






RESEARCH ARTICLE

Ultrasound assisted extraction for the recovery of phenolic compounds from waste hazelnut shell

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ABSTRACT

Hazelnut shell is the primary byproduct of hazelnut industry which has the potential source of antioxidants, and phenolics with interest of pharmaceutical, food, and cosmetic industries. The main goal of this study is to determine effects of extraction method, extraction time, solvent type, solid to liquid ratio, and particle size on extraction yield, antioxidant capacity, and total phenolic content of waste hazelnut shell. The highest extraction yield was found as 15.4% by using methanol as solvent, in combined extraction for 16 h total extraction time. As for the best antioxidant capacity, 0.0508 mg TE mL⁻¹ was observed by using methanol as a solvent in ultrasonic extraction, whereas the highest phenolic content was found as 0.188 mg GAE mL⁻¹ by Soxhlet extraction with acetone for 8 h. After extraction of hazelnut shell waste, major components were found as oleic and palmitic acids for all solvent types according to GC-MS results.

Keywords: Biomass, hazelnut shell, polyphenols, byproducts, extraction

1. INTRODUCTION

In every year, a vast amount of plant is being produced and their wastes have been disposed of to nature rather than using them [1]. Utilization of these waste biomass has great potential due to not only their abundancy, and zero carbon emission [2] but also for their valuable ingredients.

Hazelnuts are one of the most dominant nut crops in the world [3] that includes many salutary chemicals like fatty acids, amino acids, vitamins, minerals, phenolics, and antioxidants [4]. Hazelnut shell is the major byproduct of hazelnut that consist of 36.02% cellulose, 12.66% hemicellulose, 40.14% lignin, and 7.86% extractives [5].

In Turkey, each year 1 million tons of hazelnut waste have been produced and burned for heating [6]. Researchers have proposed new alternative ways to valorize hazelnut shell waste rather than burning such as production of sugars [5, 7], platform chemicals [8], bio-oil [9], antioxidants, and phenolics [10].

Antioxidants and phenolics are bioactive components coming from plants and have good effects on human health like antiradical activities, antimutagenic, anticarcinogenic, and antiproliferative potential. Presently, many antioxidants have being used to put the oxidation process off in food systems, synthetically. However, application of synthetic antioxidants in food products are strictly regulated considering health hazards [11].

Extraction is an important process in isolation of phenolics and antioxidants from plant matrix. Traditional methods like maceration, boiling, soaking, and soxhlet extraction are most commonly used extraction methods due to low cost, easy to operate, and high extraction yields. Moreover, Soxhlet extraction is well known extraction method since it shows great performance for recovering phenolics and antioxidants compared with other traditional methods [12].

Ultrasonic extraction is another attractive extraction method that decreases extraction time and solvent consumption [13]. Additionally, cavitation promotes

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solid solubility, diffusivity of the solvent, and transportation of the solutes [14-16].

In literature, antioxidant capacity and phenolic content have been reported about hazelnut kernel, green leafy cover, and brown skin in many studies [3, 4, 17, 18]. For example, antioxidant capacity and phenolics from hazelnut by-products (shells and defatted skins) have been reported by using solvent maceration at room temperature with extraction yield of 30% and 502 mg g⁻¹ GAE phenolic content in ethanol/water (80/20 v/v) mixture [3]. Another study has reported the effect of ultrasound-assisted extraction on antioxidants and phenolic compounds from hazelnut shells using acetone as solvent and determined optimum the extraction conditions using response surface methodology (RSM) [4]. The highest phenolic content (12 mg g⁻¹ GAE) was obtained in acetone as a solvent for 12 h extraction time.

The main goal of this study is to valorize waste hazelnut shell by extracting phenolic compounds from it by different extraction methods (soxhlet extraction, ultrasonic extraction and combined extraction). For this purpose, effects of extraction time, extracting solvents and solid to liquid ratio on extraction yield, antioxidant capacity, phenolic content were investigated.

2. MATERIALS AND METHODS

2.1. Feedstock and chemicals

Hazelnut shell waste provided from Ordu, Turkey, was used as a feedstock without separating husks and shells. Hazelnut shell waste was dried at 60 °C and grounded into 1 mm particle size for extraction processes by using blade-knife laboratory grinder. ACS grade ethanol, acetone, methanol and hexane were purchased from Merck. To determine total phenolic content and antioxidant capacity, sodium carbonate (99.5%), potassium persulfate (99.9%), gallic acid (97.5%), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (97%) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS+) were purchased from Sigma-Aldrich. Folin-Ciocalteu reagent was purchased from Merck.

2.2. Experimental setup and procedure

In this study, soxhlet, ultrasonic and combined (including soxhlet and ultrasonic extraction) extractions were used as extraction methods. Soxhlet extraction setup includes 500 mL solvent flask, 250 mL thimble flask, condenser, and heating mantle (Wisd, DH.WHM 12295). An ultrasonic bath (WUC-D06H, WiseClean) with 40 kHz maximum frequency was used in ultrasonic extraction part. The combined extraction was formed by two steps: extraction of waste was done first by soxhlet extraction and then the remaining waste was subjected to ultrasonic extraction. In this combined method, after 8h of soxhlet extraction, solid residue was dried in vacuum oven at 50 °C for overnight to remove remaining solvent. After drying, solid residue was reextracted by ultrasonic extraction. At the end, solid residue was

dried under the same conditions to calculate the extraction yield by using Eq. (1). Extracted oil and solvents were separated with a rotary evaporator under specific pressure and temperature according to nature of solvents. Experiments were carried out with different extracting solvents (ethanol, methanol, n-hexane, acetone) for 2 to 8 h. Initial solid to liquid ratio (4, 8 and 12 g in 250 ml) was another extraction parameter.

$$\text{Extraction yield (\%)} = \frac{\text{Mass of initial hazelnut shell} - \text{mass of final hazelnutshell}}{\text{Mass of initial hazelnut shell}} \times 100 \quad (1)$$

2.3. Analytical methods

2.3.1. Total phenolic content

The total phenolic content in liquid product was determined by Folin-Ciocalteu's method: Folin Ciocalteu reagent was diluted 10-fold with deionized water and 7.5% (75 g L⁻¹) of Na₂CO₃ was prepared with distilled water. 0.5 mL of extracted liquid product, 0.5 mL of Folin Ciocalteu solution, and 1 mL of Na₂CO₃ were mixed and then volume adjusted to 10 mL with deionized water. After this step, mixture was kept in dark room for 45 mins at room temperature. Then, the absorbance was measured at 725 nm by using distilled water as a blank. The phenolic content of liquid product was designated as milligrams of Gallic Acid Equivalents (GAE) per milliliter of liquid product.

2.3.2. Total antioxidant capacity

Total antioxidant capacity of liquid product solution was evaluated by using ABTS method: ABTS radical solution was prepared by using 14 mM ABTS solution and 4.9 mM potassium persulfate solution with volume ratio of 1:1. This solution was kept in dark room for 16 h. Then, ABTS⁺ solution was diluted with ethanol (1:50 v/v%). After dilution, 1 mL of liquid product was mixed with 4 mL of ABTS⁺ solution and kept in the dark at room temperature for 5 min. The absorbance was measured at 734 nm with water was used as a blank. The antioxidant capacity of liquid product was expressed as milligrams of Trolox Equivalents (TE) per milliliter of liquid product.

2.3.3. FTIR analysis

Functional groups in solid residue were examined in the wave number range of 4000- 650 cm⁻¹ by using Fourier Transform Infrared Spectrometry that equipped with attenuated total reflectance (ATR-FTIR) (Perkin Elmer-Spectra Two, USA).

2.3.4. GC-MS analysis

GC-MS (Agilent 6890 N/5973 N Network) was used for the analysis of hazelnut shell waste decomposition products. Stabilwax®-DA (Crossbond® Carbowax® polyethylene glycol, 30-meter-long, 0.32 mm inner diameter, 1 µm particle size) column was used. Injection volume was 1.0 µL and helium was used as a carrier gas. GC-MS analysis was conducted in SCAN

mode with the following method; initial oven temperature set as 40 °C and then, first heating (8 °C min⁻¹) to 140 °C kept for 5 minutes, second heating (10 °C min⁻¹) to 220 °C and kept for 10 minutes. Total run time of method is 35 minutes. GC-MS chromatograms were analyzed by using MSD ChemStation E.0202.1431 software and the area of specified chromatogram peaks were calculated accordingly. Moreover, product distributions were given as the ratio of peak area of governing species at given reaction to its maximum area obtained throughout the extraction process (Eq. (2)). Analyzed products were identified by using National Institute of Standard (NIST) MS search and compounds are tabulated in Table 1 in 'Results and Discussion' section.

$$\text{Relative peak area} = \frac{\text{peak area of species } i \text{ at specified extraction}}{\text{Total peak area of all extracted species}} \quad (2)$$

3. RESULTS AND DISCUSSION

In this study, effect of different solvent type, extraction time, extraction method and solid/liquid ratio were examined to determine extraction yield, total phenolic content, and antioxidant capacity of hazelnut shell waste.

3.1. Effect of solvent type

The extraction was carried out with different solvents (ethanol, methanol, n-hexane, acetone) to clarify the effects of solvent type on extraction yield, phenolic content and antioxidant capacity and the results were shown in Fig 1a-c. The total phenolic content (Fig 1-a) was found as 0.006, 0.02, 0.0185 and 0.0191 mg GAE mg mL⁻¹ for hexane, ethanol, methanol, and acetone extraction, respectively. It can be inferred that ethanol was the best solvent in terms of phenolic content which are compatible with previous studies in literature. Shahidi et al. reported phenolic content of hazelnut kernel and by-products as 214 .1 mg CE per gram of hazelnut skin in ethanol/water mixture (80:20 v/v) medium [19].

Total antioxidant capacity results were represented in Fig 1-b. The highest antioxidant capacity was found in hexane extracts as 0.055 mg TE mL⁻¹. On the other hand, the lowest value was obtained in methanol extracts as 0.049 mg TE mL⁻¹. Polarity of the solvents dominates the antioxidant capacity. Hexane is nonpolar solvent while ethanol, methanol and acetone are polar. In other words, difference in solvent polarity, dispersibility, and penetrability may affect the antioxidant capacity due to selective different extracts from the hazelnut shell [20].

Extraction yield (Fig 1-c) is another important response in extraction process. The lowest extraction yield in Fig 1-c was found in hexane as 6.94%, while the best extraction yield was obtained as 10.55% and 10.1% in methanol and ethanol, respectively. As well known, ethanol and methanol are polar protic solvents and they donate hydrogen to the medium [21]. Since they gave the best results, it is possible to say that hazelnut shell waste includes more polar extractives. In another words, polar protic solvents

provide higher extraction yield thanks to -OH bonds and probable hydrogen donation to extraction medium [9].

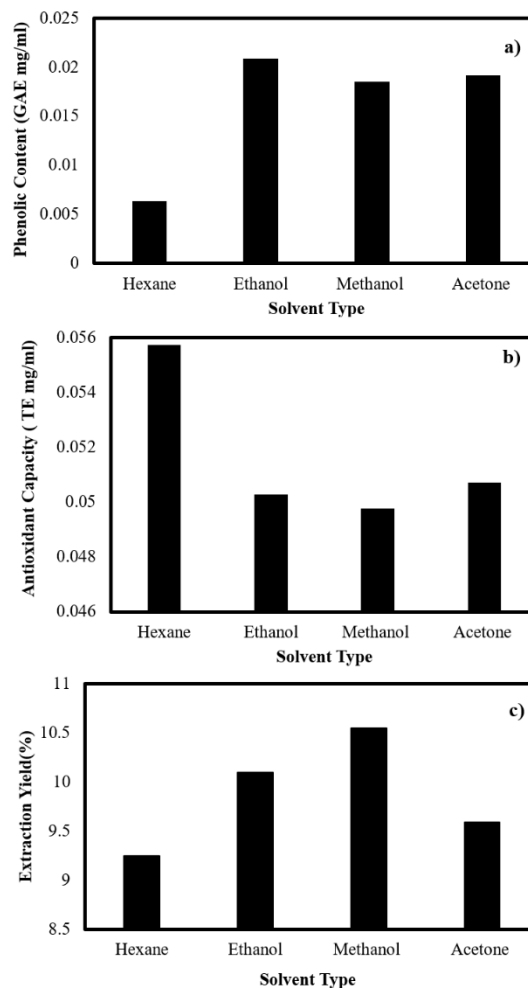


Fig 1. Effect of solvent type on a) phenolic content, b) antioxidant capacity, c) extraction yield in soxhlet extraction for 8 h

3.2. Effect of extraction method

In this work, three extraction methods (soxhlet, ultrasonic and combined) were carried out for the valorization of waste hazelnut shell and results are given in Fig 2. The highest extraction yield was obtained in combined extraction for each solvent and the maximum extraction was recorded as 15.40% with methanol.

If individual extraction methods are compared, it is possible to say that extraction yield was higher in ultrasonic extraction resulting from high diffusion rates of solvent and increment of the cavitation [22]. Furthermore, combined (soxhlet and ultrasonic) extraction gave better results compared with soxhlet extraction. This was caused from erosion, breakdown of cell, and rupturing the surface because of the generated shear forces by the ultrasound cavitation [23].

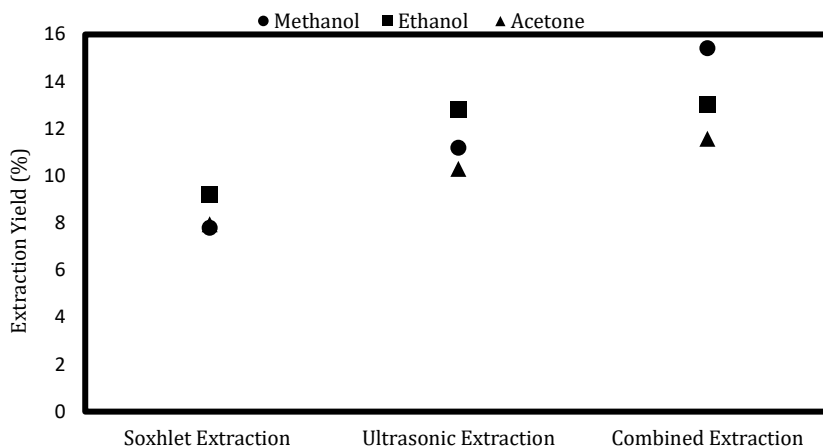


Fig. 2. Effect of extraction methods on extraction yield (Soxhlet extraction: 8 h, Ultrasonic extraction: 8 h and combined extraction: 8 h Soxhlet and 8 h ultrasonic extraction)

3.3. Effect of extraction time

Extraction time is another parameter in the extraction process due to imperative in reduction of energy and cost. In soxhlet extraction, extraction time was varied from 2, 3, and 8h for each solvent. Fig 3 indicates the effect of extraction time on extraction yield.

The highest extraction yield was found as 10.55% in methanol for 3 h. In the extraction by using ethanol as solvent, the yield for 2 h was 9.7%, while it was 10% for 8 h extraction, respectively. In methanol extraction, extraction yields were very close to each other from 2 to 8 h (10.55%). The results indicate that there is no significant difference in extraction yields after 3 h due to Fick’s second law of diffusion [12, 15]. Final equilibrium will be reached between hazelnut shell and extraction solvent at certain time of extraction. Besides, extraction yields tend to decrease after 3 h due to the fact that over-exposure of hazelnut shell to localize heating. This over exposure may cause

the degradation of extractives in the extraction medium [24, 25].

Antioxidant capacity was also investigated with different extraction times. Results were given in Fig 4. There is no significant difference in antioxidant capacity with time (except in hexane). Hexane is a nonpolar solvent and dissolves nonpolar extractives from the extraction medium, whereas other solvents are polar and extracts the polar extractives. In hexane extraction, there was an increment from 2 to 3 h and dramatic decrement from 3 h to 8 h. This dramatic difference means that extractives would be decomposed after a certain time due to exposure of excess heating [26]. The difference between antioxidant activities of polar solvents and nonpolar solvent might be concluded as follows; extractives coming from ethanol, methanol, and acetone are more stable compared with extractives coming from hexane.

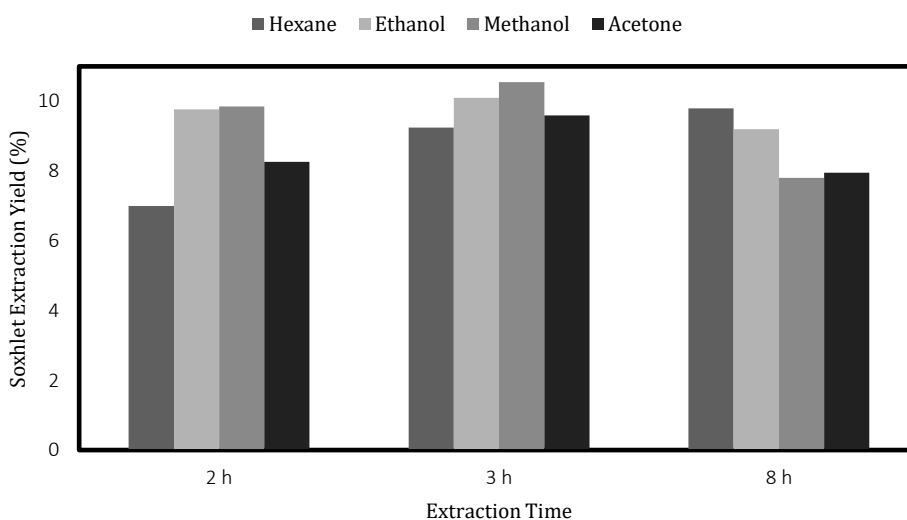


Fig 3. Effect of extraction time on extraction yield

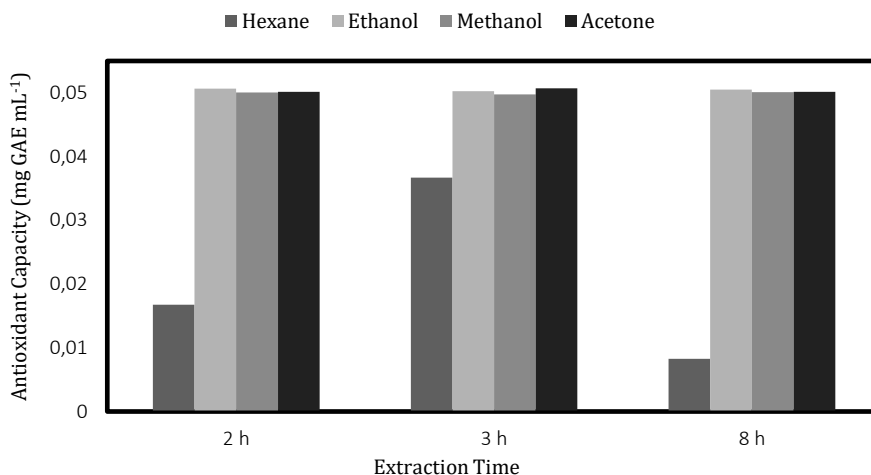


Fig 4. Effect of time on antioxidant capacity

3.4. Effect of solid/liquid ratio

The solid/liquid ratio is another parameter that affects extraction yield, total phenolic content, and antioxidant capacity. In this study, three different solid/liquid ratios (g mL⁻¹) as 4/250, 8/250, and 12/250 were investigated. Fig 5 shows how solid/liquid ratio effects extraction yield with methanol, ethanol, and acetone as extracting solvents. The extraction yield decreased with increasing solid/liquid ratio with each individual solvent. The highest extraction yield was found as 10.55% with 4/250 g mL⁻¹ solid/liquid ratio in methanol extraction,

whereas the lowest one was found as 7.62% with 12/250 g mL⁻¹ in acetone extraction. These results, which are compatible with literature, may arise from the fact that high amount of solid causes mass transfer limitations in the extraction experiments [26, 27]. Mohammadpour et. al. conducted a study about extraction of *Moringa peregrina* with hexane [26]. Increasing solid to liquid ratio resulted in a decrease in the extraction yield due to the mass transfer limitation. Also, Jadhav et al. reported increasing vanilla beans amount caused an attenuation of vanillin concentration.

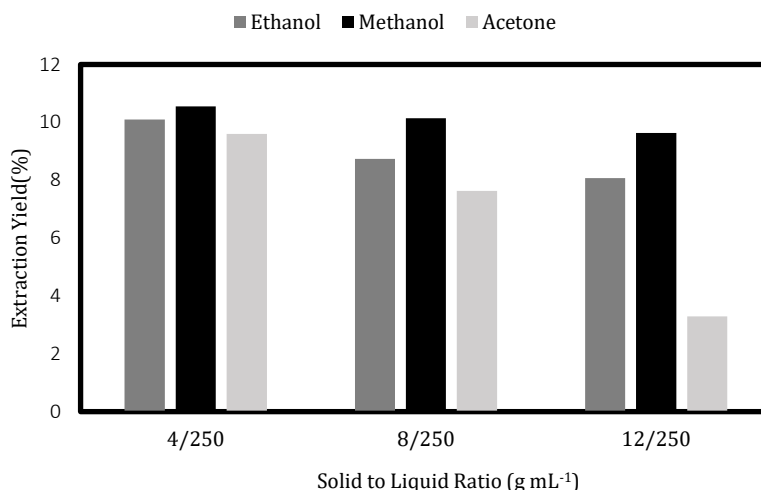


Fig 5. Effect of solid to liquid ratio on extraction yield with different solvents

Antioxidant capacity results with different solid to liquid ratios were given in the Fig 6 for different solvents. Antioxidant capacity first increased from 4/250 solid liquid ratio to 8/250, then decreased for 12/250 solid to liquid ratio when ethanol was used as solvent. On the other hand, there was gradual decrement in antioxidant capacity with acetone extraction, whereas slight increment in antioxidant

capacity was observed when ethanol was used as solvent. The highest antioxidant capacity was found as 0.0507 TE mg mL⁻¹ with 8/250 g mL⁻¹ solid to liquid ratio in methanol and the lowest one was 0.0497 TE mg mL⁻¹ with 4/250 g mL⁻¹ solid to liquid ratio. Since hexane extraction efficiency is very low, it has been removed from the system.

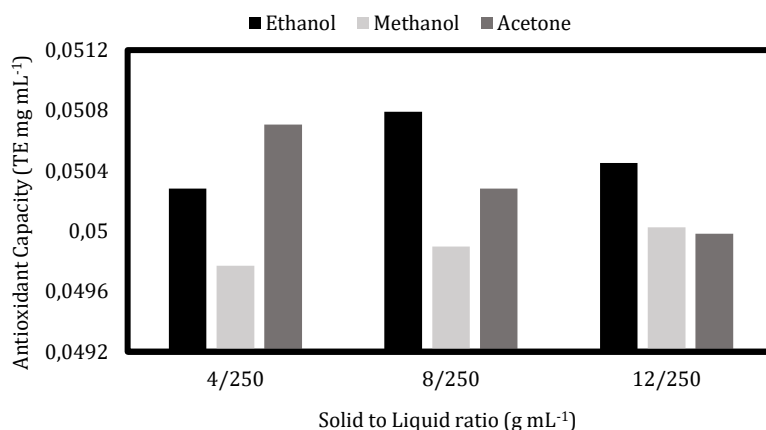


Fig 6. Effect of solid to liquid ratio on Antioxidant capacity

There were 21 major components identified by GC-MS analysis after extraction of hazelnut shell waste with various solvents. These major components were tabulated in Table 1. On this table, numbers under the given solvent type refers to the relative peak areas of components calculated from GC-MS analysis (see Eqn 2 in Materials and Methods).

Distribution of extraction components was related with the polarity [28], dielectric constant, donation of hydrogen [5, 9] to the extraction medium, and viscosity at boiling point. All solvents extracted oleic acid and palmitic acid from the hazelnut shell since they have both polar and nonpolar sites. Hexane is the most powerful solvent for extracting oleic acid with 75.52% extraction yield and methanol comes next with an extraction yield of 75.6% extraction yield.

Hydrophobic part dissolves in nonpolar hexane and hydrophilic -COOH part dissolves in polar methanol. Although both ethanol and methanol are polar protic solvents, which gives hydrogen to the medium, methanol dissolves -COOH part of the oleic acid more than ethanol due to the large dielectric constant of methanol. Product distribution of methanol and ethanol were similar except 1-pentadecene, 1-nonadecene. This may be caused from boiling point difference and degradation pathway of components.

Methyl propyl ketone is the only ketone extracted with all solvent types and acetone mainly extracts the methyl propyl and oleic acid from the hazelnut shell. Moreover, chloroform is the only solvent that extracts the Stigmasterol, 22,23-dihydro- also called as beta sitosterol. Similar results were found in literature about extraction of beta-sitosterol from plants [29]. Gamma sitosterol were detected in polar solvents such as ethanol, methanol, acetone. In literature, there is a reported extraction and isolation of gamma-sitosterol from Asteraceae by using methanol [30].

Hazelnut shell waste and products after the extraction process were investigated with FT-IR. Analysis results were shown in Fig. 7. Peaks at the 1229, 1609, 3337 cm⁻¹ represent aliphatic C=C stretching, C-C and O-H bonds, respectively. These bonds are typical lignin structure. In addition to that, peaks at 1028, 1371 and 2981 cm⁻¹ belong to cellulose and hemicellulose structures [5, 31]. 1028 cm⁻¹ represents C-O stretching of alcohols, while 1371 cm⁻¹ shows C-O stretching of carboxylic acids. Moreover, 2981 cm⁻¹ belongs to C-O stretching esters and aliphatic C-H stretching [32]. Hazelnut shell residues were also examined by using FT-IR to determine where extractives come from mostly and also how the levels of lignin, cellulose and hemicellulose decreases due to the type of solvent.

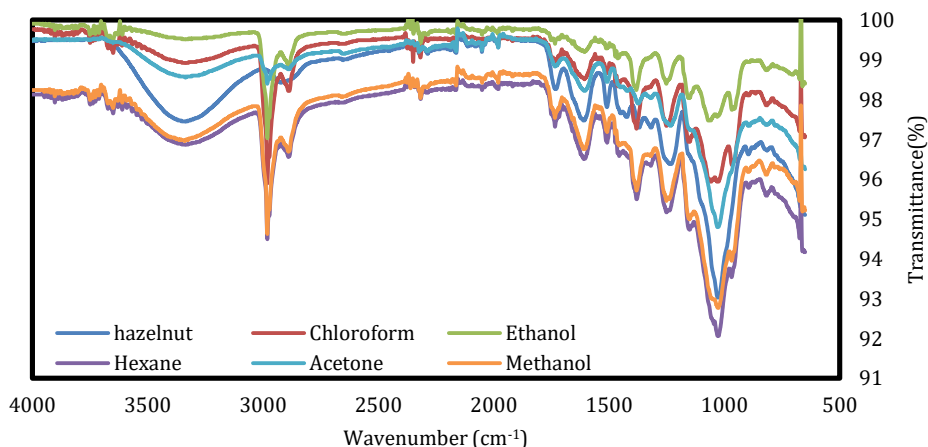


Fig 7. FT-IR spectra of hazelnut shell due to solvent type

Table 1. Major components for different solvents in extraction

Retention Time (min)	Identified Components	Relative Peak Areas of Components with Different Solvents				
		Hexane	Chloroform	Ethanol	Methanol	Acetone
4.26	methyl propyl ketone	-	-	-	-	35.43
10.7	1-Dodecene (alpha-olefin)	-	-	3.23	1.03	4.52
14.14	1-Pentadecene	-	-	4.08	-	-
14.16	1-Tetradecene	-	-	-	-	4.01
14.44	Vanillin	-	2.8	-	-	-
17.22	1-Hexadecene (palmitic acid)	-	-	2.71	0.98	-
17.24	9-Octadecene	-	-	-	-	2.76
19.99	1-Nonadecene	-	-	1.49	-	-
22.29	n-Hexadecanoic acid-palmitic acid	6.81	10.99	5.68	5.51	5.01
24.43	9-Octadecenoic acid, oleic acid	75.52	52.49	59.93	75.6	35.03
24.55	stearic acid	-	-	-	-	3.2
24.55	Ethyl Oleate	-	-	4.05	-	-
24.64	Octadecanoic acid-oleic acid	7.8	7.45	3.67	-	-
27.1	Hexanedioic acid, bis(2-ethylhexyl) ester	3.6	-	-	-	-
27.41	Oleic acid, 3-hydroxypropyl ester	5.12	-	-	-	-
27.79	9-Octadecenal	-	-	6.29	-	3.38
27.81	9-Octadecenal (Olealdehyde)	-	-	-	8.7	-
28.9	Sitosterol	-	-	8.87	8.54	5.01
28.97	Stigmasterol, 22,23-dihydro-	-	22.49	-	-	-
29.89	Heptacosane	-	3.78	-	-	-

In Fig 7, the highest lignin extraction of hazelnut shell was achieved by using hexane as a solvent, since all typical lignin peak intensities (1229, 1609, 3337 cm^{-1}) decreased with hexane extraction. On the other hand, ethanol was the most destructive agent for the O-H bonds of lignin as a consequence of disappearance of O-H peak (3334 cm^{-1}). However, other typical lignin bonds (1229 and 1609 cm^{-1}) did not disappear when ethanol was used as a solvent. Therefore, it may be said that ethanol had the lowest extraction potential in terms of lignin-based extractives. The intensity of C-O stretching esters and aliphatic C-H was mostly decreased in hexane rather than other solvents. In other words, hexane extracts more cellulose and hemicellulose-based extractives. It can be validated by

checking C-O stretching alcohols at 1028 cm^{-1} and carboxylic acid bonds at 1371 cm^{-1} . Lignin, cellulose and hemicellulose-based extractives were observed in the order of hexane > methanol > acetone > chloroform > ethanol [31, 32].

Extraction yield were statistically analyzed via Analysis of Variance (ANOVA) by considering interaction of solvent type (hexane, acetone, ethanol and methanol), extraction time (2-18 h) and solid to liquid ratio (4-8-12 g 250 mL^{-1}). Response surface methodology (RSM) was used to optimize process parameters in a way of maximizing extraction of phenolic compounds from waste hazelnut shell with a significance level as 95% ($p \leq 0.05$).

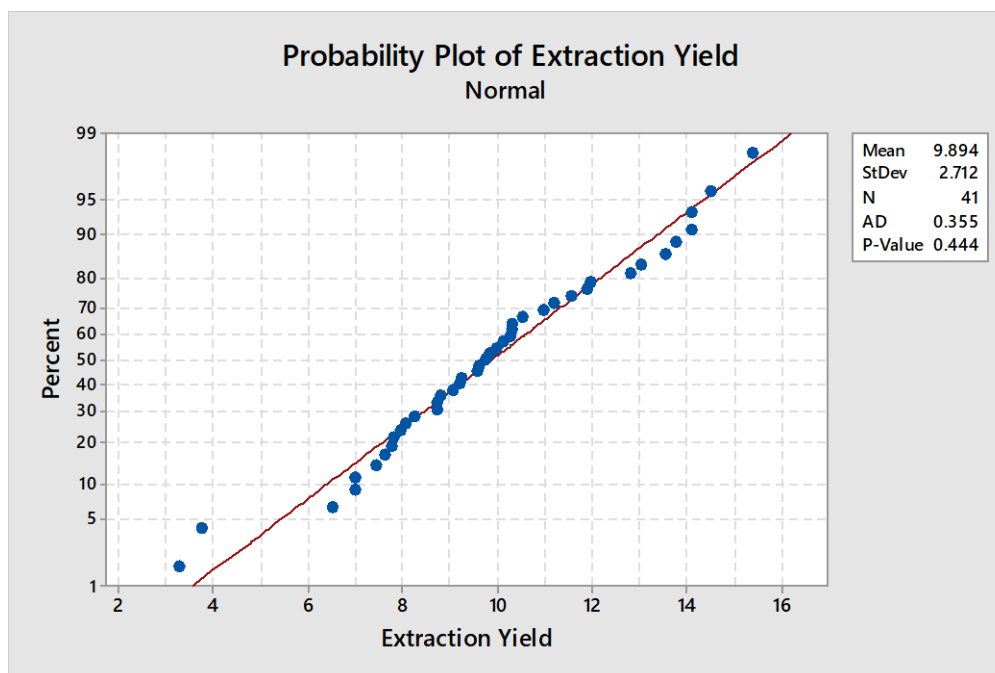


Fig 8. Normality plot of extraction yield

Normality plot of the extraction yield is shown in Fig 8 and it was checked by Anderson-darling test. As a result of ANOVA, extraction yield data was distributed normally.

Histograms and residual plots from RSM showed the linear distributed data (Fig. S1 and Fig. S2). The results were tabulated in Table S1 and Table S2. According to the results, extraction and solvent type were the only statistically significant terms since their p-values were smaller than 0.05. R^2 and adjusted R^2 values were 84% and 71%, respectively. Furthermore, solvent type was the only parameter that affected the total antioxidant capacity with a p-value of 0.013.

4. CONCLUSION

Hazelnut shell waste represent a rich and inexpensive source of natural and effective phenolic antioxidants. This study investigated the effects of different factors, such as extraction method, extraction time, solid-to-solvent ratio, solvent type, and particle size on the antioxidant capacity and recoveries of extract, and total phenolic compound from hazelnut shell waste. Response surface methodology was successful to develop an adequate model which describes total phenolic compounds and antioxidant capacity values of hazelnut shell extracts obtained by Soxhlet extraction, ultrasonic extraction and combination of them. Statistical analysis results showed that solvent type ($p < 0.05$) was demonstrated to be the most significant parameter, affecting the extraction yield and antioxidant capacity of extracts obtained from hazelnut shell waste. Compared with Soxhlet extraction, the extraction yields improved significantly with the application of both ultrasonic (14.12%) and combined extraction (15.40%) by using methanol as solvent. On the other hand, extraction time did not show significant effect on extraction yield, antioxidant capacity, and phenolic content. GC-

MS analysis results showed that major phenolic compounds obtained from hazelnut shell waste extraction were oleic acid and palmitic acid for all solvent types. In conclusion, these results indicated that selective extraction from natural sources, by an appropriate solvent, is important for obtaining fractions with high antioxidant activity and the development and utilization of hazelnut shell waste. Ultrasonic extraction and combination of it with Soxhlet extraction have been presented to be efficient methods for the extraction of phenolic compounds from hazelnut shell compared to the Soxhlet extraction.

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SUPPLEMENTARY DATA

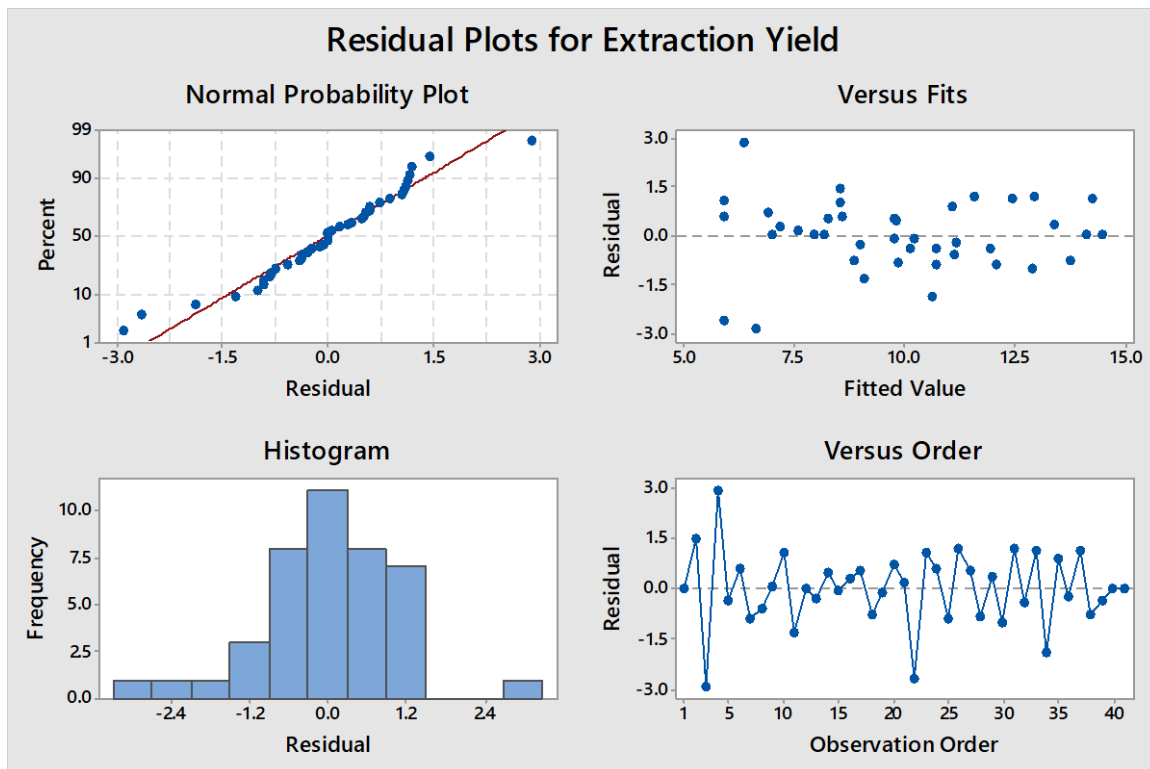


Fig S1. Residual plot for Extraction yield

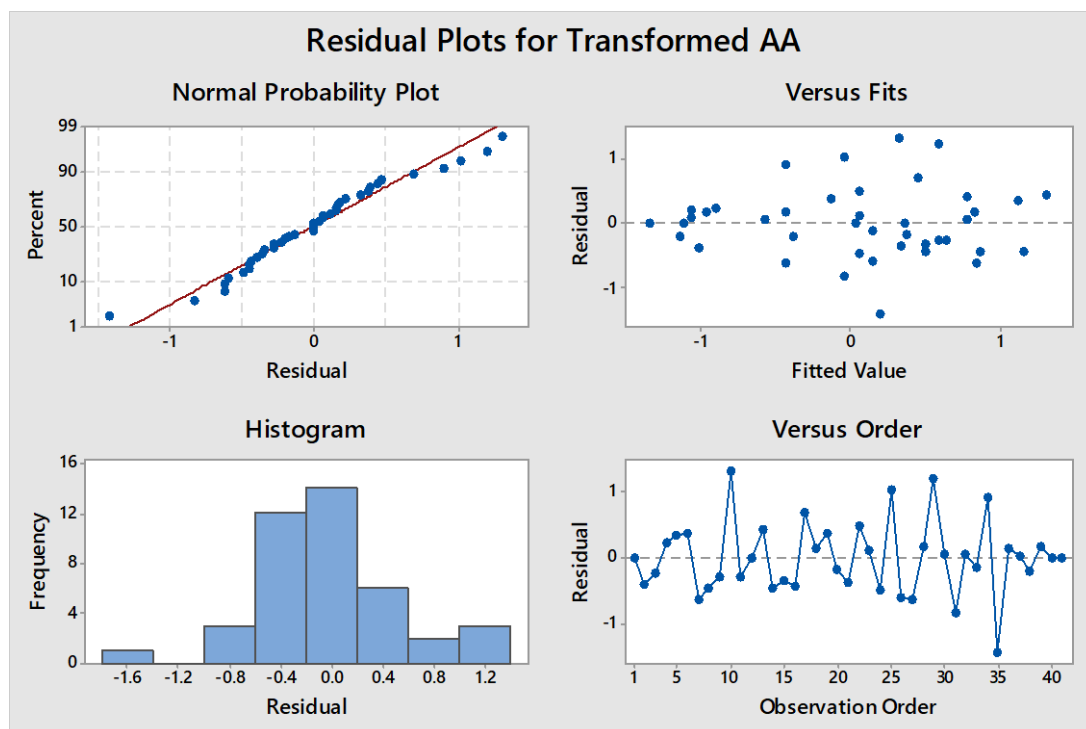


Fig. S2. Residual plot of Antioxidant Capacity after Johnson Transformation

Table S1. ANOVA Results of Extraction Yield

Analysis of Variance							
Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	18	246.839	83.93%	246.839	13.7133	6.38	0.000
Linear	12	240.21	81.68%	140.742	11.7285	5.46	0.000
Time	1	82.119	27.92%	4.231	4.2313	1.97	0.174
Solid to liquid ratio	1	7.336	2.49%	0	0	0	0.997
Extraction Type	2	73.631	25.04%	46.566	23.2829	10.84	0.001
Solvent	7	60.278	20.50%	46.798	6.6855	3.11	0.019
Square	2	2.991	1.02%	2.663	1.3317	0.62	0.547
Time*Time	1	1.93	0.66%	2.412	2.4124	1.12	0.301
Solid to liquid ratio*Solid to liquid ratio	1	1.061	0.36%	0.022	0.0217	0.01	0.921
2-Way Interaction	4	3.638	1.24%	3.638	0.9094	0.42	0.79
Time*Solid to liquid ratio	1	0.349	0.12%	0.009	0.0091	0	0.949
Solid to liquid ratio*Extraction Type	2	2.983	1.01%	2.983	1.4915	0.69	0.51
Error	22	47.256	16.07%	47.256	2.148		
Lack-of-Fit	20	39.096	13.29%	39.096	1.9548	0.48	0.85
Pure Error	2	8.16	2.77%	8.16	4.08		
Total	40	294.096	100.00%				

Table S2. ANOVA Results of Antioxidant Capacity

Analysis of Variance							
Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Model	18	20.5173	63.11%	20.5173	1.13985	2.09	0.051
Linear	12	18.4085	56.62%	18.5642	1.54702	2.84	0.016
Time	1	2.0565	6.33%	0.3593	0.35931	0.66	0.426
Solid to liquid ratio	1	0.6313	1.94%	0.1288	0.12877	0.24	0.632
Extraction Type	2	1.7182	5.28%	1.1199	0.55997	1.03	0.375
Solvent	7	13.8604	42.63%	13.0446	1.86352	3.42	0.013
Square	2	0.7721	2.37%	0.8266	0.41332	0.76	0.48
Time*Time	1	0.755	2.32%	0.7952	0.79521	1.46	0.24
Solid to liquid ratio*Solid to liquid ratio	1	0.0171	0.05%	0.0005	0.00053	0	0.975
2-Way Interaction	4	1.3367	4.11%	1.3367	0.33417	0.61	0.658
Time*Solid to liquid ratio	1	0.0369	0.11%	0.0425	0.04251	0.08	0.783
Solid to liquid ratio*Extraction Type	2	0.2624	0.81%	0.2624	0.13118	0.24	0.788
Error	22	11.9945	36.89%	11.9945	0.5452		
Lack-of-Fit	20	11.5179	35.43%	11.5179	0.57589	2.42	0.333
Pure Error	2	0.4766	1.47%	0.4766	0.23831		
Total	40	32.5118	100.00%				