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Investigation and Enhancement of the Antioxidant Compound Recovery of *Pyrus communis* Peel

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Abstract: *Pyrus communis* (*P. communis*) is the most cultivated and consumed species of pear within the European continent. This fruit has been a staple in Greece since ancient times, hence the name "Gift of the Gods". Given the extensive utilization of this fruit in the industrial sector and the focus on the exploitation of by-products to create new food and beverage products, the present research aimed to enhance the antioxidant activity of the *P. communis* peel through the implementation of a multifactor extraction system. Increased total polyphenols and ascorbic acid concentration, and enhanced antioxidant activity through radical scavenging and Fe^{3+} to Fe^{2+} reduction, all assist in boosting the health benefits of the extracts. The results indicated that the best conditions for compound yields were a 75% *v*/*v* hydroethanolic concentration, an extraction temperature of 80 °C, and 30 min of extraction time. Under the optimal conditions, the total polyphenol content was up to 4.98 mg of gallic acid equivalents (GAE)/g dried weight (dw). The radical scavenging activity by the 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) method was expressed as 18.36 µmol ascorbic acid equivalents (AAE)/g dw, while by the ferric-reducing antioxidant power (FRAP) method, it was 35.09 µmol AAE/g dw. Finally, the amount of ascorbic acid was measured at 20.16 mg/100 g dw. In this regard, this study has been conducted to assess and enhance the level of these bioactive compounds in the extract of the *P. communis* peel, leading to an extract with several applications in different food and beverage industries.

Keywords: pear peel; by-products; bioactive compounds; antioxidants; HPLC-DAD; Box–Behnken design

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1. Introduction

The pear is considered one of the main fruits cultivated in most parts of the world [1]. In fact, pears are the fifth most cultivated fruit in the world [2], where 71% of the world's total production comes from China, while other major producing regions are Europe and the USA [1]. The most prevalent pear species in Europe is *Pyrus communis* (*P. communis*), which belongs to the Rosaceae family [3]. The cultivation of this fruit in Greece alone has a history of thousands of years, with the Greek poet Homer describing pears as the "Gift of Gods" [4]. Being one of the most consumed fruits on a daily basis, the palatable flavor and affordable price, together with its phytochemical content, make *P. communis* pears very special [5]. In 2019, the global production of the *P. communis* pear exceeded 23 million tons [2], and 10% of the production is used to produce canned pears, pear juice concentrate, and fresh-cut pears [6]. Whereas, according to more contemporary data, global pear production for the year 2020 remained about 23 million tons [7], while in the year 2021–2022, it was expected to reach 1–23 million tons [8]. *P. communis* pears are typically consumed with the peels, although the peels are often discarded as a waste product [9], a practice that is also observed in the industrial sector. Industries use pears mainly as additives in processed products such as beverages, candies, canned fruits, syrups, jams, cakes, and ice creams [8].

In light of the unsustainable production of by-products by the industry, coupled with the shift in consumer preferences towards the consumption of plant-based food products and beverages rich in antioxidants [10,11], there has been a notable shift in the way in which industries manage and produce their products. In particular, food industries are attempting to address consumer demand for healthier products through the reuse of resources to create new food sources [12,13], while functional foods, defined as foods and beverages fortified with plant extracts that offer substantial health advantages [14,15], represent a significant area of interest within the food and beverage sector. In light of these considerations, it is crucial to comprehend the potential and bioactive compounds of the *P. communis* pear peel [16], a by-product, particularly within the beverage sector, given the widespread utilization of *P. communis* as an additive for distillate production [17,18].

The high consumption of pears and the diverse applications of both the fruit and peel in the food and beverage industry have prompted numerous studies on the bioactive compounds of *P. communis*. Hydroxycinnamic acids, such as chlorogenic acid—the most prevalent polyphenol—along with flavonoids like rutin, quercetin, and apigenin, as well as ascorbic acid, are among the identified bioactive compounds in pear peels [19–22]. Additionally, sugars (e.g., fructose, glucose, and sorbitol), organic acids like malic acid, and triterpenoids such as ursolic acid are the primary chemical constituents of pear peels [5]. A notable recent study by Wang et al. [20] examined five different pear varieties from Australia, using ethanol mixtures as the solvent. The highest recorded amount of polyphenols was 3.14 mg of gallic acid equivalents (GAE)/g. Besides polyphenols, antioxidant activity was evaluated using the DPPH and FRAP methods, with results showing 5.72 mg AAE/g dw and 4.37 mg AAE/g dw, respectively. Moreover, another study [23] evaluated the polyphenol content in the peel of ten different pear varieties, revealing a range from 106.78 mg/kg (0.11 mg/g) to 1446.59 mg/kg (1.45 mg/g).

Considering the above, and the widespread industrial use of ethanolic extracts prepared by simple, rapid, and cost-effective methods like stirring [24], the present study aimed to use a multifactor extraction system to produce antioxidant-rich extracts from an important agro-industrial waste, *P. communis* peels. Previous studies on the antioxidant properties of extracts from *P. communis* have been conducted, but this work systematically studied the extraction time, temperature, and hydroethanolic solvent composition variables as the main extraction parameters. Our aim was to determine the most efficient extraction parameters for maximizing the yield of essential antioxidant compounds such as total polyphenols, individual polyphenolic compounds, and ascorbic acid, as well as to measure antioxidant activity using two different protocols. The goal was to establish a refined extraction protocol that will provide a substantial basis for future research and industrial applications in the most sustainable manner.

2. Materials and Methods

2.1. Chemicals and Reagents

Anhydrous sodium carbonate, Folin–Ciocalteu reagent, DPPH$^{\bullet}$, gallic acid, 2,4,6-Tris(2-pyridyl)-*s*-triazine (TPTZ), and formic acid (98% *w*/*v*) were all purchased from Penta (Prague, Czech Republic). Ascorbic acid, methanol, iron (III) chloride, trichloroacetic acid, hydrochloric acid, acetonitrile, and all chemical standards for the chromatographic quantification of polyphenols were purchased from Sigma-Aldrich (Steinheim, Germany). Deionized water was employed for the conducted experiments from a deionizing column.

2.2. Instrumentation

Analysette 3 PRO (Fritsch GmbH, Oberstein, Germany) was used for the sieving process. A lyophilizer BK-FD10P from Biobase (Jinan, China) was used to freeze-dry the peels. The stirring process was conducted in a Heidolph stirring hotplate (Heidolph Instruments GmbH and Co. KG, Schwabach, Germany). The samples were thermostated in an Elmasonic P70H ultrasonic bath (Elma Schmidbauer GmbH, Singen, Germany) for the conducted assays and were analyzed using a Shimadzu UV-1900i UV/Vis spectrophotometer

(Kyoto, Japan). A centrifuge NEYA 16R (Remi Elektrotechnik Ltd., Palghar, India) was used to centrifuge the liquid samples and isolate the supernatant. Individual polyphenols were quantified using a Shimadzu CBM-20A liquid chromatograph and a Shimadzu SPD-M20A diode array detector, all provided by Shimadzu Europa GmbH in Duisburg, Germany. Via a high-performance liquid chromatography (HPLC) system, the compounds were separated using a Phenomenex Luna C18(2) column (Torrance, CA, USA) maintained at 40 °C (100 Å, 5 μm, and 4.6 mm × 250 mm).

2.3. Pear Collection and Handling

Pear fruits were bought from a local market in Karditsa, Central Greece. They were thoroughly cleaned with tap water to remove any dirty residue and rinsed with deionized water. Right after, they were peeled with a stainless-steel knife and lyophilized at –54 °C for 24 h. The dried pear peels were ground to a fine powder and sieved. The powder of 200–400 nm diameter was stored at –40 °C until further analysis.

2.4. Extraction Procedure

A multifactorial extraction procedure was employed for the optimized extraction of pear peels and is presented in Table 1, including the investigated parameters of the extraction (i.e., the concentration of ethanol in water (C_{EtOH}, % v/v), extraction temperature (T, °C), and extraction duration (t, min). Since polarity and temperature are known to substantially impact the recovery of bioactive chemicals in an extraction process, these parameters were investigated over a wide range (*vide infra*). Conventional stirring at 500 rounds per minute (rpm) in a stirring hotplate was employed. A 1:20 solid-to-liquid ratio was employed for all extractions, as it was found to be the most preferable after preliminary experiments. The mixture was inserted in a 50 mL Duran flask that was tightly closed in order to avoid undesirable evaporation processes. The samples were finally centrifuged at 3600× g for 10 min to separate the supernatant from the solid residue, while the supernatant was collected and stored at −40 °C until further analysis. The solid residue consisting of extracted pear-peel powder was discarded.

Table 1. The actual and coded levels of the independent variables were used to optimize the process.

Independent Variables	Coded Units	Coded Levels		
		−1	**0**	**1**
C (%, v/v)	X_1	0	50	100
T (°C)	X_2	20	50	80
t (min)	X_3	30	60	90

2.5. Optimized Extraction Investigation through the Response Surface Methodology (RSM) and Model Validation Process

Optimal extraction of bioactive compounds (i.e., total and individual polyphenolic compounds and ascorbic acid) and antioxidant capacity assessed through FRAP and DPPH assays were made possible by the RSM by investigating key extraction parameters like the solvent composition consisting of ethanol and water mixtures, temperature, and extraction time. The employed Box–Behnken methodology required 15 designs with 3 center points. Table 1 shows the three levels of process variables, including the coded and actual levels. The overall significance of the model (R^2, p-value) along with the significance of the model coefficients was determined, wherein the lack-of-fit, summary-of-fit, and analysis of variance (ANOVA) tests were employed. To further analyze the independent variables, we used a second-order polynomial model (Equation (1)) to predict the dependent variable:

$$Y_k = \beta_0 + \sum_{i=1}^{2} \beta_i X_i + \sum_{i=1}^{2} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j \quad (1)$$

where the independent variables are denoted by X_i and X_j, and the predicted response variable is defined by Y_k. In the model, the intercept and regression coefficients β_0, β_i, β_{ii}, and β_{ij} represent the linear, quadratic, and interaction terms, respectively.

Moreover, the model validation process entailed comparing the model's predictions with actual outcomes to assess its precision. This step was crucial to confirm the model's dependability for future forecasting. The data were segmented into three parts: training, validation, and test. The training data were used to learn the model parameters. The validation data helped to fine-tune these parameters and choose a well-performing model. The test data were employed to evaluate the final model's performance. In our study, we utilized *k*-fold cross-validation to ascertain the model's predictive prowess. The validation statistics are presented in Table S1.

2.6. Bioactive Compounds and Antioxidant Capacity Evaluation

All employed assays were described in detail in our previous studies [25–27]. To assess the total polyphenol content (TPC), we used the Folin–Ciocalteu assay. A calibration curve using methanol (10–100 mg/L of gallic acid, $R^2 = 0.9996$) was constructed with the results being calculated as mg GAE per g of dw. Similarly, the ascorbic acid content (AAC) was evaluated by a calibration curve using 10% TCA (50–500 mg/L of ascorbic acid, $R^2 = 0.9980$) and the results were expressed as mg of AA/100 g dw. Regarding the antioxidant assays, the chromophore DPPH$^\bullet$ probe inhibition and the ferric-reducing power assays were both employed. The DPPH$^\bullet$ inhibition calibration curve with methanol (100–1000 μM of ascorbic acid, $R^2 = 0.9926$) was calculated as μmol AAE/g dw. Finally, the ferric-reducing power (P_R) was evaluated with TPTZ as the probe with a calibration curve (50–500 μM of AAE in 0.05 M HCl, $R^2 = 0.9997$), with the results being calculated as μmol AAE/g dw.

2.7. Individual Polyphenol Determination

Quantitative analyses of individual polyphenols were conducted using the same equipment and methodology as previously discussed in detail [28]. The calibration curves employed for the quantification of individual polyphenols (i.e., chlorogenic acid, neochlorogenic acid, syringic acid, ferulic acid, kaempferol-3-glucoside, epicatechin, quercetin-3-*D*-galactoside, quercetin-3-*D*-glucoside, rutin, narirutin, and apigenin-7-*O*-glucoside) were of excellent linearity ($R^2 > 0.99$).

2.8. Statistical Analysis

Each extract was prepared in triplicate, and every extract underwent three analyses, yielding a total of nine (3×3) measurements. The data are reported as mean values with the standard deviation. A one-way ANOVA test was used to determine the statistical significance of differences in mean values; $p < 0.05$ was considered to be statistically significant. For the corresponding statistics, we used JMP® Pro 16 (SAS, Cary, NC, USA).

3. Results and Discussion

3.1. Bioactive Compound Concentration and Antioxidant Capacity of the Extracts

The RSM via the Box–Behnken design was employed with the scope of identifying the optimal extraction conditions, which were studied in relation to the three primary parameters: solvent composition, temperature, and extraction time. Water, undoubtedly one of the most commonly used solvents due to its inexpensive and environmentally friendly nature, provides exceptional efficiency for the recovery of polar molecules. Yet, some bioactive compounds may have a lower polarity than water and require an adjustment in the extraction solvent polarity. As such, organic solvents that are soluble in water and less polar than it, like alcohols, could also be employed to create binary mixtures with water at several proportions [29]. Considering the food-grade applicability of ethanol and water, these solvents could generate an exceptional binary mixture for bioactive compound recovery in the food sector [30].

To further optimize the extraction temperature and duration, and reduce energy consumption, further optimization of the extraction process was essential. Temperature usually has a major impact on bioactive compound extraction. High-temperature extraction is widely recognized to enhance extraction processes by increasing solute solubility and strengthening diffusion coefficients. However, this parameter needs to be thoroughly examined considering that some bioactive compounds may degrade due to thermolability [31]. Specifically, previous investigations [32,33] have indicated that 50–80 °C is an ideal temperature range for conventional extraction techniques to maximize bioactive compound recovery. It was previously documented that temperatures above 85 °C could be destructive for ascorbic acid [31]. Finally, regarding the extraction duration, another thoroughly demanding parameter investigation, it was previously documented that both short [34] and long [35] extraction durations were found to be efficient. Considering that these parameters can determine the severity [36] and efficiency [37] of the process, this was considered vital. The impact of these parameters was assessed by recovering bioactive compounds (specifically, polyphenols and ascorbic acid), while the antioxidant activity was also evaluated using two distinct assays.

The findings of these analyses are presented in Table 2. The results revealed that design point 7 was the most effective among the three assays (i.e., TPC, FRAP, and DPPH), whereas design points 4, 9, and 15 were found to be the least efficient combinations. However, in terms of the AAC, it exhibited a 23% reduction in efficacy compared to design point 10, which was identified as the optimal point for that particular assay. Based on our findings, it can be seen that the use of ethanol was beneficial in the recovery of bioactive compounds, and the effect was greater when the 1:1 ethanol–water binary mixture was used. On the other hand, the use of 100% ethanol was ideal for recovering ascorbic acid since design points 5, 6, and 10 had the highest yielded amount of ascorbic acid. Regarding the extraction duration, no significant difference was observed between the three time intervals. The antioxidant activity, as determined by various tests, can be strongly impacted by the solvent used to extract components from plants. Because of its polarity, ethanol is frequently used to extract a variety of compounds, including those with antioxidant properties. However, the antioxidant activity can vary depending on the solvent utilized since different solvents can dissolve different sets of molecules. This diversity should be taken into account when comparing studies or attempting to replicate findings.

Table 2. Experimental results for the three examined independent variables and the dependent responses of the four variables.

Design Point	Independent Variables			Responses			
	X_1 (*C*, %)	X_2 (*T*, °C)	X_3 (*t*, min)	TPC [1]	FRAP [2]	DPPH [3]	AAC [4]
1	0 (50)	0 (50)	0 (60)	5.03 ± 0.20	28.89 ± 1.53	14.16 ± 1.06	13.61 ± 0.50
2	0 (50)	0 (50)	0 (60)	5.01 ± 0.30	29.84 ± 1.94	14.84 ± 0.80	14.14 ± 0.38
3	0 (50)	−1 (20)	−1 (30)	5.18 ± 0.36	24.40 ± 0.66	15.80 ± 0.52	11.15 ± 0.55
4	−1 (0)	0 (50)	−1 (30)	3.19 ± 0.22	7.31 ± 0.28	2.07 ± 0.09	5.70 ± 0.12
5	1 (100)	−1 (20)	0 (60)	3.49 ± 0.08	19.55 ± 1.47	7.70 ± 0.23	19.06 ± 0.90
6	1 (100)	0 (50)	−1 (30)	3.65 ± 0.27	21.07 ± 1.37	8.00 ± 0.35	19.99 ± 1.02
7	0 (50)	1 (80)	−1 (30)	5.65 ± 0.27	33.31 ± 1.07	20.99 ± 0.78	17.23 ± 1.15
8	0 (50)	0 (50)	0 (60)	5.00 ± 0.30	30.67 ± 0.98	13.91 ± 0.79	13.73 ± 0.65
9	−1 (0)	0 (50)	1 (90)	1.63 ± 0.12	11.65 ± 0.63	3.86 ± 0.14	5.79 ± 0.28
10	1 (100)	1 (80)	0 (60)	2.29 ± 0.16	29.66 ± 0.83	11.22 ± 0.34	22.43 ± 0.85
11	0 (50)	−1 (20)	1 (90)	4.71 ± 0.34	30.42 ± 1.52	11.63 ± 0.45	11.55 ± 0.72
12	1 (100)	0 (50)	1 (90)	2.53 ± 0.14	23.68 ± 1.02	7.90 ± 0.47	18.30 ± 0.44
13	0 (50)	1 (80)	1 (90)	2.66 ± 0.10	15.89 ± 0.41	17.56 ± 1.11	16.88 ± 0.91
14	−1 (0)	−1 (20)	0 (60)	4.24 ± 0.31	18.18 ± 0.49	3.22 ± 0.14	6.94 ± 0.21
15	−1 (0)	1 (80)	0 (60)	2.10 ± 0.12	4.18 ± 0.23	9.17 ± 0.4	9.46 ± 0.56

[1] TPC in mg GAE/g dw; [2] FRAP in μmol AAE/g dw; [3] DPPH in μmol AAE/g dw; [4] AAC in mg/100 g dw.

The second-order polynomial equations (models) and their corresponding coefficients ($R^2 > 0.96$) acquired for each model are shown in Table 3 below, suggesting a good fit for the developed models. Also, all variables and their interactions are considered significant as the statistical analyses, such as ANOVA, yielded *p*-values lower than 0.05. This suggests that the variables and their interactions significantly impact the outcome. Plots of the expected and actual values for each parameter and their respective desirability functions are given in Figures S1–S4. Figure 1 shows the three-dimensional response plot for TPC, while Figures S5–S7 display the three-dimensional response plots for the remaining responses. In these plots, the effect that each variable X_1–X_3 has on each assay is shown. It can be seen that, at the points where the graph is illustrated with a red color, the maximum value of the variable is reached. For example, 50% ethanol and a low temperature achieved optimal TPC results (~5 mg GAE/g dw), as seen in Figure 1A.

Table 3. Optimization of pear-peel extraction was achieved through mathematical models developed using the RSM.

Responses	Second-Order Polynomial Equations (Models)	R^2Predicted	R^2Adjusted	*p*-Value	Eq.
TPC	$Y = 2.35 + 0.07X_1 + 0.02X_2 + 0.06X_3 - 0.0008{X_1}^2 - 0.0001{X_2}^2 - 0.0004{X_3}^2 + 0.0002X_1X_2 + 0.0001X_1X_3 - 0.0007X_2X_3$	0.9615	0.8922	0.0049	(2)
FRAP	$Y = -9.09 + 0.39X_1 + 0.25X_2 + 0.71X_3 - 0.004{X_1}^2 - 0.001{X_2}^2 - 0.003{X_3}^2 + 0.004X_1X_2 - 0.0003X_1X_3 - 0.007X_2X_3$	0.9616	0.8923	0.0049	(3)
DPPH	$Y = 5.31 + 0.43X_1 - 0.16X_2 - 0.007X_3 - 0.004{X_1}^2 + 0.003{X_2}^2 - 0.0001{X_3}^2 - 0.0004X_1X_2 - 0.0003X_1X_3 + 0.0002X_2X_3$	0.9691	0.9135	0.0029	(4)
AAC	$Y = 2.44 + 0.16X_1 - 0.06X_2 + 0.13X_3 - 0.0002{X_1}^2 + 0.001{X_2}^2 - 0.0009{X_3}^2 + 0.0001X_1X_2 - 0.0003X_1X_3 - 0.0002X_2X_3$	0.9880	0.9665	0.0003	(5)

3.2. Impact of Extraction Parameter Combinations through Pareto Plot Analysis

The extraction parameters and their combined impact on the optimization of bioactive compound extraction from pear peels were investigated through Pareto plots (Figure 2). The positive and negative impact of the extraction parameters are illustrated with blue and red bars, respectively. A gold line indicates the statistical significance level, which was set at $p < 0.05$. It was revealed that an increasing composition of ethanol had a major negative impact on the extraction of polyphenols, as illustrated in Figure 2A. The same trend was also observed in both antioxidant capacity assays since these variables are positively correlated, as seen in Figure 2B,C and also supported below. However, the opposite trend was observed in Figure 2D regarding ascorbic acid recovery, as the higher the ethanol content, the higher the ascorbic acid yield. It is known that ascorbic acid is more soluble in water than alcohol due to the reduction in attraction forces that the latter solvents provide. However, this intriguing finding could be a matter of temperature. In fact, this parameter is particularly noticeable in hydroalcoholic binary mixtures, where the solubility of ascorbic acid increases as the temperature rises, as stated by Galvão et al. [38]. Increasing temperature also increases solubility and decreases dielectric constant, a parameter that is increased with the high water content in binary hydroalcoholic solvents. However, exceeding temperatures could lead to polyphenol degradation and as such, this parameter was revealed to have a negative impact on polyphenol recovery. Finally, the extraction duration was not regarded as an impactful parameter, as a prolonged duration only negatively affected polyphenol recovery.

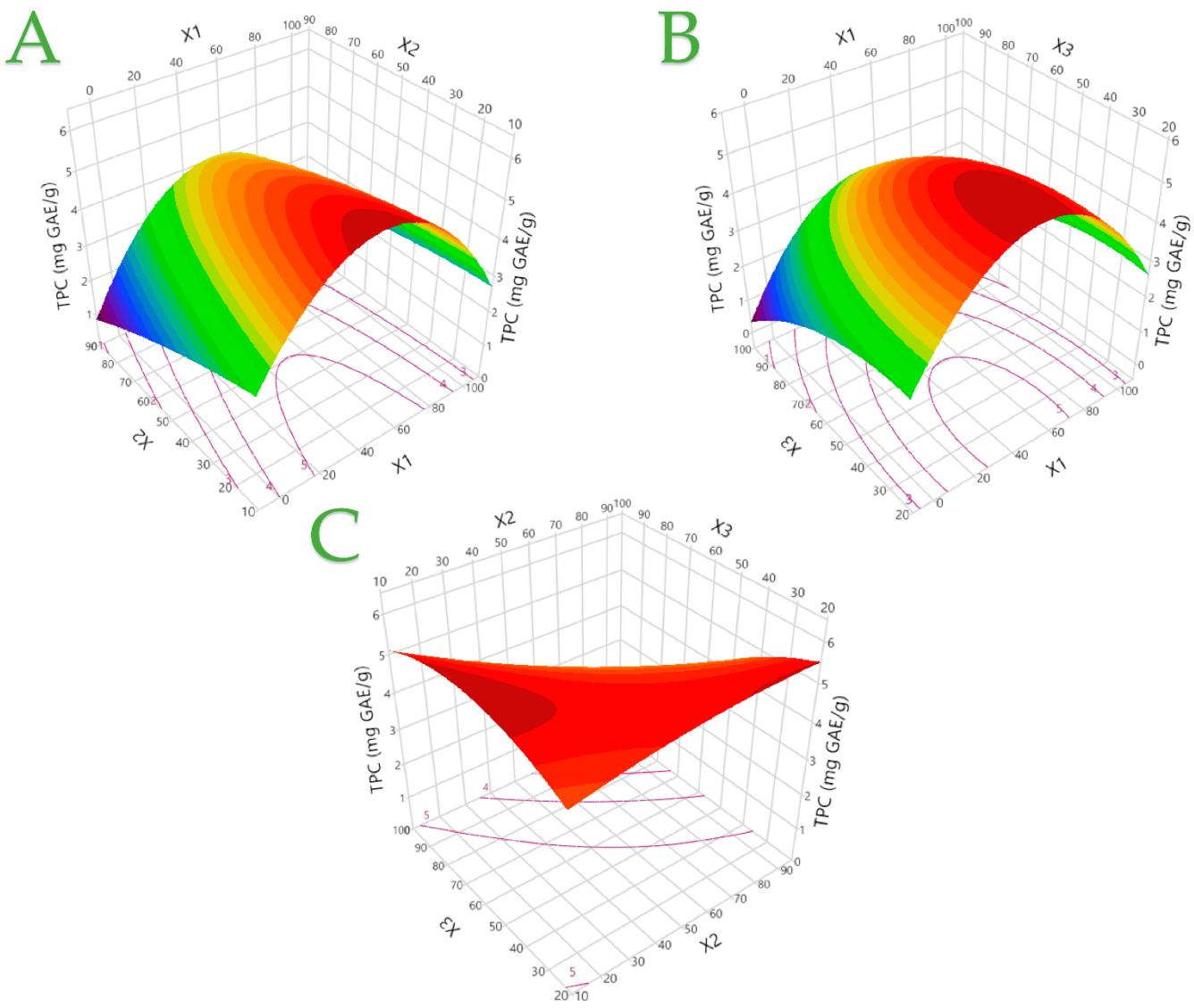

Figure 1. Graphs depicting the effects of the process variables considered in the response (TPC, mg GAE/g dw) show the ideal extraction of pear-peel extracts in three dimensions. Plot (**A**), covariation in X_1 (ethanol concentration; *C*, % *v*/*v*) and X_2 (extraction temperature; *T*, °C); plot (**B**), covariation in X_1 and X_3 (extraction duration; *t*, min); plot (**C**), covariation in X_2 and X_3.

3.3. Optimal Extraction Conditions

Pears are consumed as a fruit due to their high nutritional content and are often eaten along with their skin. Pears have has been reported to have antimicrobial activity since they modify the gut microbiota structure and have a major influence on endometrial cancer [39]. The results of the optimum extraction conditions for each parameter are shown in Table 4. As previously discussed, TPC was the only variable that required low-temperature extraction and benefited more with a 50% *v*/*v* ethanol-to-water concentration (48% *v*/*v* to be more precise), yielding 5.55 mg GAE/g dw. The antioxidant assays FRAP and DPPH demanded the highest possible temperature (i.e., 80 °C) and different solvent compositions reaching 34.90 and 19.73 µmol AAE/g dw, respectively. It should be noted that the AAC necessitated the 100% ethanol concentration, maximizing the AAC (23.45 mg/100 g dw), in full agreement with statistical prediction tools. No assay demanded the highest possible duration (90 min).

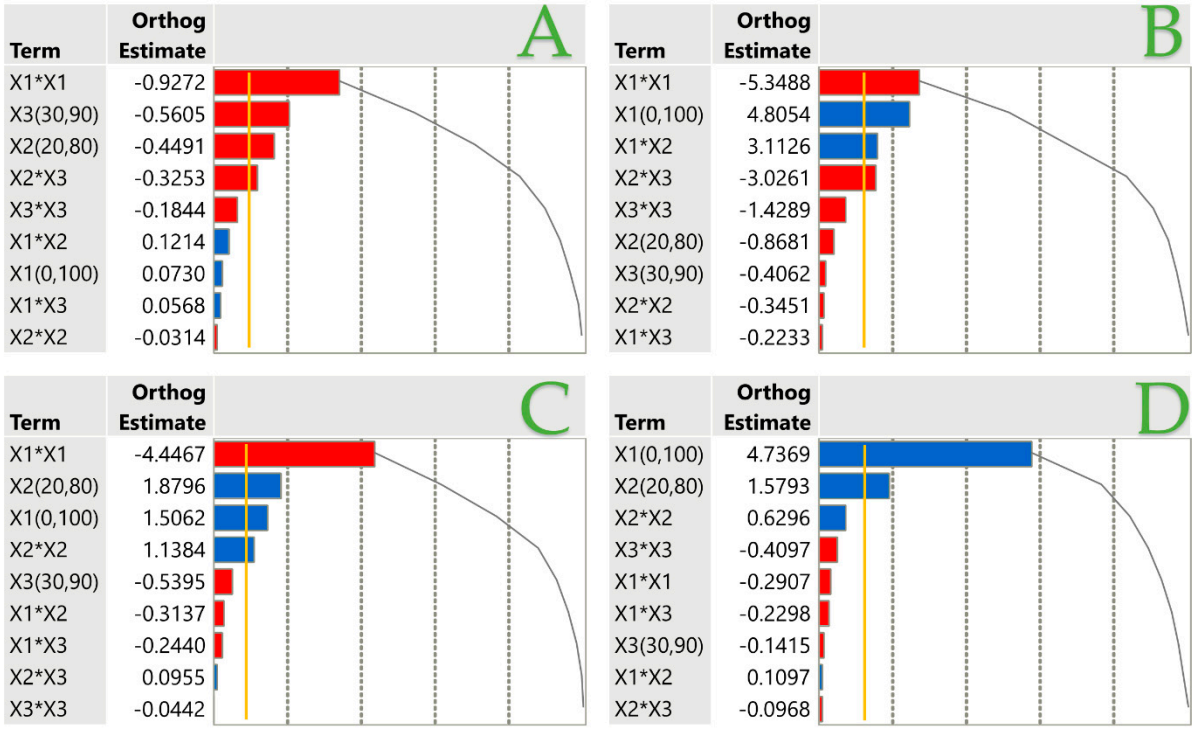

Figure 2. Pareto plots for TPC (**A**), FRAP (**B**), DPPH (**C**), and AAC (**D**) assays through transformed estimates. The significance level ($p < 0.05$) is indicated by a gold reference line. The positive and negative impact of the extraction parameters are illustrated with blue and red bars, respectively.

Table 4. Maximum predicted responses with their actual optimum extraction conditions for the four dependent variables.

Responses	Optimal Conditions			
	Maximum Predicted Response	*C* (%, *v*/*v*)	*T* (°C)	*t* (min)
TPC (mg GAE/g dw)	5.55 ± 0.70	48	20	57
FRAP (μmol AAE/g dw)	34.90 ± 6.50	77	80	34
DPPH (μmol AAE/g dw)	19.73 ± 3.61	55	80	30
AAC (mg/100 g dw)	23.45 ± 2.17	100	80	55

The TPC of pear peels may vary among different cultivars and geographical regions. A comprehensive table comparing the results of the total polyphenols recovered in previous studies along with our study is given below (Table 5). For instance, Li et al. [16] investigated the antioxidant capacity of ten pear varieties from China, Korea, and South Africa. The authors used 60% v/v methanol to water as a solvent and yielded approximately 3–11 mg GAE/g dw. In a previously mentioned study by Wang et al. [20], five different pear varieties from Australia were examined for their polyphenolic content in their pulp. The authors chose 70% v/v ethanol to water as their optimum solvent and quantified 1.89–3.14 mg GAE/g. Regarding antioxidant activity, the authors stated that both DPPH (3.25–5.72 mg AAE/g dw) and FRAP (2.15–4.37 mg AAE/g dw) had almost a two-fold range. These values are equal to 18.45–32.48 μmol AAE/g dw and 12.21–24.81 μmol AAE/g dw, values that are close to our findings. Finally, in a study by Azzini et al. [21], five ancient *S. Giovanni* varieties were investigated for their bioactive compound content. The authors employed 50% v/v methanol to water as a solvent and let the mixture stir under a low pH level for 1 h. They found that polyphenols ranged from 1.47 to 3.51 mg GAE/g fresh weight (fw), whereas ascorbic acid ranged from 17.74 to 46.84 mg/100 g fw. Ascorbic acid has several uses in the medical field as a health-promoting compound [40].

Table 5. A comparative table with the results of total yielded polyphenols.

Total Polyphenols Yielded (mg GAE/g dw)	Reference
2.81–11.21	[16]
1.89–3.14	[20]
1.47–3.51 [1]	[21]
0.11–1.45	[23]
5.49	This study

[1] These values refer to mg GAE/g fw.

3.4. Correlation Analysis

A correlation analysis was used to further clarify the association between the considered extraction variables. Hence, a principal component analysis (PCA) and multivariate correlation analysis (MCA) were applied, as illustrated in Figure 3 and Table 6, respectively. The variables were analyzed in two principal components, PC1 and PC2, which explained 62.7% and 24.7% of the variance. Particularly, the TPC, FRAP, DPPH, and AAC variables were all positively correlated with PC1, whereas the TPC and FRAP variables were negatively correlated with PC2. As explained earlier in the Pareto plot, the increased concentration of ethanol in the binary mixture with water was beneficial for the extraction of ascorbic acid. This finding was also confirmed in the PCA plot since the two variables (i.e., X_1, and AAC) were positively correlated and placed in close proximity to one another. Another observation was that TPC, FRAP, and DPPH all showed similar responses to the extraction conditions, as shown by their corresponding discrimination in the PCA plot. The MCA table revealed a quantitative correlation between the variables under examination. The high antioxidant activity of recovered polyphenols is proven since a positive correlation (>0.5) between TPC and the antioxidant assays (i.e., FRAP and DPPH) was observed, as per Table 5. However, a lower correlation coefficient was observed between the AAC and antioxidant assays. Polyphenols have a high free-radical-scavenging capacity providing impactful health-promoting compounds for consumption [41]. Finally, a low correlation was observed between the AAC and TPC, since these compounds required different solvents in order to be successfully recovered.

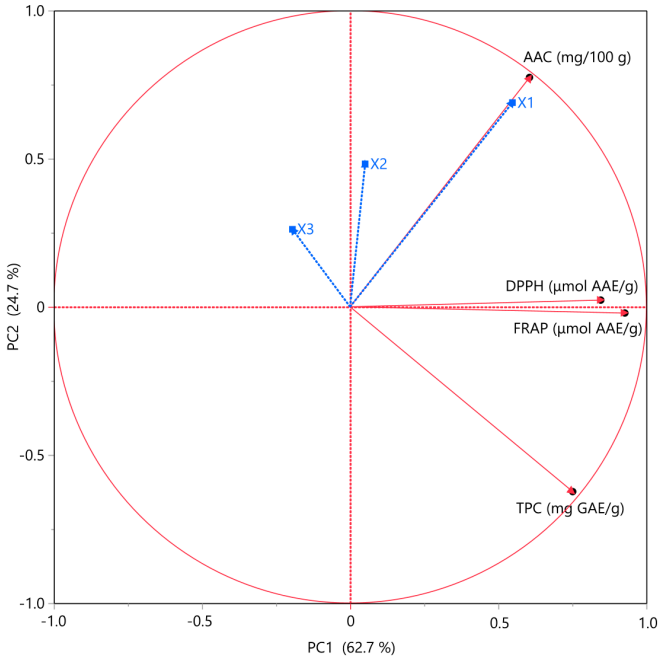

Figure 3. PCA plot for the four measured dependent variables. The blue color indicates each *X* variable.

Table 6. MCA values of four measured dependent variables.

Responses	TPC	FRAP	DPPH	AAC
TPC	–	0.7090	0.5520	0.0116
FRAP		–	0.6255	0.5531
DPPH			–	0.4613
AAC				–

3.5. Optimum Extraction Conditions through the Partial Least Squares (PLS) Analysis

A PLS model was created in Figure 4 and the load correlation plot is shown in order to assess the impact of the three extraction condition parameters (X_1, X_2, and X_3). The effects of different extraction parameters on pear-peel extracts are shown in this graph. The obtained findings were in agreement with the discussed results in Section 3.1. To start with, the increasing concentration of ethanol in the binary mixture of ethanol and water was found to have a vast impact. The plot revealed that a plateau at a precise concentration of ethanol (75% v/v) was reached. This concentration was deemed to be the most preferable to adjust the solvent polarity. A similar trend was observed in the temperature variable (X_2), as increasing values were found to be preferable for the optimization of the extraction process. Antioxidant compound recovery is higher under elevated temperatures since their solubility increases and the mass transfer rate to solvent is enhanced. Finally, concerning the extraction duration variable, it was revealed that a low extraction duration process was more beneficial for higher extraction yields. A desirability level of 0.83 also supports the reliability of the method. The impact of the extraction variables is also illustrated in Figure 4B, where it was found that hydroethanolic content contribution was of the highest significance, reaching 1.70, surpassing the threshold of 0.8 of the variable importance plot (VIP). The extraction temperature also had a vast impact on extraction enhancement as it reached a level of 0.91.

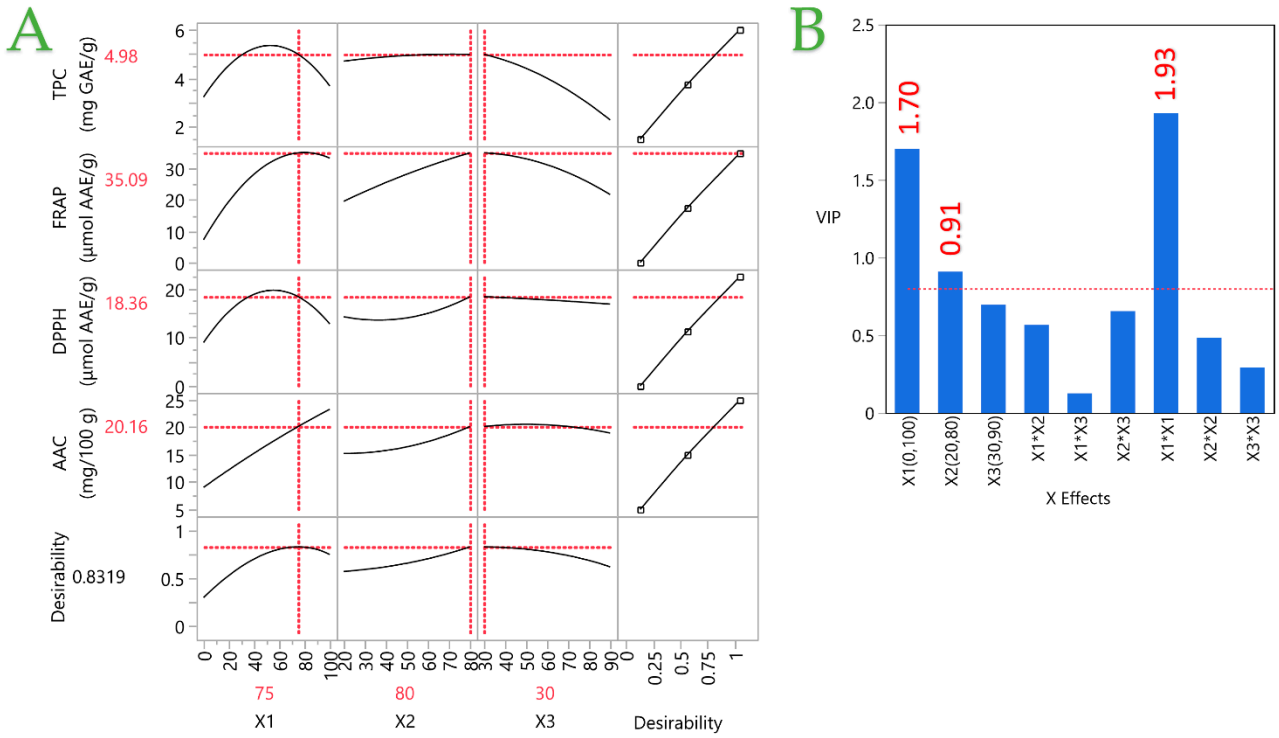

Figure 4. Plot (**A**) shows the optimization of pear-peel extracts using a PLS prediction profiler and a desirability function with extrapolation control; plot (**B**) shows the VIP option graph with the corresponding values for each predictor variable. At the 0.8 level of significance, plot (**B**) shows a red dashed line for each variable.

Excellent agreement between the experimental results and the predictions by the PLS model is shown by the high correlation coefficient of 0.9981 and the high determination coefficient (R^2) of 0.9961. The low *p*-value (<0.0001) indicates the lack of a significant variance between the expected and actual values. The experimental conditions X_1:75, X_2:80, and X_3:30 support this consistency by aligning with the data shown in Table 7, which confirms the validity of the model.

Table 7. Under optimum extraction conditions, the PLS prediction profiler maximizes the desirability of all variables (X_1:75, X_2:80, and X_3:30).

Variables	PLS Model Values	Experimental Values
TPC (mg GAE/g dw)	4.98	5.49 ± 0.37
FRAP (µmol AAE/g dw)	35.09	37.11 ± 1.26
DPPH (µmol AAE/g dw)	18.36	18.84 ± 0.38
AAC (mg/100 g dw)	20.16	21.05 ± 0.74

Finally, Table 8 lists all of the quantified polyphenolic compounds found in the pear-peel hydroethanolic extracts under optimum conditions with their corresponding % quantity, graphically illustrated by an exemplary chromatograph in Figure 5. The chromatograph showed an adequate resolution and peak area to satisfactorily identify and quantify the polyphenolic compound peaks. With 40.1% of the total identified polyphenolic compounds being chlorogenic acid, it is the most abundant polyphenolic substance. This finding is also supported by previous studies that quantified the specific compound as one of the primary polyphenols found in pears [20–22,42]. Specifically, our results were comparable to those of Liaudanskas et al. [42], who quantified 0.53 mg/g dw, and Azzini et al. [21], who recovered 0.43 mg/g fw of chlorogenic acid. The anti-diabetic and anti-obesity effects of chlorogenic acid have been associated with improvements in glucose metabolism [43]. Quercetin was also quantified in a total sum of ~21%. Since quercetin has potent antioxidant, cardiovascular, and neuroprotective properties, its presence greatly enhances the health advantages of pear-peel extract [44].

Table 8. Quantified individual polyphenols under optimum extraction conditions (X_1:75, X_2:80, and X_3:30). Percentage (%) quantity of total identified polyphenols in pear peels is also displayed.

Polyphenolic Compound	Optimal Extract (mg/g dw)	Quantity (%)
Neochlorogenic acid	0.11 ± 0.01	2.1
Chlorogenic acid	2.04 ± 0.07	40.1
Syringic acid	0.19 ± 0.01	3.6
Epicatechin	0.08 ± 0.01	1.5
Ferulic acid	0.32 ± 0.02	6.2
Rutin	0.32 ± 0.02	6.3
Quercetin-3-*D*-galactoside	0.42 ± 0.02	8.2
Quercetin 3-β-*D*-glucoside	0.64 ± 0.02	12.6
Narirutin	0.56 ± 0.02	11.0
Kaempferol-3-glucoside	0.19 ± 0.01	3.8
Apigenin-7-*O*-glucoside	0.23 ± 0.01	4.6
Total Identified	5.09 ± 0.21	

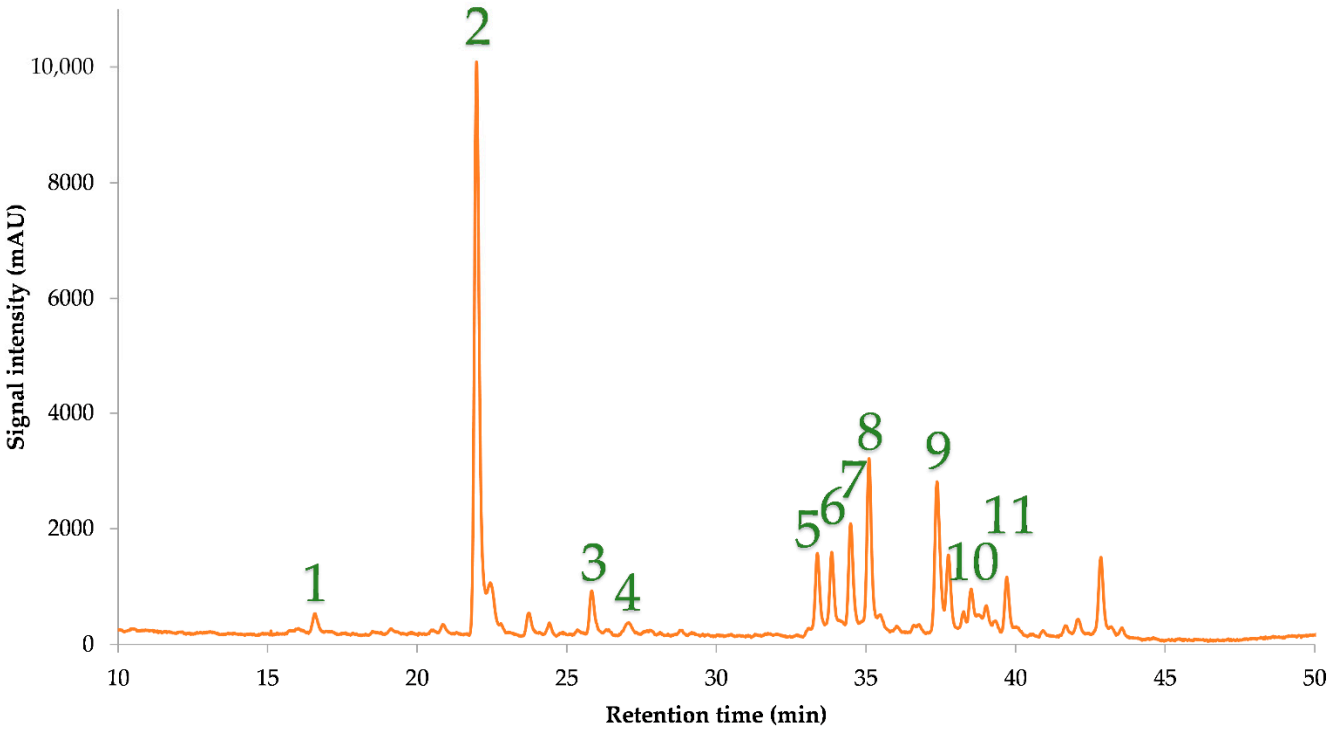

Figure 5. Exemplary HPLC chromatogram at 320 nm of pear-peel optimal extract, demonstrating polyphenolic compounds that were identified. 1: Neochlorogenic acid; 2: chlorogenic acid; 3: syringic acid; 4: epicatechin; 5: ferulic acid; 6: rutin; 7: quercetin-3-*D*-galactoside; 8: quercetin 3-β-*D*-glucoside; 9: narirutin; 10: kaempferol-3-glucoside; 11: apigenin-7-*O*-glucoside.

4. Conclusions

The food industry and consumers alike have demonstrated a growing interest in waste reduction. There is a clear preference among consumers for food and beverages that are prepared with minimal waste. This research presents the creation of a potent extract from the by-product of one of the most cultivated and consumed pear varieties on the European continent, *P. communis*, using the most suitable conditions of conventional extraction. Extraction parameters like duration, temperature, and the proportion of ethanol to water were adjusted to produce high-added-value extracts. High ascorbic acid and chlorogenic acid contents along with substantial levels of antioxidant activity in pear-peel waste were achieved through statistical models, presenting a methodology capable of being employed in several food waste matrices. Given the extensive use of *P. communis* in the food and beverage industry, this research has sought to enhance the antioxidant capacity of pear peels through detailed experimental and statistical analysis. The objective was to facilitate further investigation and utilization of the peel in the development of novel foods and beverages, or for the enhancement of existing products, with a focus on sustainable production practices. The further use of extracted pear peel could present a fascinating and innovative area of research. This residual solid matter has the potential for diverse applications. It may serve as a substrate in solid-state fermentation to produce bioactive compounds with antioxidant and antimicrobial properties. Moreover, it could be used in animal feed, composting, and biofuel production. The residual matter contains fibers, proteins, and other bioactive compounds, including hydrolyzable and condensed tannins, which were not previously extracted.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/waste2030021/s1, Table S1 presents the model validation statistics using the *k*-fold cross-validation technique. Figures S1–S4 comprise the plots for the TPC, FRAP, DPPH, and AAC that illustrate the comparison between the actual response and the predicted

response for each parameter under examination, accompanied by the desirability functions. Figures S5–S7 present the 3D response plots for the remaining responses (FRAP, DPPH, and AAC).

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