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# Development of a Low-Temperature and High-Performance Green Extraction Process for the Recovery of Polyphenolic Phytochemicals from Waste Potato Peels Using Hydroxypropyl $\beta$ -Cyclodextrin

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**Abstract:** Potato peels (PP) are a major agri-food side-stream originating from potato processing, but to date, their green valorization as a bioresource of antioxidant polyphenols is limited to extraction processes involving mainly water/ethanol-based solvents, whereas other eco-friendly methodologies are scarce. This study aimed at developing a simple, straight-forward and green extraction methodology to effectively recover PP polyphenols, using hydroxypropyl  $\beta$ -cyclodextrin (HP- $\beta$ -CD). After an initial assay to identify the optimal HP- $\beta$ -CD concentration that would provide increased extraction yield, optimization based on response surface methodology enabled maximization of the extraction performance, providing a total polyphenol yield of  $17.27 \pm 0.93$  mg chlorogenic acid equivalent  $\text{g}^{-1}$  dry mass, at  $30^\circ\text{C}$ . Testing of temperatures higher than  $30^\circ\text{C}$  and up to  $80^\circ\text{C}$  did not favor higher yields. The extracts obtained with HP- $\beta$ -CD were slightly richer in polyphenols than extracts prepared with conventional solvents, such as aqueous ethanol and methanol, displaying similar antioxidant characteristics. The major polyphenols that could be identified in the extracts were neochlorogenic, chlorogenic, caffeic and ferulic acids. The outcome of this study demonstrated that HP- $\beta$ -CD may be used as a highly effective green means of recovering PP polyphenols, at near-ambient temperature.

**Keywords:** antioxidants; extraction; hydroxypropyl  $\beta$ -cyclodextrin; polyphenols; potato peels

## 1. Introduction

Industrial activity within the agri-food sector is a major source of side-streams and wastes, which pose serious and imminent environmental risks. However, the dire necessity for proper waste management and handling does not stem merely from avoiding environmental aggravation, but also from the recognition that waste agri-food biomass is a primal bioresource of raw materials destined for the production of value-added substances [1]. Various plant tissues regularly rejected during processing of agricultural products to foods, such as stems, peels, seeds, leaves etc., constitute highly important, abundant and low-cost pools of precious phytochemicals, whose use may have wide applicability in food, pharmaceutical and cosmetic formulations [2–4].

Potato (*Solanum tuberosum*) is an indispensable element in the nutritional habits of numerous countries around the globe, and there have been estimations that world production of potato amounted 368 million tons in 2013. This makes potatoes the fourth largest food crop, after rice, wheat, and maize [5]. There is an enormous amount of by-products generated through potato tuber processing, since potatoes are regularly used to produce a spectrum of popular food commodities, such as chips, canned potatoes,

mashed potatoes, fries etc. Potato processing residues are composed almost exclusively of peels, which are regarded as a source of polyphenolic substances with significant nutritional value [6,7].

The effective recovery of bioactive polyphenols from various waste plant materials has traditionally been based on the use of common volatile solvents of appropriate polarity, such as methanol, ethanol and acetone. However, such approaches are now considered as options lower in the hierarchy of biorefinery strategies, as the principles of Green Chemistry explicitly dictate the use of alternative green solvents, possessing negligible vapor pressure, recyclability and no toxicity [8]. In this framework, the seeking and testing of novel extraction media is of undisputed significance. Cyclodextrins (CDs) are cycling supramolecular structures, containing at least 6 D-(+)-glucopyranoside units, attached to each other with  $\alpha$ -1,4-glycosidic linkages [9]. The main feature characterizing CDs is their relatively hydrophobic cavity, as opposed to their external surface, which is hydrophilic. This unique structural attribute permits CDs to form inclusion complexes with compounds possessing a variety of structures, which are stabilized through non-covalent forces, such as hydrophobic interactions, van der Waals forces and hydrogen bonds [10].

Cyclodextrins have been extensively used in recent years as means of assisting extraction of polyphenolic compounds, and several studies have appraised factors critical to an extraction process, such as the CD type, CD concentration, time, extraction technique and temperature [11]. The advantages ascribed to the use of CDs for extracting polyphenols pertain mainly to the improvement of extraction efficiency and extraction time shortening, display of improved antioxidant activity by the extracts produced, and better extract stabilization and solute bioavailability. In this frame, the current study was performed to examine polyphenol extraction from PP with the aid of HP- $\beta$ -CD, and identify key process variables, whose optimization could contribute to attaining maximized extraction yield.

## 2. Materials and Methods

### 2.1. Chemicals and Reagents

Neochlorogenic acid ( $\geq 98\%$ ) was from Merck (Darmstadt, Germany). Chlorogenic acid (95%) was from Fluorochem (Hadfield, UK). Ferulic acid, caffeic acid, Folin–Ciocalteu reagent, 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ), hydroxypropyl  $\beta$ -cyclodextrin and 2,2-diphenylpicrylhydrazyl (DPPH) were from Sigma-Aldrich (Darmstadt, Germany). Sodium hydroxide and iron chloride hexahydrate was from Merck (Darmstadt, Germany). Sodium carbonate anhydrous (99%), aluminum chloride anhydrous (98%) and ethanol (99.8%) were from Penta (Praha, Czechia). All solvents used for chromatography were HPLC grade.

### 2.2. Plant Material

Waste potato peels (PP) with a moisture level of 82%, derived from processing of brown-skin potatoes (*Solanum tuberosum* L. var Spunta), were collected from a catering facility (Karditsa, Greece) and transferred to the laboratory within 15 min after peeling. PP were then immediately placed on discs to form layers of approximate thickness of 0.5 cm, and dried in a laboratory oven (Binder BD56, Bohemia, NY, USA) for 480 min at 75 °C, to give a moisture content of approximately 4%. The dried PP were pulverized in a ball mill and sieved to provide a powder with a mean particle diameter of 0.435 mm. This feed was used for all extractions.

### 2.3. Batch Stirred-Tank Solid–Liquid Extraction Process

To test the effect of hydroxypropyl  $\beta$ -cyclodextrin (HP- $\beta$ -CD) concentration ( $C_{CD}$ ) prior to optimization, accurately weighted PP amount of 0.667 g was transferred into a 50 mL round-bottom flask and mixed with 20 mL deionized water containing varying concentrations of HP- $\beta$ -CD (0–8 mM). Extractions were performed at room temperature ( $29 \pm 2$  °C) on a magnetic stirrer (Witeg, Wertheim, Germany) at 500 rpm for 150 min. After extraction, samples were centrifuged at  $10,000 \times g$  and stored at  $-40$  °C. For the extractions carried out for the response surface optimization, the amount of PP and

the stirring speed varied according to predetermined values, dictated by experimental design. The pH of the extraction medium was adjusted at various levels with 2 M NaOH, after incorporating citric acid at a final concentration of 1 g L<sup>-1</sup>. Extractions with 60% (v/v) EtOH and 60% (v/v) MeOH were used as the control.

#### 2.4. Experimental Design and Process Optimization

Process optimization was accomplished by deploying response surface methodology through a Box–Behnken design with three central points. The objective was to evaluate the influence of selected extraction variables on the total polyphenol yield ( $Y_{TP}$ ), which was chosen as the response. The variables examined were the pH of the extraction medium, the liquid-to-solid ratio ( $R_{L/S}$ ) and the stirring speed ( $S_S$ ). These variables were assigned as  $X_1$ ,  $X_2$  and  $X_3$ , respectively (Table 1), and codified to levels, as previously reported in detail [12]. The assessment of the fitting of the model to the experimental data was based on ANOVA and lack-of-fit analysis. The equation describing the mathematical model was reported by excluding non-significant dependent terms.

**Table 1.** Actual and coded levels of the process variables considered for response surface optimization.

Independent Variables	Code Units	Coded Variable Level		
		−1	0	1
pH	$X_1$	2	3.5	5
$R_{L/S}$ (mL g <sup>-1</sup> )	$X_2$	20	50	80
$S_S$ (rpm)	$X_3$	200	500	800

#### 2.5. Total Polyphenol Determination

Total polyphenol determination was performed using the Folin–Ciocalteu methodology, as described elsewhere [12]. In an Eppendorf tube of 1.5 mL, a 0.1 mL sample followed by 0.1 mL Folin–Ciocalteu reagent were introduced and allowed to stand for 2 min. Then, 0.8 mL of sodium carbonate (5%) was added and the mixture was maintained for 20 min, at 40 °C, in a water bath (Heidolph HB digital, Schwabach, Germany). Results were given as mg chlorogenic acid equivalents per g dry mass (dm).

#### 2.6. Estimation of the Antiradical Activity ( $A_{AR}$ )

For this assay, DPPH was used as the radical probe and a stoichiometric determination was employed [12]. A volume of 0.975 mL DPPH (100  $\mu$ M in methanol) was combined with 0.025 mL of sample and incubated at room temperature. The absorbance at 515 nm was recorded at  $t = 0$  min ( $A_{515(i)}$ ) and at  $t = 30$  min ( $A_{515(f)}$ ). The  $A_{AR}$  was computed as follows:

$$A_{AR} = \frac{\Delta A}{\varepsilon \times l \times C} \times Y_{TP} \quad (1)$$

$\Delta A$  corresponds to  $A_{515(i)} - A_{515(f)}$ ,  $\varepsilon$  (DPPH) to  $11,126 \times 10^6 \mu\text{M}^{-1} \text{cm}^{-1}$ ,  $C$  to  $C_{TP} \times 0.025 \times$  sample dilution (in this case 1/50),  $Y_{TP}$  to the total polyphenol extraction yield (mg g<sup>-1</sup>) and  $l$  to the path length (1 cm).  $A_{AR}$  was given as  $\mu\text{mol DPPH g}^{-1} \text{dm}$ .

#### 2.7. Estimation of the Ferric-Reducing Power ( $P_R$ )

A published methodology was implemented to assay  $P_R$  [12]. In short, 0.05 mL of FeCl<sub>3</sub> (4 mM in 0.05 M HCl) and an equal volume of extract were mixed and incubated for 30 min at 37 °C, in a water bath. Following this, 0.9 mL of TPTZ solution (1 mM in 0.05 M HCl) was added, and the absorbance was recorded at 620 nm, after 10 min.  $P_R$  was estimated as  $\mu\text{M}$  ascorbic acid equivalents (AAE) per g dry mass.

### 2.8. High-Performance Liquid Chromatography-Diode Array (HPLC-DAD)

The equipment employed was a Shimadzu CBM-20A liquid chromatograph (Shimadzu Europa GmbH, Duisburg, Germany), coupled to a Shimadzu SPD-M20A detector, and interfaced by Shimadzu LC solution software. For the chromatographic analyses, a Phenomenex Luna C18(2) column (100 Å, 5 µm, 4.6 × 250 mm) (Phenomenex, Inc., Torrance, CA, USA) was used, at 40 °C. Separation was performed with eluents (A) 0.5% aqueous formic acid and (B) 0.5% formic acid in MeCN/water (6:4), at 1 mL min<sup>-1</sup> flow rate, using the following elution program: 100% A to 60% A in 40 min, 60% A to 50% A in 10 min, 50% A to 30% A in 10 min; then, isocratic elution for further 10 min. The injection volume was 20 µL. Quantification was performed at 325 nm, with calibration curves (0–50 µg mL<sup>-1</sup>), constructed with neochlorogenic acid ( $R^2 = 0.998$ ), chlorogenic acid ( $R^2 = 0.999$ ), caffeic acid ( $R^2 = 0.998$ ) and ferulic acid ( $R^2 = 0.998$ ).

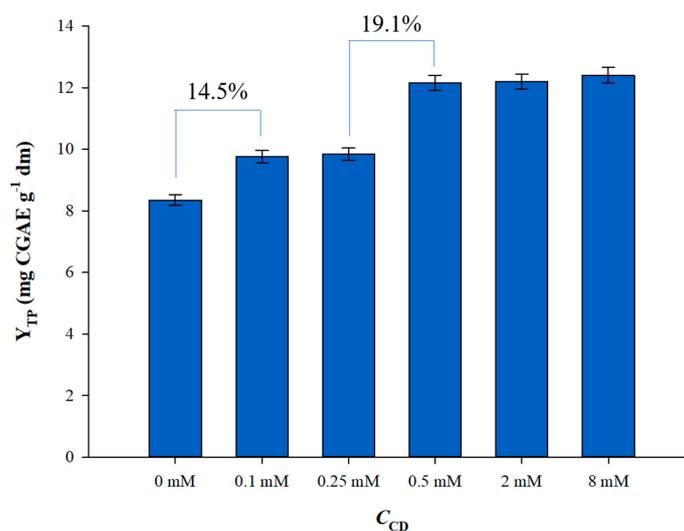
### 2.9. Statistical Processing

Extractions were repeated at least twice and analyses in triplicate. The reported values are means ± standard deviation (sd). SigmaPlot™ 12.5 (Systat Software Inc., San Jose, CA, USA) was used to establish linear correlations, at least at a 95% significance level. JMP™ Pro 13 (SAS, Cary, NC, USA) was used to carry out distribution analysis, as well as to set up the response surface experimental design and perform the response surface-associated statistics (ANOVA, lack-of-fit).

## 3. Results and Discussion

### 3.1. Effect of HP-β-CD Concentration ( $C_{CD}$ )

The initial step in the process development was to identify the most suitable  $C_{CD}$  which would provide the highest total polyphenol extraction yield ( $Y_{TP}$ ). Thus,  $C_{CD}$  was tested over a range of 0 (deionized water) to 8 mM (Figure 1). Compared to deionized water (0 mM), a solution with  $C_{CD}$  of 0.1 mM provided by 14.5% higher  $Y_{TP}$ . This fact indicated that the presence of HP-β-CD fostered polyphenol extraction to a significant extent. By raising  $C_{CD}$  levels from 0.1 to 0.25 mM, the  $Y_{TP}$  increased from  $9.76 \pm 0.20$  to  $9.84 \pm 0.87$  mg CGAE g<sup>-1</sup> dm. This difference fell within the limits of statistical error and it was non-significant ( $p > 0.05$ ). However, switching  $C_{CD}$  from 0.25 to 0.5 mM, an increase in  $Y_{TP}$  by 19.1% was recorded, whereas a further  $C_{CD}$  increase up to 8 mM afforded higher  $Y_{TP}$  by only 2%. Therefore, a  $C_{CD}$  of 0.5 mM was chosen as the most appropriate to carry out subsequent process optimization.

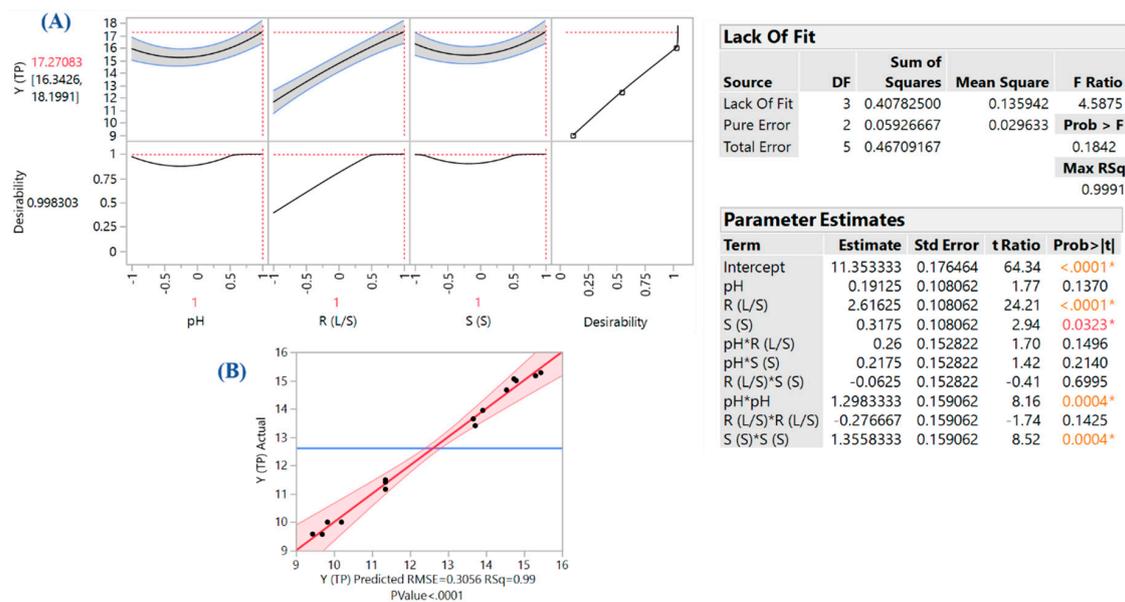


**Figure 1.** Effect of HP-β-CD concentration ( $C_{CD}$ ) on total polyphenol yield ( $Y_{TP}$ ). Extractions were carried out at ambient temperature ( $29 \pm 2$  °C), at a liquid-to-solid ratio of 30 mL g<sup>-1</sup>.

### 3.2. Optimization-Effect of Process Variables

The optimization procedure was designed to evaluate the influence exerted by three critical extraction variables, pH,  $R_{L/S}$  and  $S_S$ , on the response ( $Y_{TP}$ ), and to reveal possible synergistic effects between them. The assessment of the fitted model and the suitability of response surface were accomplished by performing ANOVA and a lack-of-fit test (Figure 2), on the basis of the proximity of measured and predicted values (Table 2). Taking into consideration only the significant terms (Parameter Estimates, Figure 2), the second-degree mathematical model derived was as follows:

$$Y_{TP} \text{ (mg CGAE g}^{-1} \text{ dm)} = 11.35 + 2.62X_2 + 0.32X_3 + 1.30X_1^2 + 1.36X_3^2 \quad (2)$$

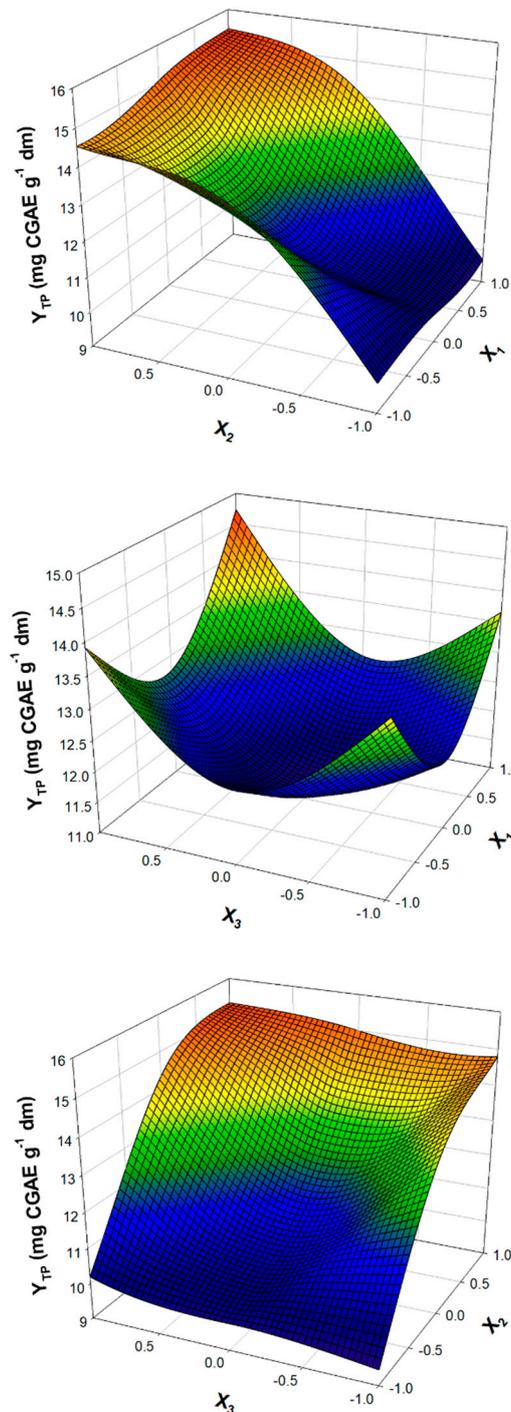


**Figure 2.** Desirability function (A), actual-by-predicted plot (B) and statistical information (lack-of-fit and parameter estimates inset tables) generated by performing response surface methodology, concerning the effect of process variables on the response. Asterisks (\*) on the “Parameter Estimates” inset table denote statistically significant terms ( $p < 0.05$ ).

**Table 2.** Analytical display of individual design points and measured and predicted values of the response.

Design Point	Independent Variables			Response ( $Y_{TP}$ , mg CGAE $g^{-1}$ dw)	
	$X_1$	$X_2$	$X_3$	Measured	Predicted
1	-1	-1	0	10.00	9.83
2	-1	1	0	14.66	14.54
3	1	-1	0	9.57	9.69
4	1	1	0	15.27	15.44
5	0	-1	-1	9.58	9.44
6	0	-1	1	10.00	10.20
7	0	1	-1	14.99	14.79
8	0	1	1	15.16	15.30
9	-1	0	-1	13.4	13.72
10	1	0	-1	13.64	13.66
11	-1	0	1	13.94	13.92
12	1	0	1	15.05	14.73
13	0	0	0	11.41	11.35
14	0	0	0	11.16	11.35
15	0	0	0	11.49	11.35

The square correlation coefficient ( $R^2$ ) provides an indication of the total variability around the mean, as determined by the model [13]. Given that  $R^2$  was 0.99 ( $p < 0.0001$ ) and the lack-of-fit was significant at least at a 95% significance level, it could be supported that the mathematical equation (Equation (2)) describing the model showed excellent adjustment to the experimental data. The 3D diagrams representing the model (Figure 3) visualize the effect of the process variables on the response ( $Y_{TP}$ ).



**Figure 3.** Three-dimensional diagrams portraying the effect of process variables on the response.

Using the desirability function (Figure 2), the maximum  $Y_{TP}$  was estimated to be  $17.27 \pm 0.93$  mg CGAE  $g^{-1}$  dm, at the following optimal settings: pH = 5.0,  $R_{L/S} = 80$  mL  $g^{-1}$  and  $S_S = 800$  rpm. To confirm

the validity of this prediction, the optimal settings were employed to carry out three individual extractions and the  $Y_{TP}$  found was  $16.86 \pm 1.75$  mg CGAE  $g^{-1}$  dm. This finding demonstrated the reliability of the predictive model. The  $Y_{TP}$  level determined in this study was of a similar magnitude to 20 mg GAE  $g^{-1}$  dm attained by employing subcritical water extraction of PP [14], but exceeded significantly 7.67 mg GAE  $g^{-1}$  dm achieved with 80% methanol and ultrasound-assisted extraction [15], 9.11 mg CAE  $g^{-1}$  dm achieved with 59% (v/v) ethanol and ultrasound-assisted extraction [16], and 11.0 mg GAE  $g^{-1}$  dm achieved with 60% ethanol and microwave-assisted extraction [17]. Lower yields of 6.4 mg  $g^{-1}$  dm obtained with 55% ethanol and ultrasound-assisted extraction [18], and 4.39 mg GAE  $g^{-1}$  dm obtained with pressurized water/ethanol mixtures [19] have also been reported. Although the total polyphenol content of PP may exhibit variations attributed to varietal, cultivation and climatic factors, in a survey on 60 different potato cultivars, no value higher than 12.59 mg GAE  $g^{-1}$  dm was found for the total polyphenol content [20]. This fact strongly evidenced that the level of  $Y_{TP}$  achieved in this study was indicative of a high-performance extraction system.

The direct effect of pH ( $X_1$ ) was non-significant, but the influence exerted by pH was manifested by its quadratic term  $X_1^2$ . The optimum pH 5 determined by the model was the upper limit of the experimental design, suggesting that extraction was not favored in a more acidic environment. The role of pH has been implicated in polyphenol–cyclodextrin interactions because it affects the dissociation of either carboxyl functions or phenolic hydroxyls. Experiments with caffeic acid (CA) and HP- $\beta$ -CD indicated that constants of complex formation were sensitive to pH and decreased with pH increases [21]. This behavior was ascribed to the hydrophobicity of CA, which depends on its ionization state. Since the main inclusion interactions are hydrophobic, developed between the HP- $\beta$ -CD cavity and the guest molecule, acidic pH would contribute to suppressing CA ionization, maintaining it in a non-ionized and thus, more hydrophobic form, hence, the greater stability constant. Results from rosmarinic acid/ $\beta$ -CD interactions were in concurrence [22]. However, the carboxyl group of the quinic moiety on CGA, which is the principal polyphenol in PP [5], has a  $pK_a$  of 3.33, and at pH 5, this group would be deprotonated [23]. Therefore, it would be expected that polyphenol extraction from PP with HP- $\beta$ -CD would be favored at lower pH. This finding might indicate that other interactions between CGA and HP- $\beta$ -CD and/or interactions with other PP constituents affected the overall extraction yield.

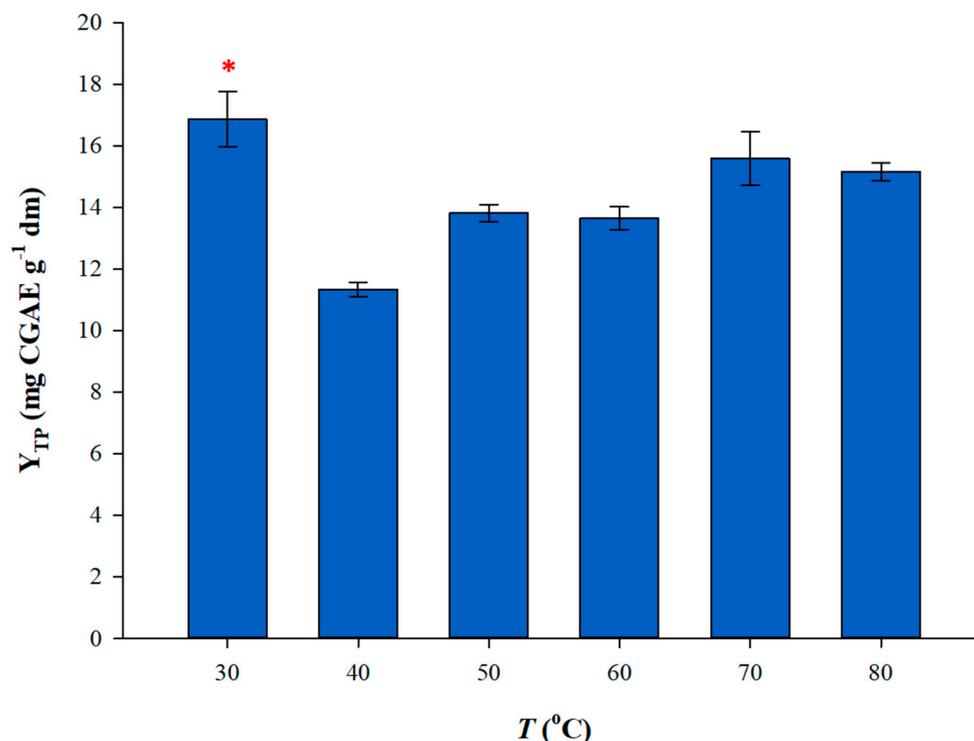
The effect of  $R_{L/S}$  and  $S_S$  was significant (Figure 2, inset table), as demonstrated for several extraction processes [24–27]. Both variables have been closely associated with diffusion phenomena that govern solid–liquid extraction, and their proper regulation might be critical in attaining high extraction yield. Regarding  $R_{L/S}$ , it defines the concentration gradient that is the driving force of diffusion, which in turn, favors mass transfer [28–30]. Thus, suitable setting of  $R_{L/S}$  would entail negligible resistance to mass transfer and effective entrainment of solute (polyphenols) into the liquid medium [30]. In this study, the optimum  $R_{L/S}$  estimated was 80 mL  $g^{-1}$ , which matches the optimum 82–84 mL  $g^{-1}$  found for polyphenol extraction from PP and eggplant peels using water/ethanol mixtures [16,31].

Likewise, careful regulation of  $S_S$  results in effective dispersion of the solute that diffuses from the internal part of the solid particles, into the liquid volume. This would minimize external resistance and increase mass transfer [32]. To achieve higher diffusivity and increased mass transfer,  $S_S$  must be properly set, since it has been shown that diffusivity is highly correlated with  $S_S$  [33]. The optimum  $S_S$  of 800 rpm determined in this study was equal to those estimated for polyphenol extraction with deep eutectic solvent from saffron processing wastes [26] and *Moringa oleifera* leaves [27], and comparable to 900 rpm found for polyphenol extraction from onion solid wastes [34]. However, optimum  $S_S$  as low as 200 rpm has also been reported [35].

### 3.3. Effect of Extraction Temperature

The extraction carried out at ambient  $T$  (approximately 30 °C) was demonstrated to be the most efficacious ( $p < 0.05$ ), giving a  $Y_{TP}$  of  $16.86 \pm 1.75$  mg CGAE  $g^{-1}$  dm, whereas extractions accomplished between 40 and 80 °C were of lower performance (Figure 4). This fact strongly emphasized that

$T > 30$  °C may not facilitate PP polyphenol extraction in the presence of HP- $\beta$ -CD. Although a similar  $T$  of 35 °C has been proposed as the optimum for ultrasound-assisted PP polyphenol extraction [18], this finding contrasted with earlier investigations, which illustrated that the most favorable  $T$  for polyphenol extraction from PP may lie from 80 [16,17,19] and 90 [36] to as high as 190 °C [14]. However, intermediate levels of 50 °C have also been suggested [37].



**Figure 4.** The effect of temperature on total polyphenol yield ( $Y_{TP}$ ), under optimized extraction conditions. Asterisk (\*) denotes statistically different value ( $p < 0.05$ ). All other values showed no statistical difference.

The aqueous solubility of sparingly soluble polyphenols, such as quercetin, has been explicitly shown to increase with increases in  $T$ , in the presence of various cyclodextrins [38]. On this ground, the results illustrated in Figure 4 might appear paradoxical.

However, in another study on polyphenol/cyclodextrin complexation, it was evidenced that the binding constants of polyphenol complexes with  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrin, decreased with a rise in  $T$  [39]. In support of this finding were results from another investigation on interactions of the stilbene (E)-piceatannol with HP- $\beta$ -CD, where a decrease in the complexation constant was observed as a response to raising  $T$  [40]. The authors ascribed this phenomenon to weakening of hydrogen bonds between the host and the guest molecule, due to heating. This hypothesis might justify the reason for reduced  $Y_{TP}$  observed at  $T > 30$  °C. Moreover, at  $T$  around 50–60 °C, there may be observed decomposition of polyphenol-CD inclusion complexes. Thus, selection of appropriate extraction  $T$  is of utmost importance [11].

### 3.4. Antioxidant Activity and Polyphenolic Composition

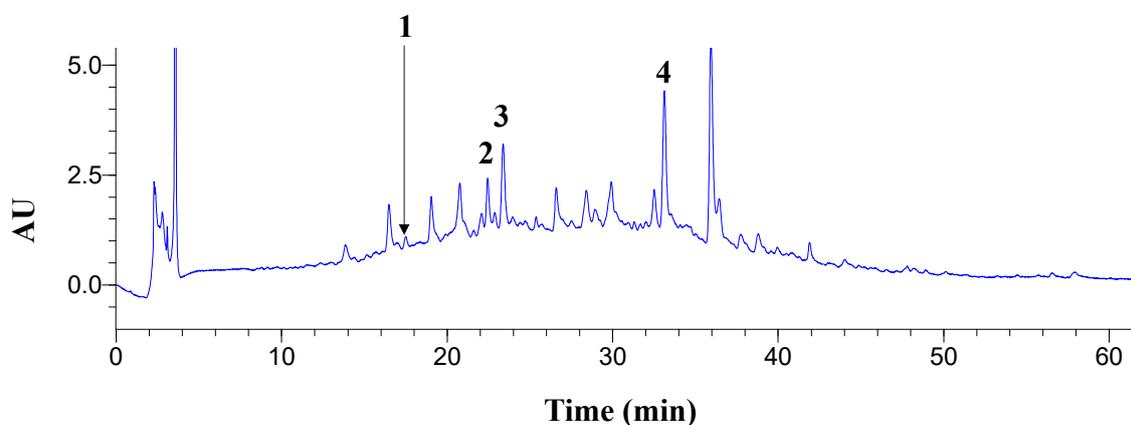
To better portray the effect of HP- $\beta$ -CD on polyphenol extraction from PP, the extracts obtained under optimized conditions, at 30 °C, were tested for antioxidant activity. The results were compared with extracts prepared using 60% aqueous ethanol, a commonly used green solvent, and 60% aqueous methanol, a common conventional solvent (Table 3).

**Table 3.** Comparison of the characteristics of the extract obtained with HP- $\beta$ -CD with those of common conventional solvents. Values reported are means  $\pm$  standard deviation.

Extraction	Y <sub>TP</sub> (mg CGAE g <sup>-1</sup> dm)	A <sub>AR</sub> ( $\mu$ mol DPPH g <sup>-1</sup> dm)	P <sub>R</sub> ( $\mu$ mol AAE g <sup>-1</sup> dm)
HP- $\beta$ -CD	16.86 $\pm$ 1.75	16.37 $\pm$ 0.49	8.83 $\pm$ 0.09
60% EtOH	13.67 $\pm$ 0.27	25.26 $\pm$ 0.76	9.47 $\pm$ 0.09
60% MeOH	13.27 $\pm$ 1.01	23.04 $\pm$ 0.69	11.49 $\pm$ 0.11

Y<sub>TP</sub>, yield in total polyphenols; A<sub>AR</sub>, antiradical activity; P<sub>R</sub>, ferric-reducing power.

Extraction with HP- $\beta$ -CD afforded almost by 19% higher Y<sub>TP</sub> compared to 60% EtOH and by 21% compared to 60% MeOH, while differences in both A<sub>AR</sub> and P<sub>R</sub> were marginal and non-significant ( $p > 0.05$ ). This outcome clearly suggested that extraction of PP with HP- $\beta$ -CD was virtually as effective as with common organic solvents. The HP- $\beta$ -CD extract was then analyzed with HPLC to identify the major polyphenolic constituents. Of the trace recorded at 325 nm (Figure 5), four phytochemicals could be tentatively identified, namely neochlorogenic acid, chlorogenic acid, caffeic acid and ferulic acid.

**Figure 5.** Chromatogram of PP extract obtained with HP- $\beta$ -CD, under optimized conditions, at 30 °C. The trace was recorded at 325 nm. Peak assignment: 1, neochlorogenic acid; 2, chlorogenic acid; 3, caffeic acid; 4, ferulic acid.

The results from the quantitative analysis are given in Table 4. The most abundant polyphenol was ferulic acid, followed by caffeic and chlorogenic acid, whereas neochlorogenic acid occurred at much lower levels. Unlike previous reports, chlorogenic and caffeic acids were not the predominant constituents. In fact, chlorogenic acid content (83.67  $\mu$ g g<sup>-1</sup> dm) was significantly low compared to 4100  $\mu$ g g<sup>-1</sup> dm reported by other studies [18]. Yet, other authors determined levels ranging from 2.16 to 267.4  $\mu$ g g<sup>-1</sup> dm [15] and from 299.51 to 904.21  $\mu$ g g<sup>-1</sup> dm [41].

**Table 4.** Contents of the major polyphenols detected in PP extracts.

Peak #	Polyphenol	Content ( $\mu$ g g <sup>-1</sup> dm) $\pm$ sd
1	Neochlorogenic acid	28.95 $\pm$ 1.60
2	Chlorogenic acid	83.67 $\pm$ 0.54
3	Caffeic acid	88.98 $\pm$ 0.28
4	Ferulic acid	108.73 $\pm$ 3.52
	Sum	310.34

Regarding caffeic acid, the content determined was comparable to 68.19–129.05  $\mu$ g g<sup>-1</sup> dm found in earlier investigations [15]. However, a yield of 592  $\mu$ g g<sup>-1</sup> dm has been achieved for PP extraction with pressurized liquids [19], but yields varying from 160 to as high as 1220  $\mu$ g g<sup>-1</sup> dm have been attained with ethanol/water mixtures and ultrasound-assisted extraction [18]. Other authors reported

values of 250 to 324  $\mu\text{g g}^{-1} \text{ dm}$  [41]. On the other hand, ferulic acid was shown to occur at levels of 1 to 28  $\mu\text{g g}^{-1} \text{ dm}$  [42].

#### 4. Conclusions

The examination presented herein illustrated the effectiveness of PP polyphenol extraction, at near-ambient temperatures, using HP- $\beta$ -CD. Such an extraction process for PP polyphenols has not been reported heretofore. The results obtained suggested that regulation of pH at 5 may enhance polyphenol extractability, but the role of  $S_5$  and  $R_{L/S}$  was also significant. Temperatures higher than 30 °C were not favorable to attaining higher extraction yields. Under optimized conditions, the total polyphenol yield and the antioxidant properties of the extracts produced were comparable to those obtained with aqueous methanol and ethanol. Some of the major polyphenols identified in the extracts were neochlorogenic, chlorogenic, caffeic and ferulic acids. The methodology proposed might be less cost-effective compared to methods employing cheaper conventional solvents. Another limitation that may arise by the use of HP- $\beta$ -CD could be its incompatibility with certain types of foods and/or cosmetics (e.g., those with high-fat content). On the other hand, it is a completely volatile solvent-free process, and thus, the use of toxic and environmentally aggravating materials is fully precluded. Furthermore, HP- $\beta$ -CD is a food-grade substance and the direct application of extracts produced with HP- $\beta$ -CD, in foods and/or cosmetics, could be particularly advantageous, without the need for additional energy-demanding and time-consuming downstream steps for extract purification. It would be proposed that future studies should focus on identifying whether extracts generated with the method proposed could be effective food antioxidants/antimicrobials and/or cosmetic constituents. Such approaches would certainly have an obvious industrial prospect for large-scale valorization of PP as abundant and low-cost bioresources of polyphenolic phytochemicals.

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