54^{eA}
4	H_2SO_4	1.23	1.51	1.15	24.62 ± 0.65^{aB}	3.37 ± 0.53^{bC}	27.99 ± 0.36^{aA}	63.92 ± 0.61^{cA}	61.42 ± 0.61^{dB}
5	HCl	1.03	1.31	0.97	19.53 ± 0.58^{bB}	1.85 ± 0.48^{cC}	21.38 ± 0.42^{bA}	67.15 ± 0.64^{bA}	67.35 ± 0.58^{bA}
Pectin from OW									
6	H_2O	5.44	4.43	4.80	4.52 ± 0.65^{dB}	2.08 ± 0.66^{bC}	6.60 ± 0.39^{eA}	30.69 ± 0.59^{fB}	33.50 ± 0.62^{fA}
7	CA	2.25	3.03	2.60	6.60 ± 0.63^{cB}	4.60 ± 0.62^{aC}	11.20 ± 0.41^{cA}	40.58 ± 0.60^{dB}	45.06 ± 0.59^{dA}
8	AA	2.98	3.79	3.58	5.05 ± 0.52^{dB}	2.95 ± 0.61^{bC}	8.00 ± 0.38^{dA}	38.19 ± 0.57^{eB}	40.27 ± 0.55^{eA}
9	H_2SO_4	1.23	1.45	1.23	24.93 ± 0.59^{aB}	3.50 ± 0.65^{aC}	28.43 ± 0.42^{aA}	62.46 ± 0.55^{cA}	63.60 ± 0.59^{cA}
10	HCl	1.03	1.28	0.98	16.47 ± 0.52^{bB}	2.80 ± 0.63^{bC}	19.27 ± 0.46^{bA}	64.75 ± 0.58^{bB}	67.04 ± 0.60^{bA}

Results were given as mean ± standard deviation

**HAE* Hot-acid extraction method, *MAE* Microwave-assisted extraction technique, *MAHE* Sequential microwave assisted and hot-acid extraction (MAHE)

Averages marked with different letters (in the same row A, B and C in the same column a, b, c, d, e, and f) are statistically different from each other ($p < 0.05$)

Table 2 Methoxyl contents (MeO) and equivalent weights (EW) of the extracted pectins from GW and OW under MAE and HAE (after MAE) techniques

Entry*	Extractant	DE (%)		MeO (%)		EW (g/mol)	
		MAE	HAE (after MAE)	MAE	HAE (after MAE)	MAE	HAE (after MAE)
Commercial Pectin (CP)		73.20 ± 0.52^{a}		12.18 ± 0.59^{a}		1000 ± 6.35^{c}	
Pectin from GW							
11	H_2O	75.00 ± 0.63^{aA}	61.90 ± 0.53^{cB}	12.47 ± 0.55^{aA}	10.39 ± 0.61^{aB}	2500 ± 6.22^{aA}	1250 ± 6.26^{bB}
12	CA	58.33 ± 0.49^{bA}	50.00 ± 0.55^{dB}	9.82 ± 0.57^{bA}	8.47 ± 0.60^{bB}	1250 ± 6.33^{bA}	833 ± 5.89^{dB}
13	AA	75.00 ± 0.59^{aA}	68.23 ± 0.56^{bB}	12.47 ± 0.57^{aA}	11.40 ± 0.65^{aA}	2500 ± 6.19^{aB}	5000 ± 5.88^{aA}
14	H_2SO_4	43.67 ± 0.55^{cA}	29.03 ± 0.63^{eB}	7.43 ± 0.63^{cA}	5.00 ± 0.58^{cB}	625 ± 5.98^{dA}	455 ± 6.55^{eB}
15	HCl	40.00 ± 0.58^{dA}	22.22 ± 0.59^{fB}	6.83 ± 0.65^{cA}	3.85 ± 0.63^{dB}	556 ± 6.28^{eA}	385 ± 6.35^{fB}
Pectin from OW							
16	H_2O	52.94 ± 0.56^{dA}	40.00 ± 0.54^{dB}	8.95 ± 0.58^{bA}	6.83 ± 0.52^{cB}	1667 ± 5.99^{aA}	1111 ± 6.22^{bB}
17	CA	66.67 ± 0.59^{bA}	54.55 ± 0.62^{cB}	11.15 ± 0.61^{aA}	9.21 ± 0.58^{bB}	1250 ± 6.15^{bA}	833 ± 5.97^{dB}
18	AA	63.50 ± 0.61^{cA}	60.00 ± 0.58^{bB}	10.65 ± 0.59^{aA}	10.09 ± 0.60^{bA}	1667 ± 6.11^{aB}	2500 ± 6.18^{aA}
19	H_2SO_4	46.15 ± 0.55^{eA}	29.03 ± 0.59^{fB}	7.84 ± 0.62^{bA}	5.00 ± 0.60^{dB}	591 ± 6.23^{dA}	455 ± 6.38^{eB}
20	HCl	51.52 ± 0.57^{dA}	31.58 ± 0.65^{eB}	8.72 ± 0.64^{bA}	5.43 ± 0.56^{dB}	556 ± 6.30^{eA}	370 ± 6.29^{fB}

Results were given as mean ± standard deviation

**HAE* Hot-acid extraction method, *MAE* Microwave-assisted extraction technique

Averages marked with different letters (in the same row A and B and in the same column a, b, c, d, e, and f) are statistically different from each other ($p < 0.05$)

also prepared from three different volume ratios (1/1, 1/3, and 3/1).

Solution pH is known to be very crucial for the efficient pectin extraction. Extraction solutions with lower pH values enable to isolate more pectin products since solubility of pectin from plant matrix increases in lower pH media due to the hydrolysis of cellulose [23, 24]. Initial pH values of 0.1 N acid solutions were pH_{H2O}:5.44, pH_{CA}: 2.25, pH_{AA}: 2.98, pH_{HCl}: 1.03 and pH_{H2SO4}: 1.23 (Table 1). The highest pectin yields from GW and OW were mainly achieved from experiments carried out in inorganic acids. Poor acidities of organic acids resulted in isolating lower pectin yields (Table 1).

Extraction of pectin from Garlic Waste (GW)

Two different pectin extraction procedures from GW were applied as following, advanced MAE and conventional HAE to the separated residue from the extraction media of MAE. Extractions were first performed under organic or inorganic acids used alone in the solution (Table 1). The highest pectin yield from GW was 24.62 ± 0.65% achieved under H_2SO_4 media by MAE method (entry 4 in Table 1). Previous report showed that pectin yield from GW by HAE under H_2SO_4 solution was 22.08% [25]. Thereby, it was observed that MAE procedure highly improved the pectin yields from GW in comparison with the HAE method. In addition to this observation, applying HAE to the separated residue from the extraction media of MAE contributed 3.37 ± 0.53% additional pectin yields which existed in the residue. Thus, utilization of MAHE technique resulted in the highest yielded pectin product (27.99 ± 0.36%). Observation of this yield showed that there was still some amount of pectin existing in the residue of MAE. Therefore, utilization of MAHE conditions was determined to be very beneficial in terms of obtaining higher pectin yields (Table 1).

Poor acidities of CA and AA solutions resulted in lower pectin yields (entries 2 and 3 in Table 1). In general, extraction performed in CA resulted in pectin with better yields compared with AA. Pectin yield from GW under CA by MAE was 9.55 ± 0.44% (entry 2 in Table 1). Applying HAE after MAE under CA gave 5.57 ± 0.41% of pectin yield. Therefore, utilization of MAHE method resulted in a total of 15.12 ± 0.33% of pectin yield from CA solution. Pectin yield from GW by HAE under CA was previously reported to be 8.13% [25]. Employing MAE technique highly increased the pectin yield compared with the reported HAE method. One of the interesting results was that utilization of water as an extractant by MAHE resulted in 11.27 ± 0.47% of pectin yield (entry 1 in Table 1).

DE and Gal-A contents are known to be two important parameters for the determination of the quality of extracted pectins. These values contribute to the gelling properties of pectins. In general, a pectin sample is expected to have a minimum of 65% Gal-A and ≥ 50 DE (high methoxyl pectin) contents for commercial applications. Gal-A and DE values of the commercial citrus pectin were calculated to be respectively 80.10 ± 0.44% and 73.20 ± 0.52% (Tables 1 and 2). If Gal-A content is below 65%, pectin product should be further purified for the utilization in commercial applications [26]. DE and Gal-A contents of the extracted pectins from GW under MAE and HAE after MAE methods were summarized in Tables 1 and 2. According to the Table 1, Gal-A contents of pectin samples from GW increased with enhanced acidity. Extractions carried out under inorganic acid solutions generally provided more acceptable Gal-A contents. For example, Gal-A contents of pectins extracted in H_2SO_4 and HCl by MAE were respectively 63.92 ± 0.61% and 67.15 ± 0.64% (entries 4 and 5 in Table 1), these values were found to be 49.96 ± 0.59% and 44.85 ± 0.57% for extractions carried out in CA and AA organic acids, respectively (entries 2 and 3 in Table 1). In addition to this observation, applying MAE method also improved Gal-A contents of extracted pectins. While Gal-A content of pectin from GW in CA under HAE condition was reported to be 32.98% [25], this value was 49.96 ± 0.59% for the pectin sample obtained from MAE technique (entry 2 in Table 1). Another interesting result was that Gal-A contents of extracted pectins under organic acids and pure water by HAE after MAE were observed to be significantly higher compared to the MAE. Applying HAE to the separated residue from the extraction media of MAE seems to be very beneficial for achieving higher Gal-A contents, especially for organic acidic media.

DE is described as the ratio of the esterified Gal-A to the total Gal-A groups of a pectin sample. According to the obtained results, DE contents of the extracted pectins under MAE method were higher in pure water and organic acid solutions compared to the inorganic acids. The highest DE value with 75.00%, which is very close to that of the commercial pectin, was observed in pectins extracted in pure water and AA media by MAE (entries 11 and 13 in Table 2). Interestingly, DE values of pectins obtained under HAE after MAE conditions were found to be lower compared with MAE (Table 2).

EW values help to determine unesterified Gal-A units and the gel-forming ability of pectins. EW values of the extracted pectins from GW are summarized in Table 2. Extraction achieved under strong acidic solutions including H_2SO_4 and HCl resulted in lower EW values for performed extraction procedures due to the degradations of pectin chains under lower pH solutions. MeO content of a pectin sample could be defined as the total number of moles of methanol per 100 mol of Gal-A [25]. According to the obtained results, MeO contents of the extracted pectins from GW under pure water and organic acids were higher compared to those of obtained under inorganic acids (Table 2). Applying HAE

to the separated residue from the extraction media of MAE also resulted in lower MeO contents compared with those of obtained from MAE.

Extraction of pectin from Onion Waste (OW)

MAE and MAHE methods were also performed for the extraction of pectin from OW, and obtained results are summarized in Tables 1 and 2. Extraction of pectin by MAE was performed under pure water, organic or inorganic acids used alone in the solution. The highest pectin yield from OW by MAE was 24.93 ± 0.59%, and achieved under inorganic H_2SO_4 media (entry 9 in Table 1). Previously, pectin yield from OW by HAE under H_2SO_4 solution was reported to be 16.22% [27]. Applying MAE procedure highly enhanced pectin yields from OW compared with the HAE method. Performing HAE to the separated residue from the extraction media of MAE under inorganic H_2SO_4 media contributed extra 3.50 ± 0.65% of pectin yield. Therefore, applying MAHE technique resulted in the total of 28.43 ± 0.42% of pectin yield (entry 9 in Table 1). Pectin extraction under MAHE conditions always resulted in increasing pectin yields whether organic or inorganic acids used as extractant (Table 1).

Weak acidities of CA and AA gave pectin with lower yields compared with inorganic acids (entries 7 and 8 in Table 1). Pectin yields from OW in CA under performed methods (entry 7 in Table 1) were higher than those of AA media (entry 8 in Table 1). Extraction of pectin from OW under CA media by MAE also resulted in more pectin yields compared with those of the reported HAE. For example, while pectin yield from OW under HAE condition in CA solution was reported to be 4.53% [27], yields from MAE and MAHE methods were found to be respectively 6.60 ± 0.63% and 11.20 ± 0.41% (entry 7 in Table 1). Performing MAE method notably increased the pectin yield in any circumstances. Extraction of pectin from OW carried out in water by MAHE also resulted in 6.60 ± 0.39% of yield (entry 6 in Table 1).

DE and Gal-A contents of the extracted pectins from OW performed under MAE and HAE after MAE are also summarized in Tables 1 and 2. Similar to the observation obtained from the extraction of pectin from GW, increased acidity resulted in increasing Gal-A contents of pectins from OW. Extraction accomplished in HCl and H_2SO_4 (entries 9 and 10 in Table 1) provided more reasonable Gal-A contents compared with those of pure water, CA and AA solutions. For instance, extractions accomplished in H_2SO_4 and HCl under MAE condition resulted in pectins with 62.46 ± 0.55% and 64.75 ± 0.58% of Gal-A contents, respectively (entries 9 and 10 in Table 1), these values were respectively found to be 30.69 ± 0.59%, 40.58 ± 0.60% and 38.19 ± 0.57% for pectins extracted in pure water, CA and AA media (entries 6, 7 and 8 in Table 1). Employing HAE after MAE also gave higher Gal-A contents of the pectin samples from OW compared with those of MAE used alone.

According to the Table 2, DE contents of pectins from OW in organic acidic and pure water media by MAE were mainly higher compared to those of the inorganic acid solutions. The highest DE value was achieved with 66.67 ± 0.59% from the extracted pectin under CA media by MAE method (entry 17 in Table 2). DE values of pectins by HAE after MAE condition were mostly lower compared with the MAE conditions (Table 2).

EW values of the pectin samples from OW are given in Table 2. Increased acidity in extraction solution was found to be inversely correlated with EW values of pectin products. EW values of pectin samples extracted in H_2SO_4 and HCl were always found to be lower than those of extracted in pure water, AA and CA (Table 2). Similar observation was observed for MeO contents of the extracted pectins from OW. MeO contents of pectins extracted in pure water, AA and CA were higher compared to those of obtained under H_2SO_4 and HCl (Table 2). In addition to this observation, MeO contents of obtained pectins from OW extracted under HAE after MAE were lower than those of MAE.

Extraction of pectin from OW and GW under Dual Acid conditions

Extraction of pectin from OW and GW under dual acidic solutions was also performed using MAE technique. Employing dual acid mixtures during the MAE procedure highly improved the pectin yields from both GW and OW when compared to especially conditions of organic acidic media. Increasing inorganic acid concentration in the dual acidic solution resulted in increasing pectin yields (Table 3).

Initial pH values of dual acid mixtures are summarized in Table 3. As expected, the highest pectin yields from GW and OW were mainly achieved from experiments carried out in HCl-H_2SO_4 mixtures. According to the Table 3, addition of strong HCl and H_2SO_4 to the organic acids resulted in increasing pectin yields due to the releasing of more pectin from plant matrix [28]. Employing mixtures of AA and CA did not improve the pectin yield. However, mixing organic and inorganic acids significantly increased the extracted pectin yields [26]. In general, extractions of pectin carried out under dual acidic media containing H_2SO_4 resulted in the highest yielded pectins from both GW and OW compared with the other dual acidic extraction solutions. While the highest pectin yield (23.36 ± 0.66%) from GW was accomplished in 1/3 HCl-H_2SO_4 mixture (entry 38 in Table 3), it was 21.88 ± 0.52% from OW carried out under 1/3 AA-H_2SO_4 mixture (entry 26 in Table 3).

Physicochemical properties (Gal-A, DE, MeO and EW) of the extracted pectins from both OW and GW are also

Table 3 Extraction of pectin from OW and GW under dual acid conditions using MAE method

Entry*	Extractant	Initial pH	Final pH (GW)	Final pH (OW)	Yields (%) from OW	Yields (%) from GW	Gal-A (%) OW	Gal-A (%) GW	DE (%) OW	DE (%) GW	MeO (%) OW	MeO (%) GW	EW (g/mol) OW	EW (g/mol) GW
Commercial pectin (CP)							80.10±0.44^{a}		73.20±0.52^{a}		12.18±0.59^{a}		1000±6.35^{e}	
CA-HCl														
21	3/1	1.64	2.66	2.58	9.00± 0.62^{dB}	10.48± 0.64^{dA}	50.38± 0.66^{fB}	55.38± 0.61^{dA}	62.96± 0.59^{cA}	58.16± 0.66^{fB}	10.56± 0.58^{aA}	9.79± 0.66^{aA}	1000± 6.22^{eA}	853±6.35^{hB}
22	1/1	1.35	2.00	1.91	15.52± 0.52^{cB}	18.58± 0.58^{bA}	55.38± 0.59^{dB}	59.13± 0.65^{cA}	56.52± 0.65^{fA}	46.67± 0.61^{iB}	9.53± 0.63^{aA}	7.93± 0.55^{aB}	625±6.33^{iA}	625±6.36^{nA}
23	1/3	1.20	1.54	1.53	16.45± 0.55^{cB}	19.83± 0.62^{bA}	59.96± 0.61^{cA}	61.21± 0.57^{cA}	53.56± 0.66^{gA}	45.45± 0.66^{iB}	9.05± 0.66^{aA}	7.73± 0.59^{aB}	591±7.08^{jA}	576±6.60^{qB}
AA-H_2SO_4														
24	3/1	1.74	3.08	2.81	10.22± 0.66^{dA}	11.17± 0.68^{dA}	45.38± 0.65^{hB}	47.88± 0.68^{fA}	60.00± 0.63^{dB}	70.00± 0.75^{bA}	10.09± 0.62^{aB}	11.68± 0.63^{aA}	1250± 6.13^{dB}	1667±6.33^{bA}
25	1/1	1.46	2.19	2.06	16.63± 0.61^{cB}	17.90± 0.66^{bA}	55.90± 0.62^{dB}	60.48± 0.63^{cA}	58.33± 0.66^{eA}	53.85± 0.63^{gB}	9.82± 0.57^{aA}	9.10± 0.58^{aA}	833±6.44^{fA}	833±6.55^{iA}
26	1/3	1.34	1.73	1.69	21.88± 0.52^{aA}	22.83± 0.62^{aA}	59.02± 0.67^{cB}	61.21± 0.59^{cA}	55.25± 0.61^{fA}	50.00± 0.64^{hB}	9.32± 0.60^{aA}	8.47± 0.57^{aA}	667±6.27^{hB}	714±6.56^{lA}
CA-H_2SO_4														
27	3/1	1.64	2.64	2.57	11.38± 0.68^{dB}	13.47± 0.55^{cA}	46.00± 0.66^{hB}	55.54± 0.57^{dA}	60.87± 0.60^{dA}	54.55± 0.62^{gB}	10.23± 0.61^{aA}	9.21± 0.67^{aA}	1000± 6.25^{eA}	1000±6.23^{fA}
28	1/1	1.43	2.08	2.04	16.07± 0.60^{cB}	19.12± 0.63^{bA}	58.81± 0.62^{cA}	58.25± 0.66^{cA}	52.00± 0.63^{gA}	47.15± 0.65^{iB}	8.80± 0.57^{aA}	8.00± 0.62^{aA}	769±6.40^{gB}	814±6.44^{jA}
29	1/3	1.19	1.72	1.69	20.83± 0.67^{aB}	22.77± 0.60^{aA}	60.17± 0.58^{cB}	61.42± 0.64^{cA}	50.00± 0.64^{gA}	45.16± 0.59^{iB}	8.47± 0.55^{aA}	7.68± 0.58^{aA}	624±6.28^{iB}	734±6.33^{kA}
AA-HCl														
30	3/1	1.60	3.03	2.82	7.03± 0.61^{eA}	7.93± 0.59^{eA}	48.60± 0.60^{gB}	54.85± 0.59^{dA}	60.00± 0.67^{dB}	68.00± 0.65^{cA}	10.09± 0.57^{aB}	11.36± 0.51^{aA}	1250± 6.18^{dB}	1450±6.21^{dA}
31	1/1	1.34	2.04	1.96	15.35± 0.61^{cB}	17.37± 0.61^{bA}	52.25± 0.55^{eB}	59.54± 0.62^{cA}	56.25± 0.64^{fA}	55.52± 0.66^{gA}	9.48± 0.61^{aA}	9.37± 0.67^{aA}	833±6.35^{fB}	975±6.34^{gA}
32	1/3	1.16	1.54	1.56	16.42± 0.57^{cB}	18.27± 0.57^{bA}	58.29± 0.66^{cB}	63.71± 0.64^{bA}	53.33± 0.63^{gA}	51.35± 0.71^{hB}	9.01± 0.63^{aA}	8.69± 0.55^{aA}	625±6.35^{iB}	655±6.39^{mA}
AA-CA														
33	3/1	2.52	3.73	3.57	5.07±0.59^{fB}	6.70± 0.63^{eA}	39.13± 0.59^{iB}	44.96± 0.59^{gA}	63.15± 0.61^{cB}	71.43± 0.68^{bA}	10.59± 0.58^{aB}	11.90± 0.61^{aA}	1567± 6.44^{aB}	1867±6.34^{aA}
34	1/1	2.42	3.48	3.33	5.93±0.54^{fB}	7.62± 0.59^{eA}	39.75± 0.61^{iB}	47.04± 0.64^{fA}	64.90± 0.67^{bA}	65.64± 0.65^{dA}	10.87± 0.61^{aA}	10.99± 0.56^{aA}	1429± 6.25^{bB}	1529±6.22^{cA}
35	1/3	2.27	3.27	3.14	7.52± 0.65^{eA}	7.80± 0.55^{eA}	40.48± 0.63^{iB}	50.06± 0.56^{eA}	66.50± 0.65^{bA}	62.50± 0.61^{eB}	11.12± 0.55^{aA}	10.49± 0.59^{aA}	1311± 6.12^{cB}	1329±6.32^{eA}
HCl-H_2SO_4														
36	3/1	1.08	1.28	1.35	18.90± 0.64^{bB}	20.35± 0.59^{bA}	63.92± 0.61^{bB}	66.50± 0.65^{bA}	51.11± 0.59^{gA}	40.74± 0.58^{jB}	8.65± 0.62^{aA}	6.95± 0.64^{aB}	566±6.39^{jA}	570±6.66^{qA}

Table 3 (continued)

Entry*	Extractant	Initial pH	Final pH (GW)	Final pH (OW)	Yields (%) from OW	Yields (%) from GW	Gal-A (%) OW	Gal-A (%) GW	DE (%) OW	DE (%) GW	MeO (%) OW	MeO (%) GW	EW (g/mol) OW	EW (g/mol) GW
Commercial pectin (CP)							80.10 ± 0.44^{a}		73.20 ± 0.52^{a}		12.18 ± 0.59^{a}		1000 ± 6.35^{e}	
37	1/1	1.14	1.34	1.37	20.52 ± 0.54^{aB}	21.90 ± 0.65^{aA}	63.40 ± 0.63^{bB}	65.03 ± 0.66^{bA}	50.00 ± 0.65^{gA}	41.86 ± 0.64^{jB}	8.47 ± 0.57^{aA}	7.14 ± 0.63^{aB}	578 ± 6.29^{jB}	590 ± 6.57^{pA}
38	1/3	1.13	1.45		21.25 ± 0.54^{aB}	23.36 ± 0.66^{aA}	62.77 ± 0.66^{bB}	64.50 ± 0.63^{bA}	46.67 ± 0.57^{hA}	42.86 ± 0.69^{jB}	7.93 ± 0.64^{aA}	7.30 ± 0.57^{aA}	583 ± 6.38^{jB}	610 ± 6.66^{oA}

*Results were given as mean ± standard deviation. Averages marked with different letters (in the same row A and B and in the same column a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p and q) are statistically different from each other ($p < 0.05$)

summarized in Table 3. In general, Gal-A contents of pectin samples from GW were higher than those of obtained from OW for all performed dual acid conditions. Increasing inorganic acid contents resulted in enhanced Gal-A contents of the pectin samples. Gal-A contents of the extracted pectins were calculated to be lower than that of the commercial citrus pectin (Table 3). However, extractions performed under dual acid conditions resulted in pectins with improved Gal-A contents compared to the acids used alone in Table 1.

This observation did not change regardless of strong acidity or types of the acids. For instance, Gal-A contents of pectins extracted from GW and OW under AA condition with MAE method were respectively $44.85 \pm 0.57\%$ and $38.19 \pm 0.57\%$ (entry 3 and 8 in Table 1), these values were calculated to be respectively $48.60 \pm 0.60\%$ and $54.85 \pm 0.59\%$ for the pectins extracted under 3/1 (v/v) mixture of AA-HCl (entry 30 in Table 3).

EW, MeO and DE values of the extracted pectins from GW and OW under dual acidic media are also given in Table 3. Addition of second acid in the extraction media resulted in moderate EW values for the extracted pectins. By mixing two acids whether organic or inorganic, EW values were observed at average values compared to the conditions in which these acids were used alone in the extraction. EW values of pectin products were observed to be directly proportional to the DE and MeO contents. Unlike showing higher Gal-A contents of pectins extracted from GW under dual acid conditions, DE and MeO values of pectins from OW were generally found to be higher than those of obtained from GW. Another interesting result is that increasing organic acid volume in the dual acidic media leads to higher DE and MeO values of pectin samples for both GW and OW (Table 3). This is probably the reason of degradation of pectic acids and demethylation with increasing inorganic acid content [25]. The highest DE and MeO contents of pectin samples were obtained respectively with $71.43 \pm 0.68\%$ and $11.90 \pm 0.61\%$ from the pectin extracted from GW under 3/1 (v/v) AA-CA solution (entry 33 in Table 3).

FT-IR spectra results of pectin samples

FT-IR spectra results of extracted samples from both GW and OW were used to characterize pectin structure, and observed vibration bands were compared with those of the commercial citrus pectin (Fig. 1). FT-IR spectra of pectin samples obtained from conditions where organic or inorganic acids used alone under MAE are shown in Fig. 1. In general, characteristic vibration bands of extracted pectin samples from GW and OW overlap with absorption bands of commercial pectin, and confirm the pectin structure. Carbonyl (C = O) and ester carboxylate (COO) vibration bands of pectin products can be seen around 1750 cm^{-1} and 1600 cm^{-1}, respectively. Absorption bands observed around

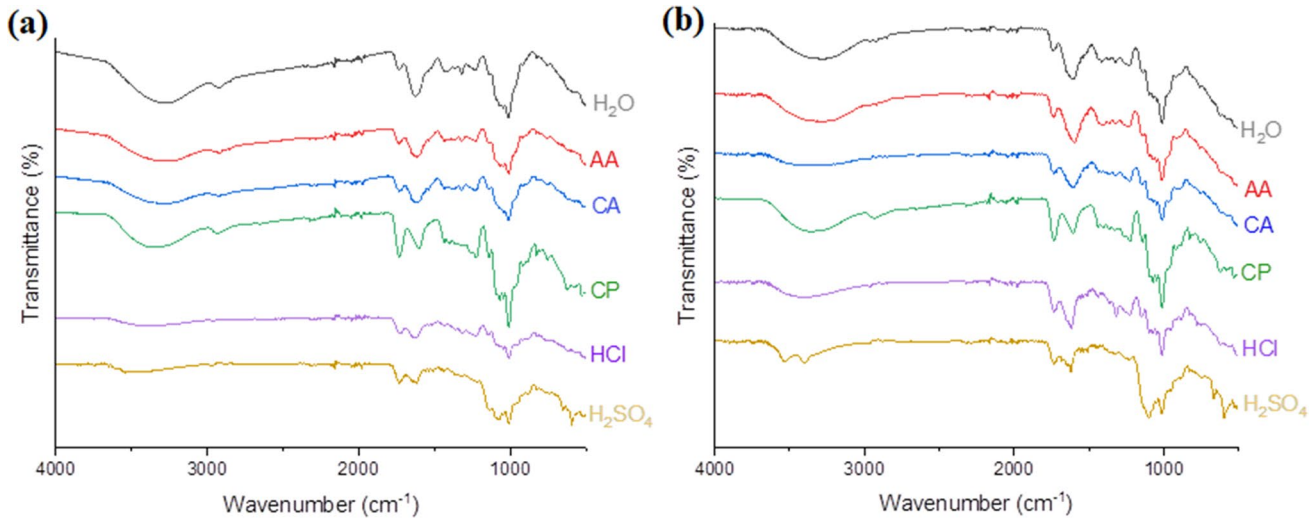

Fig. 1 FT-IR spectra results of extracted pectin from **a** OW, and **b** GW.

3400 cm^{-1} and 2900 cm^{-1} can be assigned to the presence of hydroxyl (–OH) and C-H stretching vibration bands of the pectin samples, respectively. Stretching vibration band for the glycosidic C-O-C and C-OH groups is observed at 1000 cm^{-1} [3]. FT-IR spectra results of the extracted samples confirmed the pectin structure when compared with the structure of the commercial pectin.

Conclusion

In conclusion, MAE method for the extraction of pectin from garlic and onion waste was successfully demonstrated. Extractions were accomplished under three different media including organic (citric and acetic), inorganic (sulfuric and hydrochloric) acids and their mixtures. Sequential MAHE method for the extraction of pectin from onion and garlic waste was also examined, and found to be very beneficial in terms of obtaining higher yields. Pectin yield under MAHE condition was higher than MAE. Obtained successful outcomes indicated that sequential microwave assisted-hot acid extraction (MAHE) method could be used as an efficient extraction technique in terms of obtaining higher pectin yields. Applying MAHE technique to the garlic and onion waste resulted in up to $27.99 \pm 0.36\%$ and $28.43 \pm 0.42\%$ of pectin yields, respectively. The highest pectin yields and galacturonic acid (Gal-A) contents of the extracted pectins were mostly achieved under inorganic H_2SO_4 and HCl solutions. However, degree of esterification (DE), methoxyl degree (MeO) and equivalent weights (EW) values were found to be higher for the samples extracted under citric (CA) and acetic (AA) acids. Extraction of pectin from onion and garlic waste was also accomplished in dual acidic media under MAE condition. Utilization of organic-inorganic dual acid mixtures during the extraction provided higher yields and controlled physicochemical properties for pectin. Addition of strong HCl and H_2SO_4 to the organic acidic solutions resulted in increasing pectin yields. While increasing inorganic acid contents in the dual acid solution resulted in enhanced Gal-A contents, increasing organic acid volume provided higher DE and MeO values of pectin samples from both garlic and onion waste. In general, MAE technique significantly increases yield and quality of extracted pectin, and provides decreased extraction time, utilization of less solvent and reduced cost. However, low selectivity and unavoidable reaction in high temperatures are still important concerns for the MAE method.

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Declarations

Competing interests The authors declare no competing interests.

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