

## Article

# Acid-Catalyzed Organosolv Treatment of Potato Peels to Boost Release of Polyphenolic Compounds Using 1- and 2-Propanol

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**Abstract:** The current study aimed at developing an effective organosolv treatment, with the objective to obtain potato peel extracts highly enriched in polyphenols. To this end, two low-cost solvents were employed, 1- and 2-propanol, which are considered green, but they have been rather poorly studied compared to other conventional solvents, such as ethanol. Treatment development also embraced the use of sulfuric acid, a well-examined catalyst in organosolv processes. Treatment evaluation on the basis of response surface optimization and severity demonstrated that 1-propanol was a more effective solvent, providing a maximum yield in total polyphenols of 19.28 mg chlorogenic acid equivalents per g of dry potato peel weight, attained with 40% 1-propanol/1.5% (*w/v*) sulfuric acid at a treatment time of 60 min and a temperature of 90 °C. This treatment was of lower severity compared to the one with 2-propanol, and it also provided almost 24% higher total polyphenol yield. The extracts produced contained chlorogenic acid as the major constituent, accompanied by caffeic acid and minor amounts of *p*-coumaric acid. This is the first report on such an organosolv treatment of potato peels to recover polyphenolic compounds with high efficiency.

**Keywords:** antioxidants; potato peels; organosolv; polyphenols; food waste valorization



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## 1. Introduction

The rapidly expanding world population has led to unprecedented pressure on biore-source utilization, provoking largely uncontrolled overexploitation, ecosystem degradation, and severe environmental aggravation. An issue of utmost concern pertaining to crop cultivation and food production is the generation of outstanding amounts of waste. This residual biomass consists of biological tissues of high organic load, and their improper management and excessive dumping in landfills entails imminent risks of environmental pollution as well as risks to ecosystem conservation and public health [1,2]. On the basis of the above considerations, there has been to-date a wide recognition that linear economy models are both inefficient and environment threatening, and thus circular economy aspects are gaining universal acceptance by adopting sustainable routes of agricultural production and food manufacturing. One of the major pillars associated with establishing circular economy strategies is the exploitation of food wastes in order to produce high value-added compounds, energy, and plant-form chemicals [3,4].

Plant food wastes are particularly rich in bioactive phytochemicals, such as polyphenols, which are a prominent family of phytochemicals possessing a spectrum of bioactivities [5]. This has oriented the relevant research towards the development of eco-friendly technologies for their effective recovery and valorization [6,7]. Aside from the utilization of non-toxic, benign solvents, the development of green extraction of polyphenols comprises implementing innovative techniques, such as microwave-assisted extraction, ultrasound-assisted extraction, etc., which in some instances have been proven far more

efficient than conventional extraction techniques. Furthermore, recent reports have also introduced organosolv treatments, which have been shown to be extraction processes of high efficiency [8].

The organosolv processes, originally developed for the pretreatment of biomass to increase the recovery and fermentability of cellulose, aim at disintegrating the cell wall lignocellulosic matrix [9,10]. At the same time, cell wall degradation enables intracellular metabolite (polyphenol) liberation and the entrainment of these compounds into the extraction solvent (liquid phase) [11]. This results in increased mass transfer, and, hence, improved extraction yield. Ethanol is commonly employed in organosolv processes, but other alcohols have also been used for this purpose, such as butanol, glycerol, and 2-propanol [12,13]. Additionally, acid catalysis, usually by incorporating sulfuric acid into the solvent system, may significantly enhance treatment performance [14].

Potatoes are tubers from the plant *Solanum tuberosum*, and they are consumed by large populations around the world. After cereals, the potato is the most important food crop, and the global production was over 368 million tons in 2018. Apart from being one of the most commonly consumed plant tissues, potatoes are regularly processed to produce a number of commodities, such as puree, chips, French fries, hash browns, etc. The potato processing industry is one of the largest, and accounts for the generation of waste streams caused mainly by removal of peels, which account for 15% to 40% of the initial fresh weight [15]. This is translated into the production of about 70 and 140 thousand tons of potato peels (PP) worldwide on an annual basis.

Thus, owing to their abundance and composition, PP have been the subject of extensive research regarding their exploitation through biorefinery processes but also the production of polyphenol-enriched extracts. The major polyphenol encountered in PP is chlorogenic acid, usually accompanied by other isomers (i.e., neochlorogenic acid), and simple hydroxycinnamates, such as ferulic acid and caffeic [16]. Polyphenols are considered the principal bioactives in PP, to which an array of properties have been attributed. Furthermore, PP extracts have been successfully used as natural food antioxidants, and they have been regarded as effective replacers of synthetic ones [17]. Therefore, it does not come as a surprise that several processes have been proposed for the production of PP polyphenol extraction, yet conventional methodologies reported in the literature appear to provide rather low yields in total polyphenols.

On the other hand, recent reports on organosolv treatments of plant food wastes, such as spent coffee waste [8], and onion solid wastes [18], clearly demonstrated their supremacy in achieving high-performance extractions. On this basis, this investigation was undertaken to develop an acid-catalyzed organosolv treatment based on 1- and 2-propanol, which are two benign and low-cost solvents that have been poorly studied with regard to polyphenol extraction. A critical comparison of these two alcohols was based on response surface optimization and process severity as well as liquid chromatography-tandem mass spectrometry in order to examine the possible effects on the polyphenolic profile of the extracts produced. To the best of our knowledge, the treatment developed is described for the first time.

## 2. Materials and Methods

### 2.1. Reagents and Chemicals

Caffeic acid ( $\geq 98\%$ ), *p*-coumaric acid ( $>98\%$ ), and chlorogenic acid ( $\geq 95\%$ ) were from Extrasynthese (Genay, France). For all chromatographic analyses, HPLC grade solvents were used. 2,4,6-Tripyridyl-*s*-triazine (TPTZ) and iron chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were from Honeywell/Fluka (Steinheim, Germany). Ascorbic acid and 2,2-diphenylpicrylhydrazyl (DPPH) were from Sigma-Aldrich (Darmstadt, Germany). Ethanol, 1- and 2-propanol, and sodium carbonate were purchased from Honeywell/Riedel-Haen (Seelze, Germany). Folin-Ciocalteu reagent was from Merck (Darmstadt, Germany).

## 2.2. Collection and Handling of Potato Peels (PP)

Fresh PP were collected immediately after processing (peeling) of brown-skin potatoes (*Solanum tuberosum*) from a catering facility. PP were shortly transferred to the laboratory, placed on aluminum foil trays, and dried in an oven (Binder BD56, Bohemia, NY, USA), at 60 °C, for 12 h [19]. The dried material was then comminuted in a domestic blender, and after sieving, a powder with mean particle size < 0.7 mm was collected. This powder was used in all experiments performed for the study.

## 2.3. Solvent Screening and Organosolv Treatment

The two solvents tested, 1- and 2-propanol, were first tested for their efficiency to extract polyphenolic compounds from PP. To this end, the amount of 1 g of pulverized PP was mixed with 10 mL of alcohol/water solutions with a proportion of 20, 40, 60, 80, and 100% (v/v). Extractions were accomplished for a resident period of 210 min by employing a hotplate (Witeg, Wertheim, Germany) set at 500 rpm stirring speed and a temperature of 70 °C [20]. After the extraction, centrifugation at 10,000 × g was carried out to remove cell debris, and the clear supernatant was collected for analysis.

To carry out the organosolv treatments, a previously published methodology was followed [21]. In particular, solvent with optimum alcohol/water ratio was spiked with concentrated sulfuric acid solution to give a final sulfuric acid concentration ( $C_{\text{SuAc}}$ ) of 0.5, 1, and 1.5% (w/v). Then, a volume of 10 mL of each solvent system was combined with 1 g PP, and treatments were performed for a resident time of 60, 180, and 300 min at 90 °C. Considering the boiling point of both 1- and 2-propanol, the upper limit of 90 °C was the maximum temperature that could be used, and this was for safety reasons. Upon treatment completion, mixtures were centrifuged at 10,000 × g.

## 2.4. Determination of Severity Factor

By considering the resident time and temperature, the severity of an organosolv treatment can be estimated and used to compare different processing conditions as follows [22,23]:

$$R_o = t \times e^{\left(\frac{T-100}{14.75}\right)} \quad (1)$$

$$\text{SF} = \log R_o \quad (2)$$

SF represents the severity factor,  $R_o$  the severity, and 100 °C is the reference temperature. The value 14.75 is an empirical factor, related to the treatment temperature and activation energy. An integrated form of SF, the combined severity factor (CSF) takes into consideration the pH of the solvent, which may be crucial in affecting the decomposition of the biomatrix (PP) [24]:

$$R_o' = 10^{-\text{pH}} \times t \times e^{\left(\frac{T-100}{14.75}\right)} \quad (3)$$

$$\text{CSF} = \log R_o' - \text{pH} \quad (4)$$

Finally, an approach suggested to deliver a fairer comparison of severities of different treatments, at widely different pH was also taken into account [24]:

$$\text{CSF}' = \log R_o + |\text{pH} - 7| \quad (5)$$

## 2.5. Design of Experiment and Response Surface Optimization

Optimization of the organosolv treatment was conducted by deploying response surface methodology. The experimental setup considered the catalyst (sulfuric acid) concentration,  $C_{\text{SuAc}}$ , and the resident time,  $t$ , as the process (independent) variables, and the total polyphenol yield ( $Y_{\text{TP}}$ ) as the response. The experimental design chosen was an 11-point central composite, including three central points. Both independent variables ( $t$ ,  $C$ ) were codified in 3 levels, −1, 0, and 1, as described elsewhere [25]. The codified and actual levels of each variable are given in Table 1.

**Table 1.** The process variables considered for the experimental design, and their coded and actual levels. Where  $C_{\text{SuAc}}$  is the concentration of sulfuric acid in the solvent used for the treatment.

Process Variables	Codes	Coded Variable Level		
		−1	0	1
$t$ (min)	$X_1$	60	180	300
$C_{\text{SuAc}}$ (% w/v)	$X_2$	0.5	5.0	1.5

Preliminary experiments and the recent relevant literature formed the basis to select the ranges for each variable tested [22]. Both lack-of-fit and analysis of variance (ANOVA) tests, at a minimum significance level of 95%, were used to assess the significance of the individual model coefficients, and also the overall statistical significance of the models ( $R^2$ ,  $p$ ).

### 2.6. Determinations

Analysis of total polyphenols was accomplished with a well-described Folin-Ciocalteu methodology [26]. Results were reported as chlorogenic acid equivalents, using a chlorogenic acid calibration curve (50–700 mg L<sup>−1</sup>,  $R^2 = 0.9987$ ). The antiradical activity ( $A_{\text{AR}}$ ) and the ferric-reducing power ( $P_{\text{R}}$ ) were determined using methodologies described elsewhere [26].

### 2.7. Liquid Chromatography—Tandem Mass Spectrometry (LC-MS/MS)

For the tentative identification and quantitation of the major polyphenols occurring in PP, a TSQ Quantum Access MS/MS detector (Thermo Scientific, Waltham, MA, USA) was employed, coupled with a ACQUITY Binary Solvent Manager and ACQUITY Sample manager (Waters, Milford, MA, USA). The separation was achieved with a 5  $\mu\text{L}$  injection volume at a flow rate of 0.3 mL min<sup>−1</sup> on a Fortis SpeedCore C18, 100 mm  $\times$  2.1 mm (2.6  $\mu\text{m}$ ) maintained at 40 °C. The mobile phase was (A) water containing 1% acetic acid, and (B) methanol containing 1% acetic acid, and the elution program was linear gradient, as follows: 0 min, 0% B, and 20 min, 100% B. Mass spectra acquisition was accomplished in negative ionization mode, with a sheath gas pressure of 30 (arbitrary units), a capillary temperature set at 300 °C, an auxiliary gas pressure of 15 (arbitrary units), and collision pressure at 1.5 mTorr. The quantitation of caffeic acid, *p*-coumaric acid, and chlorogenic acid was accomplished using external standards, and calibration curves were constructed using the highest intensity fragment produced during the collision-induced dissociation (CID) of the selected precursor molecular ion.

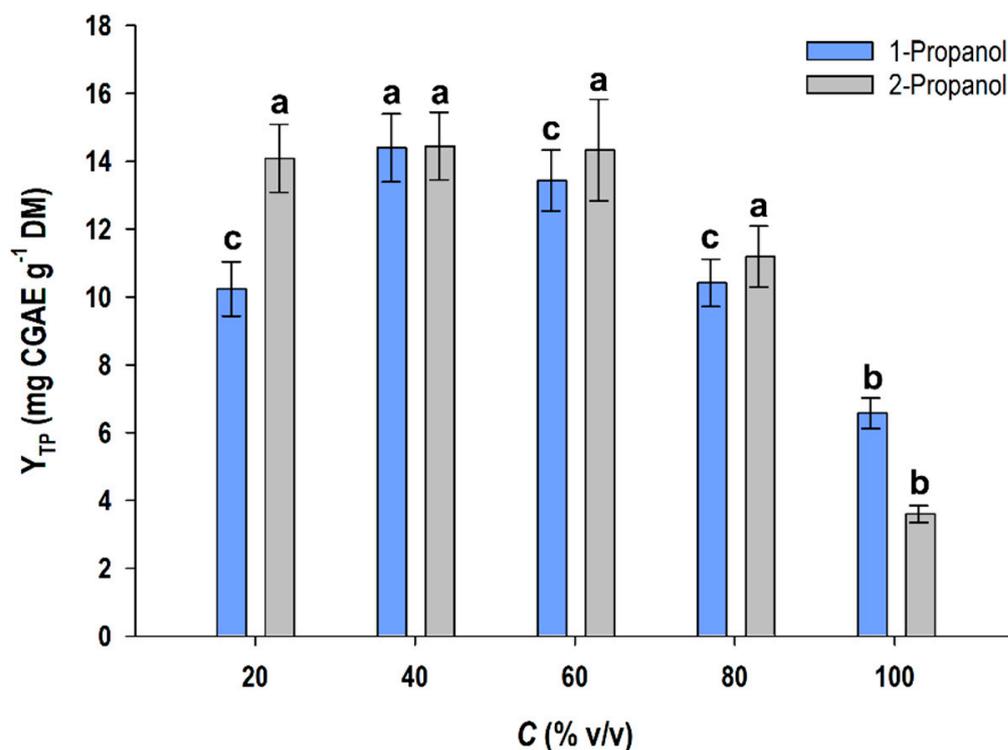
### 2.8. Statistical Analyses

JMP™ Pro 16 (SAS, Cary, NC, USA) was used to carry out distribution analysis, set up the experimental design for the response surface, and compute the accompanying statistics (ANOVA, lack-of-fit). SigmaPlot™ 15.0 (Systat Software Inc., San Jose, CA, USA) was employed for linear and non-linear regressions, at least at a 95% significance level. Organosolv treatments were carried out at least twice and all determinations in triplicate. The values presented are means  $\pm$  standard deviation (sd).

## 3. Results and Discussion

### 3.1. Solvent Assay

In order to have evidence of the capacity 1- and 2-propanol to extract polyphenolic compounds from PP, an initial assay was carried out by varying solvent concentration. In Figure 1, it can be seen that an aqueous mixture composed of 40% 1-propanol gave significantly higher  $Y_{\text{TP}}$  ( $p < 0.05$ ). A similar result was drawn from the examination of water/2-propanol mixtures, but the  $Y_{\text{TP}}$  attained with 40% 2-propanol was not statistically different from those attained with either 20 or 60%. Thus, to maintain identical levels for both 1- and 2-propanol, 40% solutions were chosen for the subsequent organosolv treatments.



**Figure 1.** Testing of water mixtures with 1- and 2-propanol for total polyphenol recovery efficiency. Extractions were carried out at 70 °C for 210 min. Columns designated with different letters (a, b, c) represent statistically different total polyphenol yield ( $Y_{TP}$ ) values. Bars indicate standard deviation.

### 3.2. Acid-Catalyzed Treatment and Solvents Effects

As mentioned above, aqueous mixtures of 40% of either 1- or 2-propanol were used to accomplish the organosolv treatment of PP by maintaining a temperature of 90 °C. The effect of acid catalysis on polyphenol recovery from PP was tested by switching sulfuric acid concentration ( $C_{SuAc}$ ) to different levels and carrying out the organosolv treatment under variable time regimes. Assessment of the severity of each treatment was determined using Equations (4) and (5), and the results drawn are analytically given in Table 2. For the treatment with 1-propanol, statistically higher  $Y_{TP}$  was achieved with  $C_{SuAc}$  of 1% at 60 min and with  $C_{SuAc}$  of 1.5% at 60 min. These treatments were characterized by CSF values of 0.28 and 0.39, respectively, which were statistically different ( $p < 0.05$ ). The corresponding CSF values were 7.28 and 7.39, which were also statistically different. This finding suggested that the maximum  $Y_{TP}$  with minimal process severity may be attained with  $C_{SuAc}$  of 1% at 60 min. Regarding the process with 2-propanol, significantly higher  $Y_{TP}$  was obtained with  $C_{SuAc}$  of 1% at 300 min, and  $C_{SuAc}$  of 1.5% at 300 min. The corresponding CSF values for these treatments were 0.82 and 0.95, which had no statistical difference ( $p > 0.05$ ).

Similarly, the corresponding CSF values were 7.82 and 7.95, which were not significantly different ( $p > 0.05$ ). Thus, with 2-propanol treatment, maximum performance with minimal severity could be obtained with  $C_{SuAc}$  of 1% at 300 min. Considering the above set of conditions, the treatment with 1-propanol would afford a  $Y_{TP}$  of 18.85 mg CGAE g<sup>-1</sup> DM, which was almost 20% higher compared to the 15.00 mg CGAE g<sup>-1</sup> DM obtained with the 2-propanol treatment. Process severity with 1-propanol was also lower compared to that performed with 2-propanol. This outcome strongly pointed to the superiority of 1- over 2-propanol in recovering PP polyphenols.

**Table 2.** Combinations of sulfuric acid concentration and time used to develop the organosolv treatment, and their corresponding severities and total polyphenol yields. Treatments were carried out at a constant temperature of 90 °C. CSF, CSF', and  $Y_{TP}$  correspond to combined severity factor, alternative combined severity factor, and the yield in total polyphenols (expressed as chlorogenic acid equivalents—CGAE).  $C_{SuAc}$  is the concentration of sulfuric acid in the solvent used for the treatment.

$C_{SuAc}$ (% w/v)	$t$ (min)	CSF		CSF'		$Y_{TP}$ (mg CGAE g <sup>-1</sup> DM)	
		1-Pr	2-Pr	1-Pr	2-Pr	1-Pr	2-Pr
0.5	60	0.07 <sup>a</sup>	−0.03 <sup>a</sup>	7.07 <sup>a</sup>	6.97 <sup>a</sup>	17.04 <sup>a</sup>	9.56 <sup>a</sup>
	180	0.55 <sup>c</sup>	0.45 <sup>c</sup>	7.55 <sup>c</sup>	7.45 <sup>c</sup>	18.00 <sup>c</sup>	11.88 <sup>c</sup>
	300	0.77 <sup>c</sup>	0.67 <sup>c</sup>	7.77 <sup>c</sup>	7.67 <sup>c</sup>	17.99 <sup>c</sup>	13.61 <sup>c</sup>
1.0	60	0.28 <sup>a</sup>	0.12 <sup>a</sup>	7.28 <sup>a</sup>	7.12 <sup>a</sup>	18.85 <sup>b</sup>	11.45 <sup>a</sup>
	180	0.76 <sup>c</sup>	0.60 <sup>c</sup>	7.76 <sup>c</sup>	7.60 <sup>c</sup>	18.30 <sup>c</sup>	14.72 <sup>c</sup>
	300	0.98 <sup>b</sup>	0.82 <sup>b</sup>	7.98 <sup>b</sup>	7.82 <sup>b</sup>	17.31 <sup>c</sup>	15.00 <sup>b</sup>
1.5	60	0.39 <sup>c</sup>	0.25 <sup>a</sup>	7.39 <sup>c</sup>	7.25 <sup>c</sup>	19.22 <sup>b</sup>	12.50 <sup>c</sup>
	180	0.87 <sup>c</sup>	0.73 <sup>c</sup>	7.87 <sup>c</sup>	7.73 <sup>c</sup>	18.00 <sup>c</sup>	15.03 <sup>b</sup>
	300	1.09 <sup>b</sup>	0.95 <sup>b</sup>	8.09 <sup>b</sup>	7.95 <sup>b</sup>	16.45 <sup>a</sup>	15.38 <sup>b</sup>

Values within columns with different superscripted letters (<sup>a</sup>, <sup>b</sup>, <sup>c</sup>), are statistically different ( $p < 0.05$ ).

To have a deeper insight into the effect of both 1- and 2-propanol on process severity and efficiency, empirical models relating  $Y_{TP}$  with either CSF or CFS were also established, as depicted in Figure 2. In the case of 1-propanol treatment, the quadratic models linking  $Y_{TP}$  with CSF and CFS were as follows:

$$Y_{TP} = -6.91CSF^2 + 7.09CSF + 16.91 \quad (R^2 = 0.78, p = 0.0109) \quad (6)$$

$$Y_{TP} = -6.91CSF'^2 + 103.77CSF' - 371.10 \quad (R^2 = 0.78, p = 0.0109) \quad (7)$$

Thus, considering Model (6), the maximum  $Y_{TP(max)}$  may be determined by the following equation:

$$Y_{TP(max)} = \frac{D}{4 \times (-6.91)} \quad (8)$$

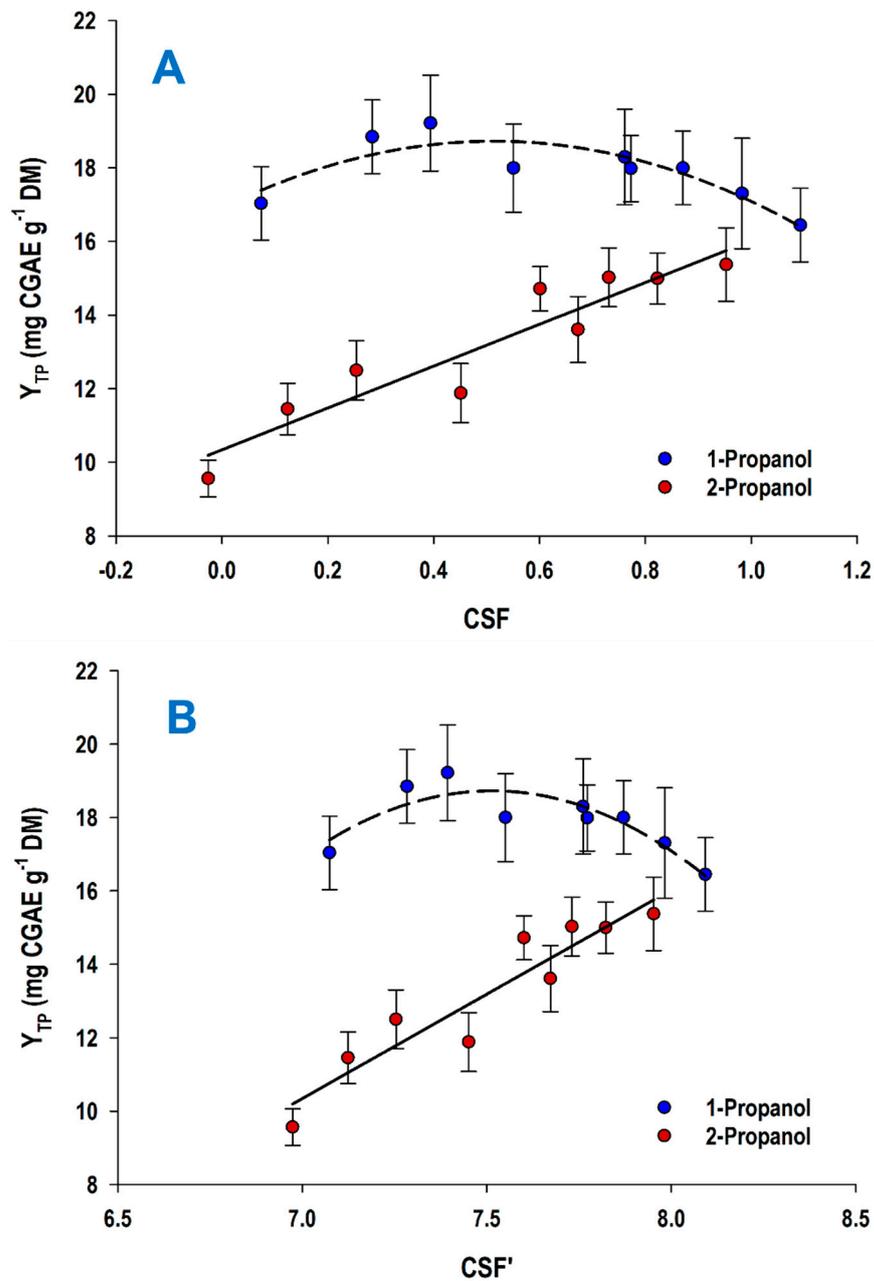
where  $D = 7.09^2 - 4 \times (-6.91) \times 16.91$ . Using Equation (8), the maximum  $Y_{TP}$  was determined to be 18.25 mg CGAE g<sup>-1</sup> DM. This was in accordance with the experimental value 18.85 mg CGAE g<sup>-1</sup> DM, which was achieved with  $C_{SuAc} = 1\%$ , at 60 min, as shown in Table 2. Likewise, when the model (7) was considered, the theoretical maximum  $Y_{TP}$  determined was 18.48 mg CGAE g<sup>-1</sup> DM. Therefore, both models provided accurate predictions.

On the other hand, for the treatments carried out with 2-propanol, the correlations between  $Y_{TP}$  with CSF and CFS were adequately described by linear models:

$$Y_{TP} = 5.68CSF + 10.34 \quad (R^2 = 0.88, p = 0.0002) \quad (9)$$

$$Y_{TP} = 5.68CSF' - 29.45 \quad (R^2 = 0.88, p = 0.0002) \quad (10)$$

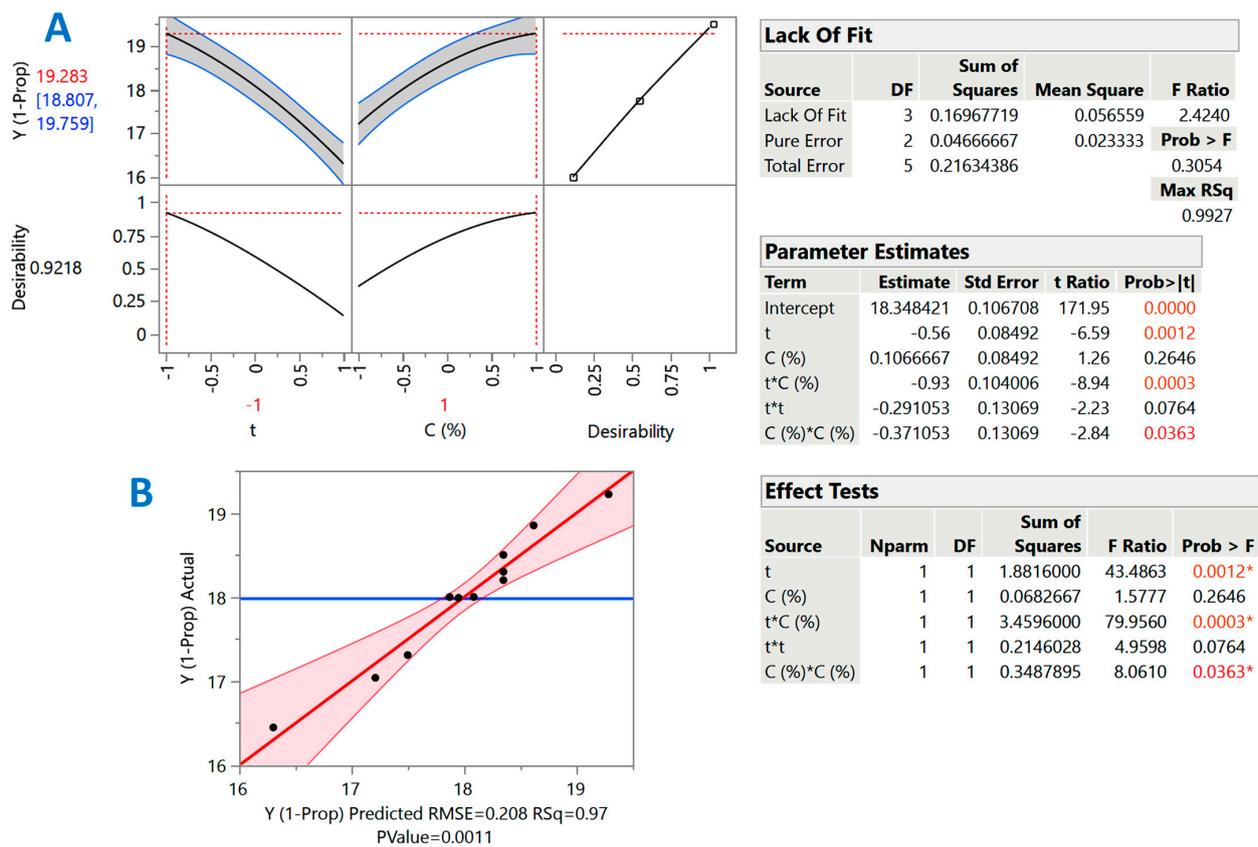
Thus,  $Y_{TP(max)}$  could be determined by using the maximum CSF and CFS, which were 0.95 and 7.95, respectively (Table 2). The  $Y_{TP(max)}$  values thus computed were 15.74 mg CGAE g<sup>-1</sup> DM and 15.71 mg CGAE g<sup>-1</sup> DM, respectively, which were virtually equal to the experimental value 15.38 mg CGAE g<sup>-1</sup> DM. In this case too, accurate predictions could be made using the models established.



**Figure 2.** Diagrams illustrating the correlations between  $Y_{TP}$  values and CSF (A), or CSF' (B). Bars indicate standard deviation. CSF, CSF', and  $Y_{TP}$  correspond to combined severity factor, alternative combined severity factor, and the yield in total polyphenols (expressed as chlorogenic acid equivalents—CGAE).

### 3.3. Response Surface Process Optimization

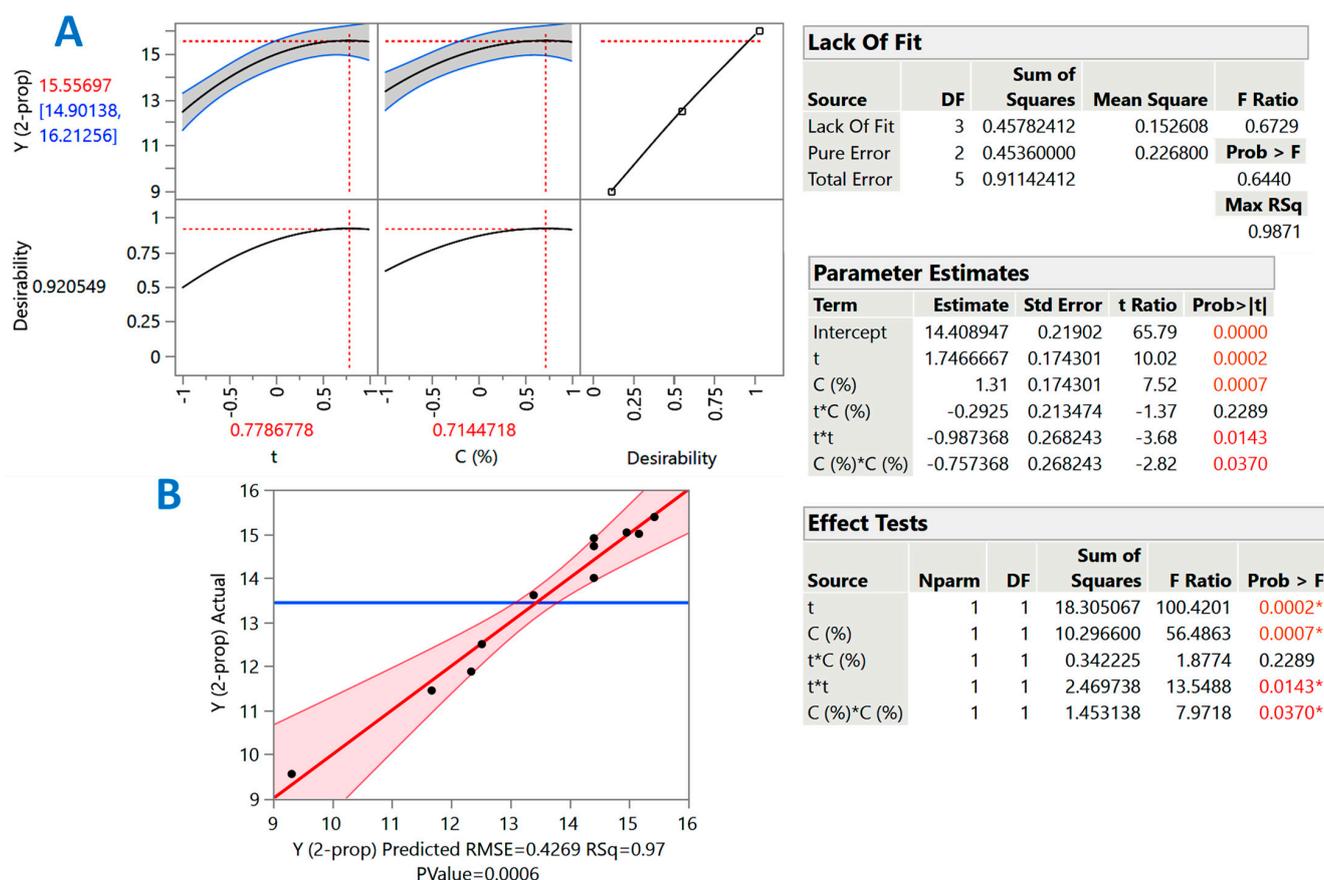
Based on the evidence derived from the severity-based models, solvent effects were pronounced and differentially affected polyphenol recovery from PP. On this ground, response surface optimization was used as a further means of modeling the organosolv treatments, by taking into account time,  $t$ , and catalyst (sulfuric acid) concentration,  $C_{SuAc}$ , as the process variables. This approach had the scope to evaluate the effects of  $t$  and  $C_{SuAc}$  on treatment performance, and to reveal possible synergistic (cross) functions. Model assessment and process optimization were based on analysis of variance (ANOVA) and lack-of-fit tests (Figures 3 and 4), considering the predicted and measured values' proximity (Table 3).



**Figure 3.** Statistical information on response surface optimization of the 1-propanol-based organosolv treatment of PP. Plot (A) shows the desirability function, through which prediction of optimized variable values could be made, as well as the estimated maximum  $Y_{TP}$ . Plot (B) shows the correlation of predicted and measured  $Y_{TP}$  values of each design point considered for the optimization. Values designated with different colors in the inset tables are statistically different.

**Table 3.** The design points included in the response surface optimization, the coded levels of the process (independent) variables, and the actual (measured) and predicted  $Y_{TP}$  values for both 1-propanol and 2-propanol-based organosolv treatments.  $Y_{TP}$  correspond to a combined severity factor, alternative combined severity factor, and the yield in total polyphenols (expressed as chlorogenic acid equivalents—CGAE).  $C_{SuAc}$  is the concentration of sulfuric acid in the solvent used for the treatment.

Design Point	Independent Variables		Response ( $Y_{TP}$ , mg CGAE $g^{-1}$ DM)			
	$X_1$ (t)	$X_2$ ( $C_{SuAc}$ )	1-Propanol		2-Propanol	
			Measured	Predicted	Measured	Predicted
1	-1	-1	17.04	17.21	9.56	9.32
2	-1	1	19.22	19.28	12.5	12.52
3	1	-1	17.99	17.95	13.61	13.39
4	1	1	16.45	16.30	15.38	15.43
5	-1	0	18.85	18.62	11.45	11.67
6	1	0	17.31	17.50	15.00	15.17
7	0	-1	18.02	17.87	11.88	12.34
8	0	1	18.07	18.08	15.03	14.96
9	0	0	18.30	18.35	14.72	14.41
10	0	0	18.22	18.35	14.01	14.41
11	0	0	18.54	18.35	14.91	14.41



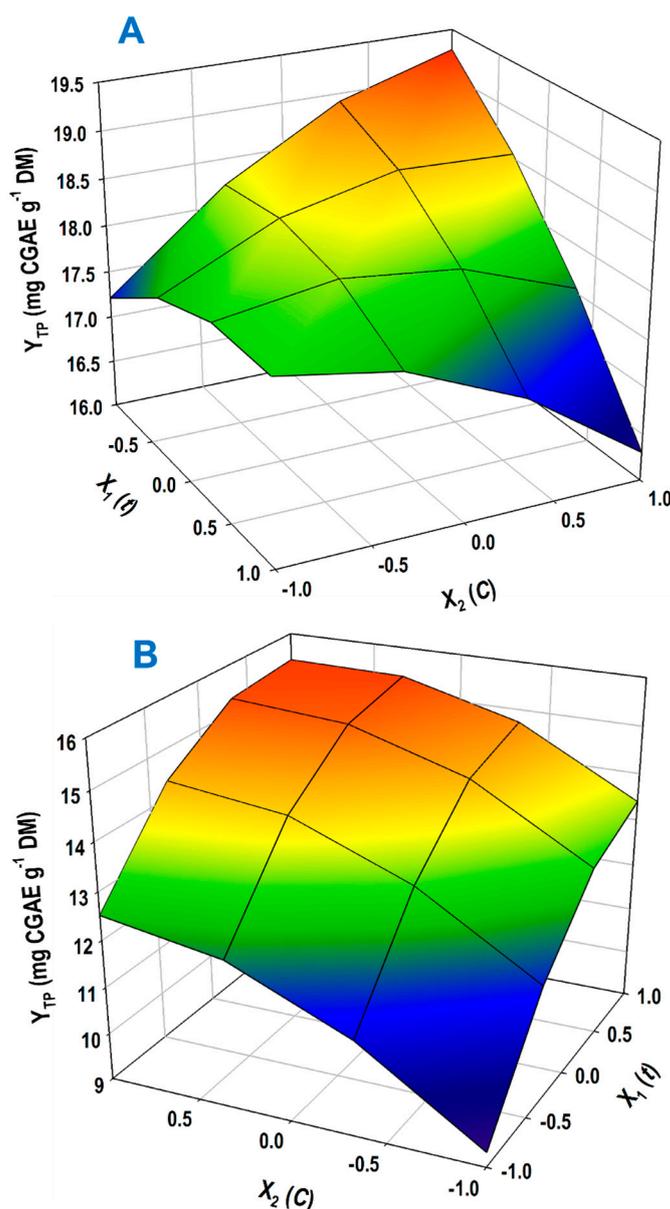
**Figure 4.** Statistical information pertaining to response surface optimization of the 2-propanol-based organosolv treatment of PP. Plot (A) shows the desirability function, through which prediction of optimized variable values could be made, as well as the estimated maximum  $Y_{TP}$ . Plot (B) shows the correlation of predicted and measured  $Y_{TP}$  values of each design point considered for the optimization. Values designated with different colors in the inset tables are statistically different.

The models derived were given in the form of equations containing only significant terms (Figures 3 and 4, inset table “Parameter estimates”), accompanied by the square correlations coefficients ( $R^2$ ), in order to provide a means of the total variability around the mean predicted by the models:

$$Y_{TP(1-Prop)} = 18.34 - 0.56X_1 - 0.93X_1X_2 - 0.37X_2^2 \quad (11)$$

$$Y_{TP(2-Prop)} = 14.41 + 1.75X_1 + 1.31X_2 - 0.99X_1^2 - 0.76X_2^2 \quad (12)$$

Both models found to have  $R^2$  were equal to 0.97 and highly significant  $p$  values for lack-of-fit for a confidence interval of at least 95% (Figures 3B and 4B). These data strongly suggested that the response surface models displayed excellent fitting to the measured (experimental) values. The 3D diagrams constructed based on the models depicted the effect of the process variables on the response ( $Y_{TP}$ ) and visualized the differences between the two solvents tested (Figure 5).

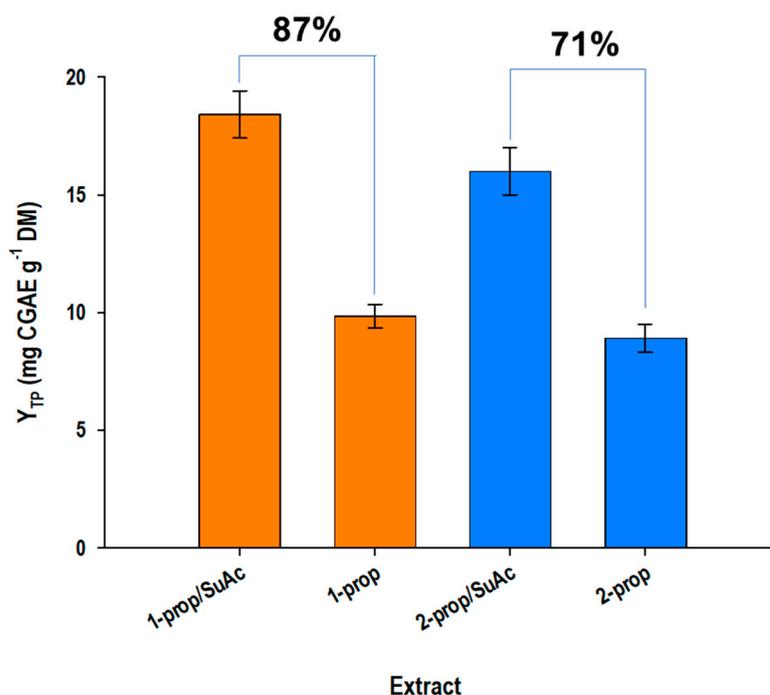


**Figure 5.** 3D graphs displaying the effect of variation of independent variables on the response ( $Y_{TP}$ ). Graph (A,B) correspond to treatments performed with 1- and 2-propanol. Where  $C_{SuAc}$  is the concentration of sulfuric acid in the solvent used for the treatment.

For the 1-propanol treatment,  $t$  ( $X_1$ ) was significant, but  $C_{SuAc}$  ( $X_2$ ) was not. However, the effect of  $C_{SuAc}$  was manifested by its cross term with  $t$  ( $X_1X_2$ ), and its quadratic term ( $X_2^2$ ). Nevertheless, quadratic effects of  $t$  were non-significant. By contrast, both  $X_1$  and  $X_2$  exhibited a significant effect on  $Y_{TP}$  when the treatment was performed with 2-propanol, and so did the quadratic terms  $X_1^2$  and  $X_2^2$ . However, no significant cross terms were seen in this case.

By employing the desirability function (Figures 3A and 4A), the theoretical optimal values for both  $t$  and  $C_{SuAc}$  could be determined, along with the predicted maximum response for each treatment. In the case of 1-propanol, maximum  $Y_{TP}$  ( $19.28 \pm 0.47$  mg CGAE  $g^{-1}$  DM) would require  $t = 60$  min and  $C_{SuAc} = 1.5\%$ . For the treatment with 2-propanol, maximum  $Y_{TP}$  was estimated to be  $15.56 \pm 0.66$  mg CGAE  $g^{-1}$  DM, with the optimum  $t$  and  $C_{SuAc}$  being 167 min and 1.36%, respectively. On the grounds of these data, it was made clear that the organosolv treatment with 1-propanol was more efficacious than that with 2-propanol, providing over 19% higher  $Y_{TP}$ . Furthermore, despite the comparable

$C_{\text{SuAc}}$ , the resident time required for the 1-propanol treatment was over than 4.5 times shorter than that determined for the 2-propanol treatment, meaning that the former was a less severe process. To bring out the role of acid catalysis in enhancing total polyphenol recovery from PP, treatments under optimal resident times but without sulfuric acid were also performed. For the treatment with 1-propanol, the presence of acid catalysts boosted  $Y_{\text{TP}}$  by 87%, while in the 2-propanol treatment, the enhancement was 71% (Figure 6). This outcome highlighted the importance of the acid catalyst in developing the organosolv treatment.



**Figure 6.** Plot portraying the effect of sulfuric acid, used as catalyst, on the treatment performance. Assignments: 1-prop/SuAc, treatment performed with 40% 1-propanol/1.5% sulfuric acid; 1-prop, treatment performed without sulfuric acid addition; 2-prop/SuAc, treatment performed with 40% 2-propanol/1.36% sulfuric acid; 2-prop, treatment performed without sulfuric acid addition. The resident time used for the treatments with 1-propanol (with or without sulfuric acid) was 60 min. The corresponding time for the 2-propanol treatments was 167 min. Bars on the columns represent standard deviation.  $Y_{\text{TP}}$  is the yield in total polyphenols, expressed as chlorogenic acid equivalents—CGAE.

A critical appraisal of the  $Y_{\text{TP}}$  levels attained by employing the 1-propanol/sulfuric acid treatment with those reported in several recent studies would illustrate the effectiveness of the process developed. Optimization of polyphenol extraction with hydroethanolic solutions has been reported to afford  $Y_{\text{TP}}$  between 9.46 to 10.31 mg CGAE g<sup>-1</sup> DM [19]. With water/methanol solvent, ultrasound-assisted extraction was of equal performance, providing  $Y_{\text{TP}}$  of 9.33 mg gallic acid equivalents g<sup>-1</sup> DM [27]. Combination of hydroethanolic solvent and microwave-assisted extraction was shown to give a level of 11 mg gallic acid equivalents g<sup>-1</sup> DM [28].

Results from another examination on ultrasound-assisted extraction of polyphenol from PP with water/ethanol solvent reported a maximum  $Y_{\text{TP}}$  of 6.20 mg gallic acid equivalents g<sup>-1</sup> DM [29]. On the other hand,  $Y_{\text{TP}}$  as high as 20 mg gallic acid equivalents g<sup>-1</sup> DM has been achieved with subcritical water extraction of PP [30], and 32.87 mg gallic acid equivalents g<sup>-1</sup> DM with sequential hydrothermal extraction [31], whereas extraction under alkaline conditions and high-pressure homogenization has afforded no more than 4.16 mg gallic acid equivalents g<sup>-1</sup> DM [32].

### 3.4. Polyphenolic Composition and Antioxidant Activity

Aside from the total polyphenol yield, the polyphenolic profile of the extracts obtained with 1- and 2-propanol was also of importance, and, thus, the extracts generated under optimized conditions were analyzed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) to tentatively identify and quantify the principal constituents. The analyses revealed that the principal compounds were chlorogenic acid, accompanied by caffeic acid and *p*-coumaric acid (see Supplementary Material). Chlorogenic acid was characterized by its molecular ion at  $m/z = 353$ , and the diagnostic fragments at  $m/z = 191.1$  and  $85.2$ . Likewise, caffeic acid was identified by the molecular ion at  $m/z = 179$  and the diagnostic fragment at  $m/z = 135.1$ , and *p*-coumaric acid by the corresponding ions at  $m/z = 163$  and  $119.3$ .

The treatment with 1-propanol/sulfuric acid and 2-propanol/sulfuric acid resulted in virtually equal caffeic acid recovery, but the former treatment afforded 50% higher chlorogenic acid recovery. Both extracts also contained minor amounts of *p*-coumaric acid, which, in the case of 2-propanol/sulfuric acid treatment, accounted for no more than 1.2% of the total hydroxycinnamates considered (Table 4). In total, the extract produced with the 1-propanol/sulfuric acid was 30% richer in hydroxycinnamates. The predominance of chlorogenic acid in PP extracts has been previously described by other authors, reporting yields of  $250.15$  [19],  $267.40$  [33], and  $904.21 \mu\text{g g}^{-1} \text{DM}$  [34]. However, yields as low as  $83.67 \mu\text{g g}^{-1} \text{DM}$  [26] and as high as  $4100 \mu\text{g g}^{-1} \text{DM}$  [29] have also been found. On the other hand, caffeic acid has been shown to accompany chlorogenic acid at significantly lower levels, ranging usually from  $89$  to  $920 \mu\text{g g}^{-1} \text{DM}$ , although its content may reach up to  $1297 \mu\text{g g}^{-1} \text{DM}$  [35].

**Table 4.** Polyphenolic composition and antioxidant characteristics of the extracts obtained under optimized conditions. Values are given along with the standard deviation. Assignments: CA, caffeic acid; CGA, chlorogenic acid; *p*-CouA, *p*-coumaric acid.

Sample	Phenolic Acid Content ( $\mu\text{g g}^{-1} \text{DM}$ )			Total	$A_{AR}$ ( $\mu\text{mol DPPH}$ $\text{g}^{-1} \text{DM}$ )	$P_R$ ( $\mu\text{mol AAE}$ $\text{g}^{-1} \text{DM}$ )
	CA	CGA	<i>p</i> -CouA			
40% 1-prop/1.5% SuAc	$772.25 \pm 54.30$	$1771.84 \pm 98.52$	$17.00 \pm 2.34$	2561.00	$148.66 \pm 10.32$	$29.94 \pm 1.85$
40% 2-prop/1.36% SuAc	$764.20 \pm 63.02$	$1181.80 \pm 84.61$	$24.04 \pm 1.87$	1970.00	$192.03 \pm 14.20$	$24.88 \pm 2.02$

Both extracts were also tested for antioxidant activity by determining the ferric-reducing power ( $P_R$ ) and the antiradical activity ( $A_{AR}$ ). With reference to  $A_{AR}$ , the extract obtained with 2-propanol/sulfuric acid treatment displayed 29% higher value compared to the extract produced with 1-propanol/sulfuric acid. Conversely, the 1-propanol/sulfuric acid treatment afforded extract with 20% higher  $P_R$  compared to the control extract obtained using with 2-propanol/sulfuric acid (Table 4). These discrepancies revealed a diversified response of the extracts to the  $A_{AR}$  and  $P_R$  tests. Such a disagreement of the results from the two antioxidants tests would not come as a surprise, given that the antioxidant responses of mixtures of antioxidant compounds may depend on several factors, such as the relevant proportion of each compound in the mixture tested. Evidence arising from the examination of the radical-scavenging activity of polyphenolic mixtures indicated the manifestation of antagonistic and/or synergistic effects, which depended on the nature of polyphenols in the mixture [36].

The study of several binary antioxidant mixtures at varying proportions with cyclic voltammetry and a chemiluminescence-based test confirmed such behavior, demonstrating again the expression of either antagonism or synergism, depending on the nature of the antioxidants interacting and their relative ratio [37,38].

#### 4. Conclusions

The examination presented herein clearly demonstrated that the organosolv treatment developed employing 1-propanol and sulfuric acid as a catalyst may be a highly effective means of recovering antioxidant polyphenols from waste potato peels. Models based on both response surface optimization and severity revealed that the 1-propanol-based treatment was significantly more effective compared to the one developed with 2-propanol, but also less severe. Furthermore, a critical comparison with the literature data suggested the treatment developed to be a high-performance process. The analysis of the extract generated under optimized conditions showed chlorogenic acid to be the predominant polyphenolic constituent, accompanied by caffeic acid and minor amounts of *p*-coumaric acid. Based on the evidence that has emerged out of this study, it could be argued that acid-catalyzed, 1-propanol organosolv treatments may have important prospects as effective processes for the recovery of high valued-added substances, such as chlorogenic acid, from potato-processing residues. Such a process could be integrated into a wider frame of a potato waste biorefinery to establish strategies of holistic waste valorization, which would contribute towards development of circular economy routes and sustainable food production.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app13169484/s1>, Figure S1: A representative total ion chromatogram of 1-propanol extract obtained under optimized conditions: RT 4.41 min, chlorogenic acid; RT 4.56 min, caffeic acid; RT 6.16 min, *p*-coumaric acid.

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