

Article

Potato Peels as a Source of Novel Green Extracts Suitable as Antioxidant Additives for Fresh-Cut Fruits

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Featured Application: An innovative green procedure to efficiently recover value added compounds from potato peels was proposed in order to formulate food-grade additives useful to replace or at least reduce synthetic preservatives in minimally processed fruits.

Abstract: Potato is a source of different bioactive compounds, and the potato transformation industry produces conspicuous quantities of potato peels as waste. In this context, the objective of this research was twofold: (i) the evaluation of the recovery of bioactive compounds from organic potato byproducts through an innovative multistep green extraction process; (ii) to evaluate the preservation during storage of the main quality-physicochemical parameters of minimally processed apples treated with two different natural extracts obtained. The potato extracts were obtained by solid CO₂ cryomaceration followed by solid/liquid extraction based on water or 10% ethanol/water solutions. The efficacy of potato extracts, with or without 1% of citric acid, was tested in comparison with traditional preserving compounds in minimally processed apple preparation. All the extracts were characterized by a high antioxidant power and were rich in phenol compounds, showing a good activity in keeping the qualitative parameters of fresh-cut apple. A significant anti-browning effect as well as a slowing down of the softening of fruits during storage were observed. The obtained results suggest the suitability of the potato extracts as antioxidant additives for fresh-cut fruits, thus avoiding the use of unsafe chemicals.

Keywords: minimally processed fruits; fresh-cut apples; potato waste; potato peels; natural antioxidant; phenols green extraction; shelf life

1. Introduction

Changes in consumer lifestyle, together with the increasing desire for fresh quality in all products, have led to the development of a new category of minimally processed (MP) foods [1]. Among them, ready-to-eat fresh-cut fruits are an important vehicle of antioxidant-compound intake for an ever-growing number of consumers and represent one of the fast-growing segments in food retail establishments [2]. Fruits and vegetables are indeed rich in antioxidants, gaining wider interest as a

nutritional strategy to prevent various pathologies [3]. The aims of minimally processing technologies are mainly to retain as much as possible the desired characteristics in terms of flavor, color, and texture of fresh-food products and to provide a foodstuff chemically and microbiologically safe [4]. Besides, the main critical point for the postharvest life of fresh-cut fruit slices is the development of physiological disorders mainly due to browning on the cut surface because of physical stresses imposed on cells during preparation. To inhibit this occurrence, several chemical treatments, including reducing agents and chelating compounds, have been used as food additives [5]. However, certain synthetic compounds such as BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) tend to form toxic and carcinogenic derivatives, suggesting the need for alternative disinfectants or other techniques [6].

In the last two decades, natural compounds with antioxidant capacity aroused a growing interest [7] as possible natural products useful to replace synthetic additives. Polyphenols, carotenoids, and vitamins (mainly E and C) may be considered a valid challenge for the shelf life of healthy MP fruits thanks to their ability to scavenge free radicals and reactive oxygen species associated with the development of cardiovascular diseases and several cancers [3].

An interesting source of natural value-added compounds could be found in the waste derived from food-processing industries [8]. The recovery and valorization of these waste products can represent a promising strategy to manage the environmental and economic problems posed by the increasing amount of vegetal waste and residues generated worldwide by food-processing industries.

One of the most widely consumed vegetables worldwide is potato (*Solanum tuberosum*) whose consumption patterns are gradually shifting from fresh to processed formulation (e.g., mashed potatoes, chip potatoes, etc.) thus resulting in an increase in waste generation [9]. Due to their high potential for pollution, the management of potato byproducts represents an important environmental problem for food-processing companies [10].

Potato is rich in starch, dietary fiber, amino acids, minerals, vitamins, and phenolics [11]. Potato peels represent the major waste from the potato processing industry, and they can be revalorized as a source of functional and bioactive compounds with particular attention to phenolic acids [12]. Thus, potato waste represents promising cheap resources and its recovery and recycling within the food chain could be a sustainable strategy to address the present challenges of the industrialized world [13].

Extraction of bioactive compounds, especially polyphenols, (mainly polyphenols) from potato skin by means of mild technologies permits to preserve the nutritional and pharmacological properties as well as the antioxidant power of these chemicals [14]. The application of conventional solvent extraction methods (CSE) to extract phenols from plant material is widely diffused, but it usually requires long extraction times, large amounts of organic solvents, and high temperatures that can cause the degradation of thermo-sensible molecules as well as contamination with trace amounts of potentially toxic solvents [14]. Moreover, the sustainability of the extraction technology and the safety of the extract is of the utmost importance [15,16].

Robles-Ramírez and Fritsch [17,18] investigated the effectiveness of bioactive compounds extracted from potato peel waste to reduce the oxidative degradation of different lipid food matrices, but to the best of our knowledge, no data about their possible application for minimally-processed fruit storage are available in literature.

In this context the objective of this research was twofold: (i) to verify the effectiveness of an innovative multi-step green extraction process to recover some high-added-value antioxidant compounds from organic potato byproducts; (ii) to evaluate the preservation during postharvest storage of the main quality physicochemical parameters of MP fruits. In order to improve the extraction yield, as well as to avoid the oxidation of extracted compounds [19–22], the potato peels were cryomacerated with the use of solid CO₂ before their utilization as substrate in solid/liquid extraction with different solutions. Finally, the obtained extracts were utilized alone or in combination with citric acid in the pretreatment of cubes of fresh-cut apples, and the results obtained in terms of

shelf life extension were compared with those collected in the same experimental conditions when traditional preserving solutions (i.e., ascorbic acid, citric acid, and BHT) were utilized.

2. Materials and Methods

2.1. Potato Peel Extraction

Organic yellow potatoes “Bologna” PDO (protected designation of origin) were purchased from a local large-scale retail market in Pisa (Italy). The peels with a thin periderm layer (total average thickness: 0.5–1.0 mm) collected from manually peeled tubers by means of a ceramic knife to avoid the interference with metallic ions, thus slowing down the start of oxidation processes, were immediately stored in an inert atmosphere (N_2) in a stainless-steel vat provided with devices for the automated temperature control.

To maximize the recovery of the bioactive compounds from potato waste, the peels stored as described were maintained in direct contact with solid CO_2 (ratio peels/ CO_2 , $s = 1/1$ w/w) over a period of 24 h. The addition of a cryogen to vegetal matrix induces, indeed, intracellular water freezing, and as a consequence of the greater volume occupied by the same amount of water in solid state than in the liquid phase, the consequent laceration of cellular membranes (cellular break) occurs permitting the immediate diffusion of many cellular compounds in the liquid phase [20]. The bioactive compounds present in potato peels (P) were then protected by oxidation due to the sublimation of solid CO_2 that at room temperature and 1 atm of pressure passes to the gaseous phase, thus forming an inert gas layer in storage atmosphere [19]. The cryomaceration was stopped by the increasing of the temperature, thus promoting a controlled defrosting phase in inert atmosphere (N_2 flow).

In order to optimize the best operating conditions to be adopted, we utilized either of two different solvent solutions: distilled water (named W) or 10% Ethanol/water solution (named E10). In each extraction run, the cryomacerated and defrosted potato peels were then extracted by solid/liquid extraction (ratio 1/20 w/w) starting from 20 g of fresh weight. The extractions were prolonged for 24 h in the dark and inert atmosphere (N_2), and the following conditions were maintained: $T = 27$ °C, stirring rate = 650 rpm.

All the extracts were filtered under vacuum and maintained in inert atmosphere (N_2) at $T = -20$ °C until analysis.

2.2. Potato Peel Extracts Characterization

2.2.1. Total Phenols Content

The total phenols content of both extracts were determined colorimetrically at 700 nm, using the Folin–Ciocalteu reagent [23]: in a 100 mL flask, 60 mL of deionized water, 1 mL of each extract were added and mixed with 5% of Folin and 15% of sodium carbonate (20%). After a waiting phase of 30 min the samples were ready for the spectrophotometric reading at 700 nm.

Moisture content of potato peels was determined according to standard International Official Method of Analysis (AOACs) [24] and the values of gallic acid equivalent [25] were used to represent the phenolic content as mg/g dry weight.

2.2.2. Antioxidant Capacity of the Extracts Determined by ABTS and FRAP Assays

Because traditional assays can provide only an estimation of the real antioxidant potential of the natural plant extracts, we used two different methods to obtain a more complete view of the antioxidant ability of our samples and to compare the effects of the different extraction protocols.

2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulphonic acid Antioxidant assay (ABTS) of both extracts was performed as reported in a previous paper [26].

The radical solution was diluted in water in order to obtain at 734 nm an absorbance of 0.70 ± 0.05 . The decrease in absorbance was monitored after 5 min from the addition of the extract (1%

v/v) and compared to a dose-response curve of standard Trolox in the 0.2–1.5 mM range. The activities of the extracts were expressed as Trolox equivalent antioxidant capacity (TEAC) L⁻¹ extract.

The ferric reducing antioxidant power (FRAP) was carried out using a freshly prepared reagent that contained 2 mM ferric chloride and 1 mM TPTZ (2,4,6-tris(2-pyridyl)-s-triazine). A total of 0.25 M acetate buffer at pH 3.6 (2.0 mL), the FRAP reagent (900 µL), and the plant extract (100 µL) were mixed in a spectrophotometric cuvette. A calibration curve was prepared with standard solutions of ferrous ammonium sulphate in the range 0–1000 µM Fe (II). The working wavelength was 593 nm.

2.3. Fresh-Cut Apple Processing and Sample Preparation

Fruits were prepared according to safety statements and recommendations for MP apples [27]. ‘Golden Delicious’ organic apples (*Malus domestica Borkh*) were purchased from a local large-scale retail market in Pisa (Italy) and stored at room temperature before being utilized in experiments. Apples (category II, diameter 75–85 mm) were selected for uniform size and lack of defects.

Apples were washed in running water, hand-peeled and cored with a ceramic knife, longitudinally cut into 4 wedges, and each one cut into 3 cubes that were placed in baskets and completely dipped in different preserving solutions (apples/solution, 1:4 w/w) for 2 min, manually stirring. The solutions (Table 1) were represented by standard chemical compounds usually adopted in MP apple and novel natural compounds obtained from potato peels (P). The P extracts were utilized alone or in combination with citric acid, widely used commercially as an antibrowning agent [28]. Moreover, the pH of solutions, determined with a pH-meter (3310 (Jenway, UK), was indicated.

Table 1. Different preservative media used for dipping of fresh-cut apple cubes: - standard compounds; - novel compounds: water (W) and ethanol 10% (E10) extracts from potato peels (P) and control.

Code	Composition of Solutions	pH of Solutions
DW	distilled water, control	7.00
BHT *	1% butylated hydroxytoluene	7.75
CA *	1.0% citric acid	2.01
AA *	0.5% ascorbic acid	2.66
AA-CA *	1.5% ascorbic acid + citric acid	2.00
PE **	water solution of E10 1:1	6.10
PE-CA **	PE +1% citric acid	2.18
PW **	water solution of W 1:1	6.10
PW-CA **	PW +1% citric acid	2.17

* Conventional preserving compounds, ** Novel preservative solutions.

Washing, dipping treatments, and measurements of the pH of solutions were carried out at room temperature (20 ± 1 °C). All reagents used were of analytical grade (Sigma Chemical, Co., St. Louis, MO, USA).

After dipping, the apple cubes were drained on absorbent paper and placed in plastic lidded containers (150 cc from Cuki, Turin, Italy) with air as storage atmosphere. Containers containing three cubes each coming from different apples were stored in controlled chambers at different temperatures and times: (a) 20 ± 1 °C (16/8 h photoperiod) to stimulate a short browning reaction; (b) 4 ± 1 °C (dark conditions for 3 days) to simulate the average standard cool retail storage condition.

Each dipping treatment consisted of 3 replicates represented by 3 different containers.

2.4. Assessment of Shelflife Analysis

Shelf life can be defined as the length of time during which the food retains the required level of quality that appeals to the consumer [29,30]. The main specific markers, color, total soluble solids, and apple flesh firmness for fresh-cut apple quality, were monitored in the first hours after preparation at room temperature and during a short period of cold storage.

Color of apple surface was quantified using a benchtop tristimulus colorimeter (Eoptis, Mod. CLM-196 Benchtop, Trento, Italy) supplied with its own white reference standard. Color was evaluated on the basis of CIE L*a*b* color System accepted by the Commission International Eclairage, where L* is the lightness, a* and b* are the red-greenness and blue-yellowness components, respectively.

According to [31], the results were expressed as Δ Browning Index (Δ BI) values by the following equation:

$$BI = 100 * (x - 0.31) / 0.172 \quad (1)$$

where

$$x = (a^* + 1.75L^*) / (5.645L^* + a^* - 3.012b^*) \quad (2)$$

and

$$\Delta BI = BI_f - BI_s \quad (3)$$

where: BI_f = BI at the end of each observation time, BI_s = BI at the start of each experiment.

Total soluble solids (TSS) obtained from the fresh-tissue sap of apple flesh cubes were measured using a hand refractometer (Mod. 2369-Bertuzzi, Milan, Italy) and expressed as °Brix. Flesh firmness or texture of apple flesh cubes was evaluated by a manual penetrometer (Mod. 53205, TR Turoni & C. snc Forli, Italy), measuring the resistance of flesh to the entrance of a metal probe (8 mm diameter and depth). The force needed to break parenchyma cells in the cortex was expressed in kilogram-force ($\text{kg}/0.5 \text{ cm}^2$).

Moreover, at every storage time the water loss from the apple cubes was gravimetrically monitored computing the weight loss percentage.

2.5. Statistical Analysis

Statistical analysis of obtained data was conducted by GraphPad Prism (version 5.00 for Windows, GraphPad Software, La Jolla, San Diego, CA, USA). Analysis of variance (ANOVA) and the test of mean comparisons according to Bonferroni were applied; Student *t*-test was also performed at $p \leq 0.05$. All data are reported as mean values \pm SE (standard error).

3. Results

3.1. Extraction Yield and Chemical Characterization of the Potato Peel Extracts

The content of bioactive compounds in potato peels appears directly affected by cultivar, growing practices, and storage conditions before sampling; moreover, the extraction yield is greatly influenced by solvent composition as well as extraction process utilized [32], so data related to phenolic content of potato peels available in the literature appear affected by a great variability [32–34].

In the experimental conditions adopted, both potato extracts showed a very interesting concentration in total phenol compounds, and the sample obtained using ethanol 10% as extraction medium was characterized by the highest value (Table 2).

Table 2. Phenolic content and antioxidant capacity of potato water extract and potato ethanol extract. Data are reported as mean \pm SE (n.3). For each row, asterisks indicate significant differences between solvents (W = water, E = 10% ethanol) used for the extraction of potato peels (P) according to Student *t* test at $p < 0.05$ * or $p < 0.001$ **.

	W	E10
Phenolic content (gallic acid mg/g dry weight)	2.92 \pm 0.41	3.95 \pm 0.02 *
Antioxidant capacity ($\mu\text{mol TEAC/mL}$)	0.17 \pm 0.02	0.21 \pm 0.01 *
Ferric reducing antioxidant power ($\mu\text{molFe}^{2+}/\text{mL}$)	0.19 \pm 0.004	0.28 \pm 0.007 **

As the effect of antioxidants on ABTS and FRAP radical scavenging was related to their hydrogen-donating ability, this activity of the extracts on ABTS and FRAP was examined as a

function of the different extraction procedure (water or ethanol 10% solvent). As expected on the basis of its phenolic content, the sample obtained using ethanol 10% exhibited also the highest antioxidant capacity (Table 2).

According to the literature [20–22,35], cryomaceration of vegetal byproducts by means of solid carbon dioxide can be profitably applied to improve the green extraction of bioactive compounds, favouring the next mass transfer processes in solid/liquid extraction. Furthermore, the concentration of phenolic compounds in both of the proposed extracts appears comparable with data obtained by our group when Sc-CO₂ was utilized in combination with ethanol to promote the supercritical fluid extraction (SFE) of phenolic compounds from potato byproducts [36]. For this reason, it was possible to suggest that the cryomaceration of potato peels can represent an interesting and cheap process easy to make without too complex equipment to efficiently improve the extraction yield of bioactive compounds from potato peels.

According to Friedman and co-workers [37], potato peels are a good source of glycoalkaloids (i.e., α -chaconine and α -solanine) and phenolics, mainly represented by chlorogenic acid, chlorogenic acid isomer, and caffeic acid. While the dual biological functions of potato glycoalkaloids and controversial safe levels are still a matter of discussion in scientific communities [38,39], as far as we know, adverse effects of potato glycoalkaloids in humans have not been detected when their exposure dose was below 1.25 mg/kg body weight (BW) [40]. On the other hand, beneficial health properties of phenolic compounds in potatoes and byproducts are well recognized [11,41], and they were profitably investigated as food additives in reducing the lipid oxidation [42] and improving the nutritional quality of cakes [43].

3.2. Effect of Dipping on Browning

The visual impact is an important trait associated with quality of fresh fruits and vegetables as well as of fresh-cut products. In particular, the quality is expressed by the surface color of fresh cuts and their changes during storage, parameters which greatly influence the purchase decision of consumers [44]. Fresh-cut products are subject to enzymatic browning of cut tissues due to the contact between enzymes and cytoplasmic and nucleic substrates, normally protected in different cell compartments [45]. Enzymatic browning reaction in fruits is primarily catalyzed by polyphenoloxidase (PPO) in the presence of oxygen [46]. PPO released during cutting acts on phenols, primarily causing browning of cut-apple surface [47]. Wounding may also determine the ethylene-induced activation of phenylalanine ammonia lyase (PAL) that regulates the biosynthesis of phenolic compounds, thus affecting their metabolism [48].

During the storage at 20 °C, differences in surface color of apple cubes among dipping treatments adopted in these experimental conditions were observed (Figure 1).

After 2 h of storage time (Figure 2), the browning appearance was evident in control dipping (DW) which showed the highest Δ BI, while adding the preservative agents, the tissue browning was significantly reduced ($p < 0.05$). The potato extracts, both water (PW) and ethanol (PE) solutions, showed an anti-browning effect comparable to the standard compounds. The beneficial effect exerted by P extracts could be linked to their phenolic content. Phenols have shown different behavior in enzymatic browning, depending on the type of compounds involved [49]. In the case of potato peels, the phenolic fraction contains substances, such as chlorogenic acid and caffeic acid [34], able to inhibit the PPO activity [28].

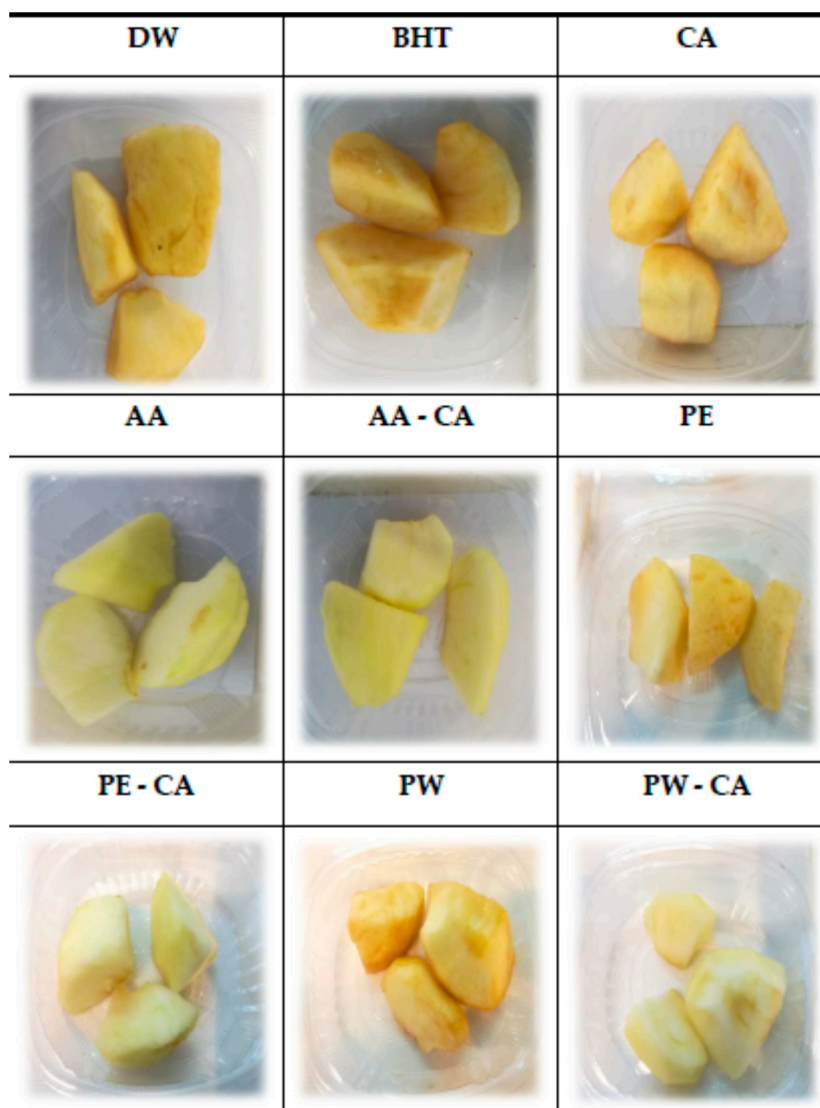


Figure 1. Changes of browning index (BI) expressed as values of Δ Browning Index (Δ BI) of fresh-cut apples treated with different preservative media (Table 1) Data are referred to storage at 20 ± 1 °C ($t = 2$ and 4 h) and 4 ± 1 °C ($t = 1$ and 3 days). Values are means \pm SE and different letters indicate significant statistical difference ($p \leq 0.05$).

In particular, both potato extracts, used in combination with CA had a beneficial effect also after 4 h of storage similar to AA-CA, confirming the efficacy of organic acids in preserving low pH values. In this experimental trial, the AA alone showed a higher efficiency than AC. However, their combination was proved to exert the maximum anti-browning effect.

The storage condition at 4 °C (Figure 2) showed a less severe browning degree in comparison to storage at room temperature. In general, the oxidation grade of tissues dipped with PE (Figure 2) was similar to DW. When PE and CA were combined, they produced a synergic effect inducing a strong browning inhibition. Thus, PE were able to retain color and control enzymatic browning alone or in combination with CA, similarly to results obtained at room temperature.

This finding could be due to the influence of CA whose anti-browning effect in MP fruits and vegetables has been well known [28,50] because of its copper chelating or acidulant role inactivating the PPO [51].

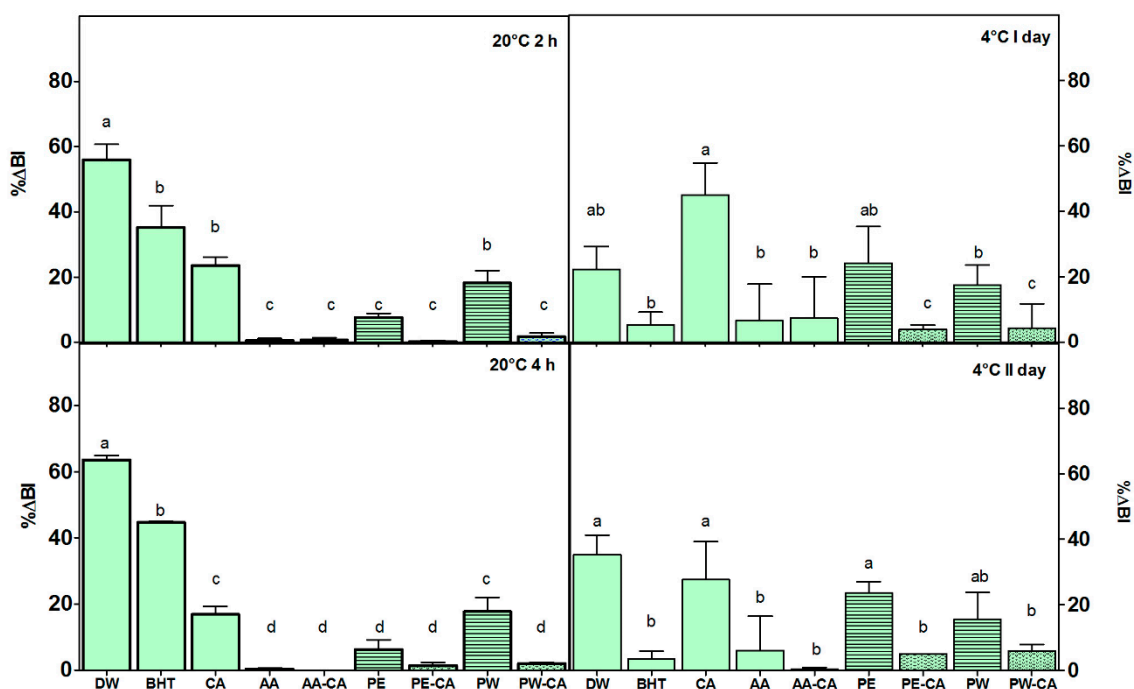


Figure 2. Visual appearance of browning in fresh-cut apples treated with different preservative media (sample codes are described in Table 1). Samples were stored at 20 ± 1 °C (2 and 4 h) and 4 ± 1 °C (1 and 3 days).

3.3. Effect of Dipping on TSS

Maintaining the original TSS content is a key requisite in storage to preserve fresh-cut apples sensory qualities. Indeed, sweetness is a fruit quality trait which is crucial for consumer acceptance [52]. In particular, sweetness in apples is related to sucrose, glucose and fructose content, with 50% of sugar present being fructose [53].

Just after cutting, Golden Delicious apple fresh-cuts were characterized by a TSS content of about 12 °Brix; at this commercial stage, the changes associated with ripening were already accomplished, obtaining the maximum soluble levels.

During the storage at 20 °C (after 2 and 4 h) the water control (DW) maintained the initial TSS values while a reduction was observed in all the other treatments (Figure 3).

This occurrence could be due to the highest water loss recorded in DW samples (about 0.4% fresh-weight reduction) in comparison with losses observed in the other treatments (about 0.2% fresh-weight reduction). The TSS changes related to the water loss rate were in agreement with studies carried out during the storage of apple fresh cuts [2,54]. Both potato PE and standard compounds used in this experiment demonstrated a protective effect in minimizing the water loss in comparison with DW. In particular, the role of AA in lowering physiological loss in tissue weight was observed in different fruit species [55,56]. The reduction of TSS in PE and PW treated apple cubes could be related with the enhanced respiration activity during storage at room temperature, as observed by Rux and co-workers [57]. It is important to stress that using PE and PW extracts, TSS values remained at acceptable levels within a changing range of 8%, similarly to what obtained in other studies, even in 'Golden Delicious' apple slices where the TSS of samples did not substantially change during storage [57,58].

In contrast to the effect observed at 20 °C, in which a decrease in the TSS values was recorded, a weaker TSS decrement was measured in samples stored at 4 °C (Figure 3). This could be attributed to the reduction in the respiratory rate, as observed by several authors in analogous conditions. The lowest temperature was more efficacious to maintain the TSS degree, in accordance with several researches reporting no substantial changes in apple slices: [59] found values that ranged from 14.6

to 12.8 °Brix for cv. Gala apples coated with alginate and stored at 5 °C. Fontes et al. [60] obtained similar results treating apples (cv. Gala) with a solution of ascorbic acid (1%), citric acid (0.5%), calcium chloride (0.25%), and sodium chloride (0.7%) stored at 2 °C [61].

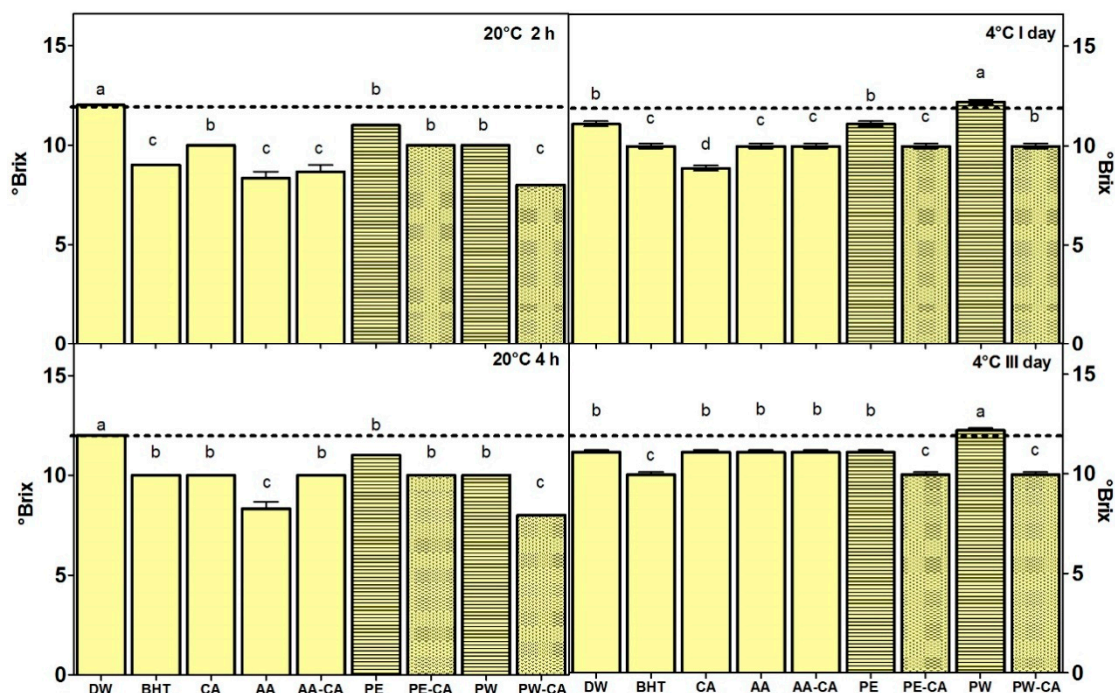


Figure 3. Total solid content (TSS) expressed as °Brix of fresh-cut apples treated with different preservative media (sample codes are described in Table 1). Dotted line represents the initial value. Data are referred to storage at 20 ± 1 °C (2 and 4 h) and 4 ± 1 °C (1 and 3 days). Values are means \pm SE and different letters indicate significant statistical difference ($p \leq 0.05$).

3.4. Effect of Dipping on Firmness

The maintenance of firmness is considered a positive attribute in minimally processed apples and it is also a major quality criterion for consumer acceptability. Cell size, cell-to-cell adhesion, tissue turgor biochemical and biophysical cell wall properties define tissue strength characteristics [44,57]. The loss of texture and the degradation of tissues determine the softening of fruits not only during the ripening but also under particular conditions such as the wounding procedures for obtaining minimal processed products.

In the present study, a firmness average of 2.70 kg/0.5 cm² was recorded on apple wedges prior the processing procedures starting. After storage at 20 °C, apple cubes maintained a good texture without differences between the two times (Figure 4). However, apples treated with the standard compounds presented the lowest values of firmness, usually due to ruptured cell wall and weakened cell-to-cell adhesion, which in turn negatively influenced tissue strength [57]. Previous results reported in the literature showed how physical and chemical changes could affect integrity of tissue structure and enzymatic hydrolysis of cell wall pectic substances [62]. Hydrolysis of protopectins to water soluble pectins, diffusion of sugar into intercellular spaces, decrease in cellulose crystallinity, ion movement from the cell wall, and thinning of cell walls are assumed to intensify softening [44]. Interestingly, the firmness of apples treated with potato extracts PE-CA and PW-CA remained unchanged during storage, inhibiting the softening of flesh tissues. A synergic effect stood out comparing the results obtained with CA, PE, and PW, alone or combined with each other.

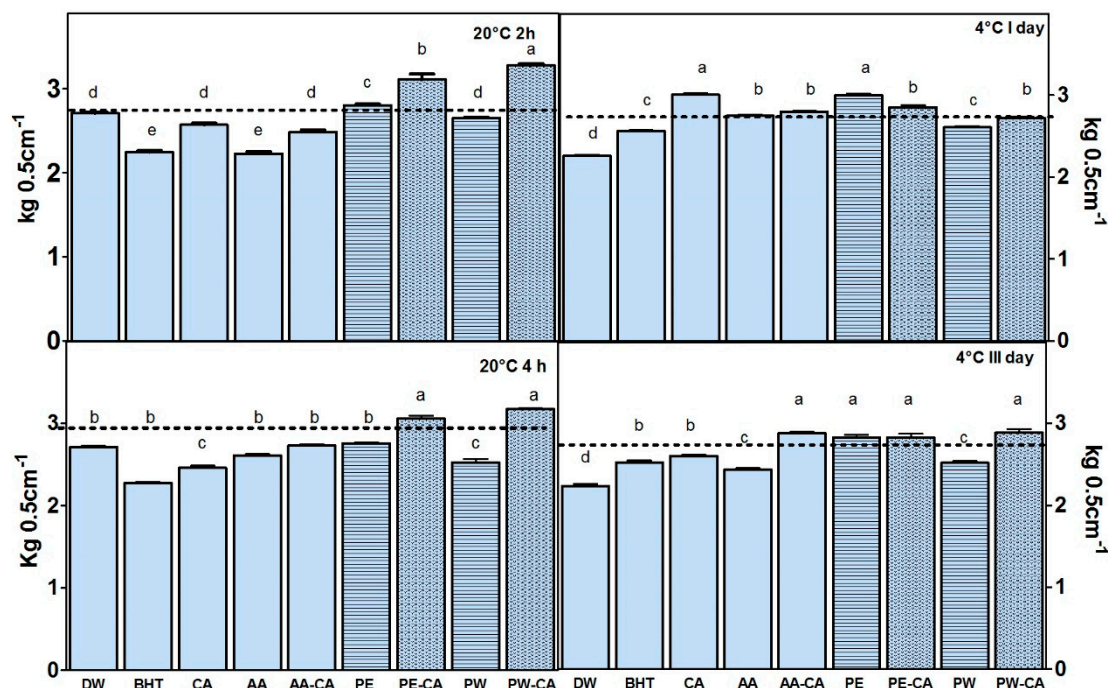


Figure 4. Flesh firmness expressed in kilogram-force (kg/0.5 cm²) of fresh-cut apples treated with different preservative media (sample codes are described in Table 1). Data are referred to storage at 20 ± 1 °C (2 and 4 h) and 4 ± 1 °C (1 and 3 days). Values are means ± SE and different letters indicate significant statistical difference ($p \leq 0.05$).

Under cold temperature at 4 °C (Figure 4), in DW dipping treatment a texture decrease was observed with a tissue strength decline of about 17% after 1 day of storage. All the other agents, particularly PE and PE-CA, showed effectiveness in maintaining the cut surface firmness until 3 days of storage.

4. Discussion

In this context, the results from this study support the possibility to propose an efficient green procedure, using water (PW) or ethanol aqueous solution (10%) (PE) to recover value added compounds from potato peels in order to formulate food-grade additives useful to replace or at least reduce synthetic preservatives in freshly stored vegetables.

While the final validation of the proposed method requires the comparison of the results obtained with those derived from other known extraction techniques (i.e., other solvent composition, ultrasound assisted, etc.), the results showed appear encouraging, and the cryomaceration of potato peels appears as a very efficient as well as easy way to realize the pre-treatment phase, thus promoting the extraction of bioactive compounds from these wastes.

The novel formulations (PE and PW) were particularly rich in phenol compounds. As a consequence of their interesting antioxidant power, PE and PW exhibited a good activity in keeping the quality of fresh-cut apple, regardless of the solvent utilized during extraction. In particular, a significant anti-browning effect as well as a slowing down of softening of fruits were observed.

Although this study is the first step in this direction, the potato peel extracts could represent potential novel natural additives of interest with the possibility of replacing or at least reducing synthetic preservatives in post-harvest treatments for the production of MP fruits. Furthermore, the employment of potato peels proposed in this study may contribute to their valorization as a promising strategy to manage the environmental and economic problems caused by the increasing amount of potato waste and residues from food-processing industries.

In the present study our attention has been focused on the overall effect showed by different antioxidant compounds present in the potato extract as a whole [63]. Future experimental investigations are needed to estimate the suitability as well as the economic feasibility of the replacement of unsafe chemicals with potato extracts in extending fresh-cut fruit. In particular, the antimicrobial effects, the sensory impact, and a more detailed chemical characterization of PE and PW need to be performed.

Author Contributions: F.V., S.B., and A.Z. conceived and designed the experiments; M.O., A.T., C.S., I.T., and M.M. performed the experiments; M.L. analyzed the data and made graphs; F.V., C.S., S.B., and A.M. wrote the paper. A.M. coordinated the project.

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References

1. Varela, P.; Salvador, A.; Fiszman, S.M. The use of calcium chloride in minimally processed apples: A sensory approach. *Eur. Food Res. Technol.* **2007**, *224*, 461–467. [[CrossRef](#)]
2. Tappi, S.; Tylewicz, U.; Romani, S.; Dalla Rosa, M.; Rizzi, F.; Rocculi, P. Study on the quality and stability of minimally processed apples impregnated with green tea polyphenols during storage. *Innov. Food Sci. Emerg. Technol.* **2017**, *39*, 148–155. [[CrossRef](#)]
3. Trivellini, A.; Lucchesini, M.; Maggini, R.; Mosadegha, H.; Villamarin, T.S.S.; Vernieri, P.; Mensuali-Sodi, A.; Pardossi, A. Lamiaceae phenols as multifaceted compounds: Bioactivity, industrial prospects and role of positive-stress. *Ind. Crops Prod.* **2016**, *83*, 241–254. [[CrossRef](#)]
4. Bansal, V.; Rahman, M.S.; Siddiqui, M.W. Minimally processed foods: Overview. A review. In *Minimally Processed Foods*, 1st ed.; Siddiqui, M.W., Rahman, M.S., Eds.; Springer International Publishing: Basel, Switzerland, 2015; pp. 1–15.
5. Paiva-Martins, F.; Correia, R.; Felix, S.; Ferreira, P.; Gordon, M.H. Effects of enrichment of refined olive oil with phenolic compounds from olive leaves. *J. Agric. Food Chem.* **2007**, *55*, 4139–4143. [[CrossRef](#)] [[PubMed](#)]
6. Chen, C.; Hu, W.; He, Y.; Jiang, A.; Zhang, R. Effect of citric acid combined with UV-C on the quality of fresh-cut apples. *Postharvest Biol. Technol.* **2016**, *111*, 126–131. [[CrossRef](#)]
7. Prior, R.L.; Wu, X.; Schaich, K. Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. *J. Agric. Food Chem.* **2005**, *53*, 4290–4302. [[CrossRef](#)]
8. Vardanega, R.; Prado, J.M.; Meireles, M.A.A. Adding value to agri-food residues by means of supercritical technology. *J. Supercrit. Fluids* **2015**, *96*, 217–227. [[CrossRef](#)]
9. Rodríguez Amado, I.; Franco, D.; Sánchez, M.; Zapata, C.; Vázquez, J.A. Optimization of antioxidant extraction from *Solanum tuberosum* potato peel waste by surface response methodology. *Food Chem.* **2014**, *165*, 290–299. [[CrossRef](#)]
10. Strati, I.F.; Oreopoulou, V. Recovery of carotenoids from tomato processing by-products—A review. *Food Res. Int.* **2014**, *65*, 311–321. [[CrossRef](#)]
11. Akyol, H.; Riciputi, Y.; Capanoglu, E.; Caboni, M.F.; Verardo, V. Phenolic Compounds in the Potato and Its Byproducts: An Overview. *Int. J. Mol. Sci.* **2016**, *17*, 835. [[CrossRef](#)]
12. Schieber, A.; Aranda Saldaña, M.D. Potato Peels: A Source of Nutritionally and Pharmacologically Interesting Compounds—A Review. *Food* **2009**, *3*, 23–29.
13. Pinela, J.; Prieto, M.A.; Barreiro, M.F.; Carvalho, A.M.; Oliveira, M.B.P.P.; Curran, T.P.; Ferreira, I.C.F.R. Valorisation of tomato wastes for development of nutrient-rich antioxidant ingredients: A sustainable approach towards the needs of the today’s society. *Innov. Food Sci. Emerg. Technol.* **2017**, *41*, 160–171. [[CrossRef](#)]
14. Durante, M.; Lenucci, M.S.; Mita, G. Supercritical Carbon Dioxide Extraction of Carotenoids from Pumpkin (*Cucurbita* spp.): A Review. *Int. J. Mol. Sci.* **2014**, *15*, 6725–6740. [[CrossRef](#)] [[PubMed](#)]
15. Venturi, F.; Sanmartin, C.; Taglieri, I.; Andrich, G.; Zinnai, A. A simplified method to estimate Sc-CO₂ extraction of bioactive compounds from different matrices: Chili pepper vs. tomato by-products. *Appl. Sci.* **2017**, *7*, 361. [[CrossRef](#)]

16. Sánchez-Camargo, A.P.; García-Cañas, V.; Herrero, M.; Cifuentes, A.; Ibáñez, E. Comparative study of green sub- and supercritical processes to obtain carnosic acid and carnosol-enriched rosemary extracts with in vitro anti-proliferative activity on colon cancer cells. *Int. J. Mol. Sci.* **2016**, *17*, 2046. [[CrossRef](#)]
17. Robles-Ramírez, M.C.; Monterrubio-López, R.; Mora-Escobedo, R.; Beltrán-Orozco, M.D. Evaluation of extracts from potato and tomato wastes as natural antioxidant additives. *Archivos Latinoamericanos de Nutrición Órgano Oficial de la Sociedad Latinoamericana de Nutrición* **2016**, *66*, 66–73.
18. Fritsch, C.; Staebler, A.; Happel, A.; Cubero Márquez, M.A.; Aguiló-Aguayo, I.; Abadias, M.; Gallur, M.; Cigognini, I.M.; Montanari, A.; López, M.J.; et al. Processing, Valorization and Application of Bio-Waste Derived Compounds from Potato, Tomato, Olive and Cereals: A Review. *Sustainability* **2017**, *9*, 1492. [[CrossRef](#)]
19. Zinnai, A.; Venturi, F.; Andrich, G. Time evolution of phenols extractions from Sangiovese grapes with and without the addition of solid carbon dioxide. *Agrochimica* **2011**, *55*, 193–202.
20. Zinnai, A.; Venturi, F.; Sanmartin, C.; Taglieri, I.; Andrich, G. The utilization of solid carbon dioxide in the extraction of extra-virgin olive oil. *Agro-Food Ind. Hi Technol.* **2015**, *26*, 24–26.
21. Zinnai, A.; Venturi, F.; Quartacci, M.F.; Sanmartin, C.; Favati, F.; Andrich, G. Solid carbon dioxide to promote the extraction of extra-virgin olive oil. *Grasas Y Aceites* **2016**, *67*, e121. [[CrossRef](#)]
22. Nari, A.; Taglieri, I.; Pistelli, L.; Ascrizzi, R.; Andrich, G.; Zinnai, A. The effect of ripening degree and irrigation regimes of fruits on the quality of extra-virgin olive oil extracted with or without the addition of carbonic snow. *Agrochimica* **2018**, *62*, 79–91.
23. Venturi, F.; Andrich, G.; Sanmartin, C.; Taglieri, I.; Serni, E.; Zinnai, A. Winemaking of Sangiovese grapes with and without the addition of different oenological tannins in order to increase the colour intensity of Chianti wine. *Agrochimica* **2015**, *59*, 261–271.
24. Horwitz, W.; Latimer, G.W., Jr. *AOAC International Official Methods of Analysis*, 21st ed.; Latimer, G.W., Ed.; AOAC International: Rockville, MD, USA, 2019.
25. Liu, X.; Yang, Q.; Lu, Y.; Li, Y.; Li, T.; Zhou, B.; Qiao, L. Effect of purslane (*Portulaca oleracea* L.) extract on anti-browning of fresh cut potato slices during storage. *Food Chem.* **2019**, *283*, 445–453. [[CrossRef](#)] [[PubMed](#)]
26. Sanmartin, C.; Venturi, F.; Macaluso, M.; Nari, A.; Quartacci, M.F.; Sgherri, C.; Flamini, G.; Taglieri, I.; Ascrizzi, R.; Andrich, G.; et al. Preliminary results about the use of argon and carbon dioxide in the extra virgin olive oil (EVOO) storage to extend oil shelf life: Chemical and sensorial point of view. *Eur. J. Lipid. Sci. Technol.* **2018**, *120*, 1800156. [[CrossRef](#)]
27. Dávila-Aviña, J.; Solis, L.; Rojas-Verde, G.; Salas, N. Sustainability and challenges of minimally processed foods. In: *Washing, Peeling and Cutting of Fresh-Cut Fruits and Vegetables. Food Eng. Ser.* **2015**. [[CrossRef](#)]
28. Son, S.M.; Moon, K.D.; Lee, C.Y. Inhibitory effects of various antibrowning agents on apple slices. *Food Chem.* **2001**, *73*, 23–30. [[CrossRef](#)]
29. Delaquis, P.J.; Stewart, S.; Toivonen, P.M.A.; Moyls, A. Effect of warm, chlorinated water on the microbial flora of shredded iceberg lettuce. *Food Res. Int.* **1999**, *32*, 7–14. [[CrossRef](#)]
30. Nicoli, M.C. *Shelf Life Assessment of Food*; Barbosa-Cánovas, G.V., Ed.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 2012.
31. Buera, M.P.; Lozano, R.D.; Petriella, C. Definition of colour in the non-enzymatic browning process. *Die Farbe* **1985**, *32–33*, 318–322.
32. Albishi, T.; John, J.A.; Al-Khalifa, A.S.; Shahidi, F. Phenolic content and antioxidant activities of selected potato varieties and their processing by-products. *J. Funct. Foods* **2013**, *5*, 590–600. [[CrossRef](#)]
33. Jin, C.Y.; Liu, H.; Xu, D.; Zeng, F.K.; Zhao, Y.C.; Zhang, H.; Liu, G. Glycoalkaloids and phenolic compounds in three commercial potato cultivars grown in Hebei, China. *Food Sci. Hum. Wellness* **2018**, *7*, 156–162. [[CrossRef](#)]
34. Choi, S.H.; Kozukue, N.; Kim, H.J.; Friedman, M. Analysis of protein amino acids, non-protein amino acids and metabolites, dietary protein, glucose, fructose, sucrose, phenolic, and flavonoid content and antioxidative properties of potato tubers, peels, and cortexes (pulp). *J. Food Compos. Anal.* **2016**, *50*, 77–87. [[CrossRef](#)]
35. Ascrizzi, R.; Taglieri, I.; Sgherri, C.; Flamini, G.; Macaluso, M.; Sanmartin, C.; Venturi, F.; Quartacci, M.F.; Pistelli, L.; Zinnai, A. Nutraceutical Oils Produced by Olives and Citrus Peel of Tuscany Varieties as Sources of Functional Ingredients. *Molecules* **2019**, *24*, 65. [[CrossRef](#)] [[PubMed](#)]
36. Andrich, G.; Stevanin, E.; Zinnai, A.; Venturi, F.; Fiorentini, R. *Extraction Kinetics of Natural Antioxidants from Potato Industry by-Products*; ISASF: Versailles, France, 2003; pp. 159–163.

37. Friedman, M.; Kozukue, N.; Kim, H.J.; Choi, S.H.; Mizuno, M. Glycoalkaloid, phenolic, and flavonoid content and antioxidative activities of conventional nonorganic and organic potato peel powders from commercial gold, red, and Russet potatoes. *J. Food Compos. Anal.* **2017**, *62*, 69–75. [[CrossRef](#)]
38. Friedman, M. Potato glycoalkaloids and metabolites: Roles in the plant and in the diet. *J. Agric. Food Chem.* **2006**, *54*, 8655–8681. [[CrossRef](#)] [[PubMed](#)]
39. Friedman, M.; Levin, C.E. Glycoalkaloids and calystegine alkaloids in potatoes. In *Advances in Potato Chemistry and Technology*, 2nd ed.; Singh, J., Kaur, L., Eds.; Elsevier: Oxford, UK, 2016; pp. 167–194.
40. Mensinga, T.T.; Sips, A.J.A.M.; Rempelberg, C.J.M.; van Twillert, K.; Meulenbelt, J.; van den Top, H.J.; van Egmond, H.P. Potato glycoalkaloids and adverse effects on humans: An ascending dose study. *Regul. Toxicol. Pharmacol.* **2005**, *41*, 66–72. [[CrossRef](#)]
41. Vinson, J.A.; Demkosky, C.A.; Navarre, D.A.; Smyda, M.A. High-antioxidant potatoes: Acute in vivo antioxidant source and hypotensive agent in humans after supplementation to hypertensive subjects. *J. Agric. Food Chem.* **2012**, *60*, 6749–6754. [[CrossRef](#)] [[PubMed](#)]
42. Franco, D.; Pateiro, M.; Rodríguez Amado, I.; López Pedrouso, M.; Zapata, C.; Vázquez, J.A.; Lorenzo, J.M. Antioxidant ability of potato (*Solanum tuberosum*) peel extracts to inhibit soybean oil oxidation. *Eur. J. Lipid Sci. Technol.* **2016**, *118*, 1891–1902. [[CrossRef](#)]
43. Ben Jeddou, K.; Bouaziz, F.; Zouari-Ellouzi, S.; Chaari, F.; Ellouz-Chaabouni, S.; Ellouz-Ghorbel, R.; Nouri-Ellouz, O. Improvement of texture and sensory properties of cakes by addition of potato peel powder with high level of dietary fiber and protein. *Food Chem.* **2017**, *217*, 668–677. [[CrossRef](#)]
44. Toivonen, P.M.; Brummell, D.A. Biochemical bases of appearance and texture changes in fresh-cut fruit and vegetables. *Postharvest Biol. Technol.* **2008**, *48*, 1–14. [[CrossRef](#)]
45. Artés, F.; Gómez, P.A.; Artés-Hernández, F. Physical, physiological and microbial deterioration of minimally fresh processed fruits and vegetables. *Revista de Agaroquímica y Tecnología de Alimentos* **2007**, *13*, 177–188. [[CrossRef](#)]
46. Martinez, M.; Whitaker, J.R. The biochemistry and control of enzymatic browning. *Trends Food Sci. Technol.* **1995**, *6*, 195–200. [[CrossRef](#)]
47. Amiot, M.J.; Tacchini, M.; Aubert, S.Y.; Oleszek, W. Influence of Cultivar, Maturity Stage, and Storage Conditions on Phenolic Composition and Enzymic Browning of Pear Fruits. *J. Agric. Food Chem.* **1995**, *43*, 1132–1137. [[CrossRef](#)]
48. Saltveit, M.E. Wound induced changes in phenolic metabolism and tissue browning are altered by heat shock. *Postharvest Biol. Technol.* **2000**, *21*, 61–69. [[CrossRef](#)]
49. Amiot, M.J.; Tacchini, M.; Aubert, S.; Nicholas, J. Phenolic composition and browning susceptibility of various apple cultivars at maturity. *J. Food Sci.* **1992**, *57*, 958–962. [[CrossRef](#)]
50. Hakkim, F.L.; Essa, M.M.; Arivazhagan, G.; Guizani, N.; Hyuk, S. Evaluation of food protective property of five natural products using fresh-cut apple alice model. *Pakistan J. Biol. Sci.* **2012**, *15*, 10–18. [[CrossRef](#)]
51. Gurbuz, G.; Lee, C.Y. Color of minimally processed potatoes as affected by modified atmosphere packaging and antibrowning agents. *J. Food Sci.* **1997**, *62*, 572–575.
52. Musacchi, S.; Serra, S. Apple fruit quality: Overview on pre-harvest factors. *Sci. Hortic.* **2018**, *234*, 409–430. [[CrossRef](#)]
53. Yahia, E.M. Apple Flavor. In *Horticultural Reviews*; Janick, J., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1994; Chapter 6; Volume 16, pp. 197–234.
54. Augusto, A.; Simões, T.; Pedrosa, R.; Silva, S.F.J. Evaluation of seaweed extracts functionality as post-harvest treatment for minimally processed Fuji apples. *IFSET* **2016**, *33*, 589–595. [[CrossRef](#)]
55. Ling, L.; Li, Q.P.; Wang, B.G.; Cao, J.K.; Jiang, W.B. Inhibition of core browning in yali pear fruit by post-harvest treatment with ascorbic acid. *J. Hortic. Sci. Biotechnol.* **2007**, *82*, 397402.
56. Singh, J.; Mirza, A. Influence of ascorbic acid application on quality and storage life of fruits. *Int. J. Curr. Microbiol. Appl. Sci.* **2018**, *7*, 4319–4328. [[CrossRef](#)]
57. Rux, G.; Caleb, O.J.; Fröhling, A.; Herppich, W.B.; Mahajan, P.V. Respiration and Storage Quality of Fresh-Cut Apple Slices Immersed in Sugar Syrup and Orange Juice. *Food Bioprocess. Technol.* **2017**, *10*, 2081–2091. [[CrossRef](#)]
58. Rocculi, P.; Dalla Rosa, M.; Romani, S. Evaluation of physico-chemical parameters of MP apples packed in non-conventional modified atmosphere. *Food Res. Int.* **2004**, *37*, 329–335. [[CrossRef](#)]

59. Olivas, G.I.; Mattinson, D.S.; Barbosa-Canovas, G.V. Alginate coatings of minimally processed ‘Gala’ apples. *Postharvest Biol. Technol.* **2007**, *1*, 89–96. [[CrossRef](#)]
60. Fontes, L.C.B.; Sarmiento, S.B.S.; Spoto, M.H.F.; Dias, C.T.S. Conservação de maçã minimamente processada com o uso de películas comestíveis. *Ciência Tecnol. Aliment.* **2008**, *28*, 1–9. [[CrossRef](#)]
61. Fagundes, C.; Carciofi, B.A.M.; Monteiro, A.R. Estimate of respiration rate and physicochemical changes of fresh-cut apples stored under different temperatures. *Food Sci. Technol.* **2013**, *33*, 60–67. [[CrossRef](#)]
62. Van Buggenhout, S.; Sila, D.N.; Duvetter, T.; Van Loey, A.; Hendrickx, M. Pectins in processed fruits and vegetables: Part III—Texture engineering. *Compr. Rev. Food Sci. Food Saf.* **2009**, *8*, 105–117. [[CrossRef](#)]
63. Nayak, A.; Bhushan, B. An overview of the recent trends on the waste valorization techniques for food wastes. *J. Environ. Manag.* **2019**, *233*, 352–370. [[CrossRef](#)] [[PubMed](#)]



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