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# On the Path to Sustainable Cosmetics: Development of a Value-Added Formulation of Solid Shampoo Incorporating Mango Peel Extract

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**Abstract:** The excessive use of water and plastic packaging in the cosmetic industry imposes the need to develop sustainable alternatives. Moreover, agricultural by-products are reported in the literature to be rich in bioactive properties, namely high antioxidant capacity, suggesting their potential use in cosmetic formulations as substitutes for commercial additives. The aim of this work was the development of a sustainable formulation of solid shampoo, incorporating extracts from mango peel as antioxidants. The characterization of the extracts revealed the presence of several phenolic compounds and a strong antioxidant capacity. Six formulations of solid shampoo were produced by varying the quantity of the additives: tocopherol and butylated hydroxytoluene, used as positive controls, and mango peel (MP) extract. The antioxidant capacity assays demonstrated that the MP extract increased the antioxidant activity of the shampoos, in comparison to the positive controls and the stability tests revealed that the MP extract is a stable ingredient. Hence, it was concluded that the MP extract is a strong source of antioxidants with the potential to replace commercial antioxidants in cosmetics. Thus, it was possible to develop a value-added formulation of solid shampoo, eliminating the use of water and plastic for the packaging, and reusing waste from the food sector.

**Keywords:** solid shampoo; mango peel; phenolic compounds; antioxidant; sustainability



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## 1. Introduction

Water is one of the most important natural resources as it is essential for the subsistence of life [1]. Water resources are renewable due to their cyclical nature. Nonetheless, the water cycle system is undergoing rapid changes as a consequence of climate change, which has led to cryosphere shrinkage, falling groundwater levels, water pollution and water shortages [2].

As a result of a rapidly growing global population and increasing industrialization, the 21st century faces one of its most significant challenges in ensuring the sufficient availability of clean water for drinking, sanitation, and industrial purposes [3]. Currently, between two and three billion people face water scarcity for at least one month per year [4]. Water scarcity has severe consequences, which involve negative impacts on human and ecosystem health, restrictions on industrial and agricultural production and a wide range of social, economic, and political disruptions [5]. Therefore, industries need to adopt cleaner production technologies to save this natural resource.

The cosmetics industry is one of the most influential in our society and represents a growing economic sector worldwide. The EU market was valued at EUR 88 billion in 2022 [6]. Unfortunately, this industry depends deeply on water in the production of cosmetics, contributing to its substantial consumption and pollution. In most cosmetic

products, the amount of water accounts for more than 65% of the total formula volume. For instance, a usual cream contains from 60 to 80% water, and a shampoo up to 95%. Additionally, water is also required in cultivation of raw materials, manufacturing processes, and packaging production [7].

Another significant issue associated with the cosmetics industry is the high amount of packaging used for the finished products, with plastic being one of the main materials used [8]. Research has shown that plastics are some of the major contributors to global greenhouse emissions and the release of those gases occurs at every stage of the plastic lifecycle [9]. Despite the broad use of plastics, their reuse and recycling are very low. Around 25.8 million tons of plastic waste are generated annually in Europe. Less than 30% of such waste is collected for recycling, whereas 31% and 39% are for landfilling and incineration, respectively. When it comes to cosmetic packaging, recycling is very often impractical due to the presence of "greasy" products, which are challenging to remove through simple washing processes [10].

Moreover, consumers are increasingly gaining awareness about environmental issues and reflecting from an ethical point of view before purchasing cosmetics, which forces cosmetic companies to keep up with the expectations from consumers and develop sustainable products [11,12]. Today, there is a huge demand for solid cosmetics. Because of their anhydrous formulation, the use of water is substantially reduced, as well as the amount of packaging, which is usually made of biodegradable paper, avoiding plastic use [7].

Furthermore, an essential aspect of achieving sustainable development lies not only in diminishing the utilization of natural resources and synthetic materials but also in promoting reuse and recycling to create a circular economy. Every year, millions of tons of by-products from the food industry, including peels and seeds, go to waste since they are not edible, resulting in increased waste and environmental pollution [13]. According to the literature, those by-products are rich in phenolic compounds (PC), which are characterized for their high antioxidant capacity and anti-inflammatory and antibacterial effects [14,15]. Several studies in the literature proved that phenolic extracts from certain food by-products can be incorporated in the cosmetics, food, or pharmaceutical industries and replace synthetic preservatives, contributing to the creation of a circular economy. Suleria et al. [16] performed a study to determine the polyphenol content in twenty fruit peels as well as their antioxidant potential. The results of this study demonstrated that most of the selected peels presented a high phenolic content with very high antioxidant potential, with mango peel (MP) presenting the highest phenolic content. Since mango is the second most produced tropical fruit worldwide, leading to the generation of around 20–30 million tonnes of peels and seeds every year, globally, it is relevant when studying the possibility of reusing this waste [17,18]. Figure 1 presents a scheme with the most common phenolic compounds identified in MP, according to the literature.

The present study aimed to develop a value-added solid shampoo, imposing an alternative to commercial liquid shampoos, which are one of the most used cosmetic products worldwide. The goal was to incorporate extracts from agricultural by-products, particularly mango peels; to evaluate their effect on the performance of the produced shampoo; and to determine the possibility of the extracts to replace commercial antioxidants. This way, the use of water is eliminated, as is the use of plastics for the packaging, and waste from the food sector is reused, contributing to a circular economy.

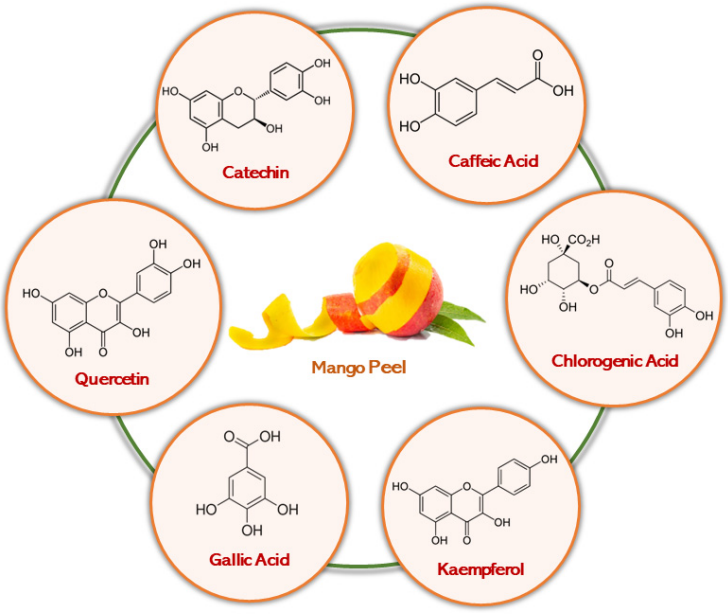


**Figure 1.** Main phenolic compounds found in mango peel extracts, according to several studies from the literature [16,19,20].

## 2. Materials and Methods

### *2.1. Chemicals and Reagents*

The mango and orange peels were provided by a local restaurant in Porto. The mangoes were of the Palmer variety and the oranges were cultivated in Algarve. Ethanol (Ref. 1.02371.1000, $C_2H_6O$, CAS 64–17-5) used as solvent for the extraction of phenolic compounds was obtained from VWR (Rosny-sous-Bois, France). Milli-Q water was purified using water purification equipment, with 18.2 Ω of electrical resistance (Millipore, Burlington, MA, USA). To analyse the total phenolic content, *Folin–Ciocalteu* reagent (Ref. 47641), from Sigma-Aldrich (St. Louis, MO, USA), and sodium carbonate (Ref. 1.06392, $Na_2CO_3$, CAS 497-19-8), from Merck (Darmstadt, Germany), were used. To evaluate the antioxidant capacity, 2,2-diphenyl-1-picrylhydrazyl (Ref. D9132, $C_{18}H_{12}N_5O_6$, CAS 1898-66-4) and 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (Ref. A1888, $C_{18}H_{24}N_6O_6S_4$, CAS 30931-67-0) were purchased from Sigma-Aldrich (St. Louis, MO, USA). To produce the solid shampoos, sodium cocoyl isethionate (Ref. CAS 61789-32-0), coco glucoside (Ref. ADK-COSM-04874), shea butter (Ref. IT-ACEI-00498), beeswax (CM-CERA-01314), panthenol (Ref. SPC-COSM-02983), and tocopherol (Ref. CAS 7695-91-2) were acquired from GranVelada (Zaragoza, Spain). Butylated hydroxytoluene (BHT) (Ref. 47168, $C_{15}H_{24}O$, CAS 128–37-0) was purchased from Sigma Aldrich. For the lipid oxidation test, barium chloride dihydrate (Ref. 217565, $BaCl_2{\cdot}2H_2O$, CAS 10326–27-9) and iron chloride III (Ref. F2877, $FeCl_3{\cdot}7H_2O$, CAS 10025–77-1) were obtained from Sigma Aldrich (St. Louis, MO, USA); iron sulfate (II) heptahydrate (Ref. 24,244.232, $FeSO_4{\cdot}7H_2O$, CAS 7782-63-0) and hydrochloric acid (Ref. 20,255.290, HCl, CAS 7647-01-0) were bought from VWR (Rosnysous-Bois, France); ammonium thiocyanate (Ref.A10632, $CH_4N_2S$, CAS 1762-95-4) was acquired from Alfa Aesar (Haverhill, MA, USA); and chloroform (Ref.438607, $CH_3Cl$, CAS 67–66-3) and methanol (Ref. 414,816, $CH_3OH$, CAS 67–56-1) were purchased from Carlo Erba (Barcelona, Spain). The samples of human hair were provided by a local hair salon.

### *2.2. Extraction Methods*

#### 2.2.1. Extraction of Phenolic Compounds from Mango Peel

To obtain the extracts from MP, the peels underwent an initial pre-treatment process. The peels with the least signs of degradation were washed to remove impurities and cut into smaller pieces. Subsequently, they were frozen at −80 °C and lyophilized to remove

the water present in them. Afterwards, the peels were ground using a coffee mill and sieved to achieve a homogeneous sample, with a diameter within the range 0.149–0.297 mm. The extraction of the phenolic content was performed via solid–liquid extraction, with a Soxhlet apparatus, using pure ethanol as the extraction solvent, at a proportion of 1:20 (m/V) for 2 h, according to the literature [21]. Additionally, the solvent was removed using a rotary evaporator (Büchi R-200, Flaiwil, Switzerland), with a bath temperature of 40 °C and automatic pressure adjustment. Lastly, the extracts were subjected to a constant stream of nitrogen to achieve the total evaporation of the solvent. Finally, they were covered with foil paper to prevent light degradation and stored in a refrigerator until further use. The average yield obtained was 62.9 ± 0.3% (dry basis), which is in accordance with the literature values, between 21.5–71%, using maceration and ultrasound as extraction techniques [22,23].

#### 2.2.2. Essential Oil Extraction from Orange Peel

To obtain a natural fragrance for the solid shampoo, hydrodistillation was performed to extract the essential oil from orange peels, in accordance with the literature [24]. Ultrapure water was used as solvent in a proportion of 1:2 (m/V), and the total extraction time was 1 h. Afterwards, the layer of oil was removed using a micropipette and stored in the refrigerator until further use. The average yield obtained was 1.8 ± 0.2%, which is within the range of the values reported in the literature, between 0.5–2.1% for the same extraction method [25,26].

### *2.3. Characterization of the Mango Peel Extract*

#### 2.3.1. Total Phenolic Content

The total phenolic content (TPC) was determined using the assay with the *Folin–Ciocalteu* reagent described in the literature with slight changes [27]. A solution of 333.3 $g \cdot L^{-1}$ of sodium carbonate in ultrapure water and a solution of 1000 $mg \cdot L^{-1}$ of extract were prepared. In a cuvette of 2 mL, 20 µL of the extract solution, 100 µL of *Folin–Ciocalteu* reagent, and 1580 µL of ultrapure water were added. After 6 min, 300 µL of the sodium carbonate solution was added and the cuvette was left to incubate in the dark for 2 h. A blank was made with 20 µL of extract solution and 1980 µL of water. The absorbance was measured at 750 nm with a spectrophotometer (V-530, Jasco, OK, USA). The gallic acid equivalents (GAE) were estimated through Equation (1).

$$\mathrm{TPC}\left[\mathrm{mg_{GAE}} \cdot \mathrm{g_{extract}^{-1}}\right] = \frac{Abs_{\mathrm{sample}} - Abs_{\mathrm{blank}}}{\mathrm{m} \times C_{\mathrm{sample}}} \times 100 \quad (1)$$

where $C_{\mathrm{sample}}$ refers to the extract concentration in the cuvette, 100 to the dilution factor of the sample, and m = 0.0748 refers to the slope of the calibration curve prepared using different concentrations of gallic acid [28].

#### 2.3.2. Antioxidant Capacity

For the determination of the antioxidant potential of the phenolic extracts from MP, the assays with DPPH (2,2-diphenyl-1-picrylhydrazy) radical and the ABTS (2,2-azinobis (3-ethyl-benzothiazolin-6-sulfonic acid)) radical were performed.

The DPPH assay was performed according to the literature with minor changes [29]. In a 96-well microplate, 20 µL of MP extract was added at concentrations ranging from 100–1000 $mg \cdot L^{-1}$ as well as 20 µL of Trolox at concentrations ranging from 50–250 $mg \cdot L^{-1}$ for the calibration curves, followed by 180 µL of $\mu mol \cdot L^{-1}$ DPPH solution. A control and a blank were made with 20 µL of water instead of the extract solution. For the blank, 180 µL of ethanol instead of DPPH solution was added. The plate was wrapped with foil paper and left to incubate for 40 min, after which the absorbance was read at 515 nm

using a spectrophotometer (V-530, Jasco, OK, USA). Equation (2) was used to calculate the percentage of DPPH inhibition (%).

$$\text{DPPH inhibition } (\%) = 1 - \frac{Abs_{\text{sample}} - Abs_{\text{blank}}}{Abs_{\text{control}} - Abs_{\text{blank}}} \times 100 \quad (2)$$

The ABTS assay was performed according to the literature with slight changes [30]. Initially, a 7.5 mmol·L$^{-1}$ solution of ABTS and a solution of 2.5 mmol·L$^{-1}$ potassium persulfate were prepared in sodium acetate buffer (0.05 M, pH 4.6). The ABTS and the potassium persulfate solutions were added at a proportion of 1:1 to form the solution of reactive ABTS, which was left to incubate at ambient temperature for 16 h. Subsequently, the solution was diluted in acetate buffer at a proportion of 1:40 and left to incubate for 30 min. Afterwards, the optical density (OD) of the solution was adjusted with acetate buffer to 0.74 at 734 nm. Finally, in a 96-well microplate, 20 µL of MP extract was added at concentrations ranging from 50–500 mg·L$^{-1}$ as well as 20 µL of Trolox at concentrations ranging from 50–250 mg·L$^{-1}$ for the calibration curve, followed by 180 µL of ABTS solution. A control was made with 20 µL of water to replace the solution. The plate was wrapped with foil paper and left to incubate for 15 min, after which the absorbance was read at 734 nm using a spectrophotometer (V-530, Jasco, OK, USA). Equation (3) was used to calculate the percentage of ABTS inhibition (%).

$$\text{ABTS inhibition } (\%) = \frac{Abs_{\text{control}} - Abs_{\text{sample}}}{Abs_{\text{control}}} \times 100 \quad (3)$$

For both assays, $IC_{50}$, which is the concentration of extract that translates into 50% of radical inhibition, was determined through the corresponding calibration curves of the absorbance in function of the concentration.

#### 2.3.3. High-Performance Liquid Chromatography (HPLC-DAD)

For the analysis of the MP extract, the identification and quantification of the phenolic compounds was performed through high-performance liquid chromatography (HPLC) using an Elite LaChrom HPLC system (Hitachi, Japan), equipped with a Hitachi L-2200 autosampler, L-2130 pump, and L-2455 diode array detector (DAD). A Puroshper® STAR RP-18 endcapped LiChroCART® chromatography column (Merck, Germany) and acetonitrile:water:ethanol (2:1:1 $v/v/v$) as a solvent were used to prepare the standards and sample solutions. For the preparation of the sample solutions, the MP extract was dissolved in ethanol and then filtered using a syringe filter with a pore size of 0.45 µm into a 2 mL vial. For the mobile phases A and B, ultrapure water with 0.5% of orthophosphoric acid and methanol:acetonitrile (80:20 $v/v$) as eluents were used, respectively. The eluent flow rate was 0.8 mL·min$^{-1}$, and the injection volume was 40 µL. The phenolic compounds were identified via the external standard method.

### *2.4. Solid Shampoo Production*

To evaluate the capacity of the MP extract to act as an antioxidant in solid shampoo, as well as its effect in the stability of the product, six formulations of solid shampoo were produced, according to the literature with slight modifications [31]. These comprised a negative control (NC) with no additives; two formulations containing commercial antioxidants frequently used in shampoos used as positive controls—one with tocopherol ($PC_1$), which is a natural antioxidant in various plants and another with butylated hydroxytoluene (BHT), which is of synthetic origin ($PC_2$); two formulations varying in the concentration of MP extract ($M_1$ and $M_2$); and a formulation containing a mixture of tocopherol and MP extract (Mix). The composition of each formulation is presented in Table 1. The percentages of antioxidants were added to each formulation by reducing the corresponding percentage of sodium cocoyl isethionate.

**Table 1.** Composition of the produced solid shampoo formulations.

| Phase | Ingredient | | | Function | | % (*w*/*w*) |
|---|---|---|---|---|---|---|
| **A** | Sodium Cocoyl Isethionate<br>Coco Glucoside | | | Primary Surfactant<br>Secondary Surfactant | | 65.5<br>20 |
| **B** | Beeswax<br>Shea Butter<br>Panthenol | | | Consistency adjustment<br>Emollient<br>Humectant | | 8<br>5<br>1 |
| **D** | Essential Oil | | | Fragrance | | 0.5 |
| **E** | Lactic Acid | | | Buffer | | 0.05 |
| | | | **Formulation** | | | |
| **Additives (Phase C)** | NC | $PC_1$ | $PC_2$ | $M_1$ | $M_2$ | Mix |
| Tocopherol | - | 1 | - | - | - | 0.5 |
| BHT | - | - | 0.5 | - | - | - |
| MP Extract | - | - | - | 1 | 2 | 0.5 |

NC: negative control; $PC_1$: positive control with tocopherol; $PC_2$: positive control with butylated hydroxytoluene (BHT); $M_1$: formulation with 1% of mango peel extract; $M_2$: formulation with 2% of MP extract; Mix: formulation with 0.5% of tocopherol and 0.5% of MP extract.

The solid shampoos were stored in refrigerator bags and protected from daylight throughout the entire study period. All formulations were subjected to stability and performance tests over 4 weeks at three distinct analysis times: t0 (same week of the production of the shampoos), t1 (second week), and t2 (fourth week).

### *2.5. Stability and Performance Analysis*

#### 2.5.1. Determination of pH

For the determination of the pH of the solid shampoos, a solution of 10% *w*/*v* in ultrapure water for each formulation was prepared. Then, the pH was measured using a conductivity meter.

#### 2.5.2. Dirt Dispersion Test

To evaluate the capacity of the solid shampoos to remove dirt, a test described in the literature was performed with slight changes [32]. Initially, one drop of China ink was added to 10 mL of a 10% *w*/*v* solution of solid shampoo in ultrapure water. Afterwards, the solution was shaken for 10 s, and the dispersion of ink was observed after 1 min to determine whether the ink concentrated in the foam or in the water portion.

#### 2.5.3. Surface Tension Measurement

The surface tension of the solid shampoos was determined using a K6 Force Tensiometer (KRÜSS), following the *Du Noüy* ring method. For the measurements, a 10% *w*/*v* solution of each solid shampoo in ultrapure water was prepared.

#### 2.5.4. Accelerated Thermal Stability Test

Before cosmetic products are brought to market, they need to be subjected to rigorous stability and shelf-life testing. To evaluate the thermal stability of the solid shampoos, the samples were incubated at 50 °C for 24 h, and the following day they were left to rest at ambient temperature; afterwards, they were incubated at 4 °C, and then they were left to rest once more. The organoleptic properties of the samples were evaluated, and the changes were registered.

#### 2.5.5. Oxidative Stability Test

To assess the oxidative stability of the solid shampoos, the peroxide value (PV) was determined according to the literature, with slight changes [33]. Briefly, 0.5 g of each

shampoo formulation were added to 9.8 mL of chloroform:methanol (7:3 $v/v$). Afterward, 50 µL of an ammonium thiocyanate:water (3:10 $w/v$) solution was added and the mixture was vortexed for 4 s. Subsequently, 50 µL of an iron (II) solution were added and the mixture was vortexed once again for 4 s. Lastly, the solution was incubated in the dark at room temperature for 5 min, and the absorbance was measured at 500 nm. The peroxide value was determined using Equation (4).

$$\mathrm{PV} = \frac{\left(Abs_{\mathrm{sample}} - Abs_{\mathrm{blank}}\right) \times \mathrm{m}}{m_{\mathrm{sample}} \times \mathrm{MM_{iron}} \times 2} \quad (4)$$

where $Abs_{\mathrm{sample}}$ and $Abs_{\mathrm{blank}}$ refer to the absorbance of the sample and the blank prepared without solid shampoo, respectively; m = 12.25 refers to the slope value of the calibration curve of $Fe^{3+}$; $m_{\mathrm{sample}}$ refers to the mass of the solid shampoo (g); $\mathrm{MM_{iron}}$ is the molar mass of iron; and the factor 2 is necessary to express the PV in milliequivalents of peroxide instead of milliequivalents of oxygen.

#### 2.5.6. Determination of the Total Phenolic Content and Antioxidant Capacity

For the extraction of the phenolic compounds from solid shampoo formulations, 8 mL of ethanol was added to 2 g of each formulation. The solution was homogenized in a vortex for 1 min and placed in an ultrasound bath for 5 min. These steps were repeated three times. Then, the solution was centrifuged for 10 min at 1502× $g$. The supernatant was collected, covered with foil paper to prevent light degradation, and stored in the refrigerator. These solutions were used to determine the total phenolic content and the antioxidant capacity of the shampoo formulations, according to the same protocols described in Section 2.3.

#### 2.5.7. Microscope Observation

To study the influence of the solid shampoo on the structure of the hair, two different samples of human hair provided by a local hair salon were observed, before and after the wash with Formulation $M_1$, in a Nikon ECLIPSE Ci Microscope with a DS-Qi2 Digital Camera. A random hair strand was collected from each sample before and after the wash for observation.

#### 2.5.8. Statistical Analysis

A statistical analysis of the results was performed using a statistical one-way analysis of variance (ANOVA) by calculating the $p$-value (95% confidence), where results with $p$-values less than 0.05 were considered significantly different.

## 3. Results and Discussion

### *3.1. Characterization of the Mango Peel Extract*

The results of the characterization of the MP extract regarding the antioxidant capacity and the presence of phenolic compounds are expressed in Table 2.

**Table 2.** Results of the characterization of the mango peel extract.

| | | |
|---|---|---|
| **TPC ($\mathbf{mg_{GAE} \cdot g^{-1}_{extract}}$)** | | 12.4 ± 0.8 |
| **DPPH** | $IC_{50}$ ($mg_{extract} \cdot L^{-1}$) | 51.5 ± 2.0 |
| | TE/ $mg_{Trolox} \cdot g^{-1}_{extract}$ | 330.5 ± 13.1 |
| **ABTS** | $IC_{50}$ ($mg_{extract} \cdot L^{-1}$) | 28.6 ± 1.0 |
| | TEAC ($mg_{Trolox} \cdot g^{-1}_{extract}$) | 315.0 ± 18.1 |

**Table 2.** *Cont.*

| HPLC-DAD | |
|---|---|
| **Compound Identified** | **Concentration ($\mu g \cdot g_{dried\ extract}^{-1}$)** |
| Catechin | 192.0 ± 3.2 |
| Chlorogenic Acid | 46.8 ± 3.6 |
| Quercetin | 114.0 ± 1.9 |
| Rosmarinic Acid | 186.1 ± 1.1 |

The results are expressed as mean ± standard deviations of three independent measurements. TPC: total phenolic content; GAE: gallic acid equivalents; $IC_{50}$: concentration of extract necessary to prevent the formation of the radical in 50%; TE: Trolox equivalents; TEAC: Trolox equivalent antioxidant capacity.

A literature review of the studies concerned with the characterization of mango peel extracts was performed, and the results are summarized in Table 3.

**Table 3.** Characterization of mango peel extracts, according to several studies in the literature.

| Extraction Method | TPC/$mg_{GAE} \cdot g^{-1}$ | AO Capacity/$mg \cdot L^{-1}$ | Main Phenolic Compounds | | Reference |
|---|---|---|---|---|---|
| Soxhlet<br>Ethanol | 55.8 | $IC_{50}$ =51.1 | Gallic acid<br>Chlorogenic acid | Catechin<br>Kaempferol | [19] |
| MAE<br>Ethanol:Water (60:40) | 52.1 | $IC_{50}$ =23.0 | Gallic acid<br>Mangiferin | Quercetin<br>Quinic acid | [34] |
| MAE<br>Ethanol:Water (70:30) | 0.7 | - | Oleanolic acid<br>Chlorogenic acid | Gallic acid<br>Caffeic acid | [20] |
| Soxhlet<br>Methanol | 18.4 | - | Gallic acid<br>derivatives | Mangiferin | [35] |
| Maceration<br>Ethanol:Water (70:30) | 27.5 | - | Gallic acid<br>Chlorogenic acid | Catechin<br>Quercetin | [16] |

TPC: total phenolic content; GAE: gallic acid equivalents; $IC_{50}$: concentration of extract necessary to prevent the formation of the DPPH radical in 50%; AO: antioxidant; MAE: microwave-assisted extraction.

The obtained TPC of the MP extract (12.4 ± 0.8 $mg_{GAE} \cdot g^{-1}$) is in the range of the values displayed in Table 2 (0.7–55.8 $mg_{GAE} \cdot g^{-1}$). However, it is inferior to the value obtained for the same extraction conditions (Soxhlet extraction an ethanol as solvent). The phenolic content varies depending on the fruit species, cultivars, and the geographical regions where they are grown. Additionally, factors such as climate, soil characteristics, and cultivation methods further contribute to differences in the composition of the peels [16]. Consequently, these variations in the composition may lead to fluctuations in the TPC value.

Regarding antioxidant capacity, the results demonstrate that the extract has very strong antioxidant properties, according to the literature, since the $IC_{50}$ values are below 50 $mg \cdot L^{-1}$ [36]. Additionally, those values suggest that the MP extract exhibits a higher antioxidant capacity towards the ABTS radical, since a lower quantity of extract is required to inhibit the radical to the same extent. Another study also reported higher capacity to inhibit ABTS compared to DPPH in mango peel extract [20]. Additionally, these results are in the range of the values obtained in previous studies, as displayed in Table 3.

The TE and TEAC indicate the concentration of Trolox (the standard antioxidant) required to inhibit DPPH and ABTS to the same extent as the MP extract, respectively. The higher those values, the higher antioxidant capacity of the extract. Del Pilar Sánchez-Camargo et al. [34] obtained a value of 660.8 $mg_{Trolox} \cdot g^{-1}{}_{extract}$ for the TEAC using maceration and methanol as solvent. On the other hand, Sogi et al. [37] achieved values of 49.3 $mg_{Trolox} \cdot g^{-1}{}_{extract}$ and 54.8 $mg_{Trolox} \cdot g^{-1}{}_{extract}$ for the TEAC and TE, respectively, also using maceration. The results obtained in this study are within the range of the values reported in the literature.

The antioxidant capacity is highly influenced by the presence of phenolic compounds in the plant matrix and their concentration. This is because the molecular structures of these

compounds play a crucial role in determining their ability to scavenge free radicals [38]. Hence, to better understand the bioactive properties of the extract, HPLC-DAD was utilized to identify the main phenolic compounds. From the data presented in Table 2, it can be concluded that catechin was the main phenolic compound identified in the MP extract, followed by rosmarinic acid, quercetin, and chlorogenic acid. Previous studies have also reported the presence of these compounds in MP extracts, except for rosmarinic acid, as seen in Table 3.

In one study, catechin, quercetin, and chlorogenic acid were quantified in mango peels at concentrations of 7.1, 11.9, and 13.8 $mg \cdot g^{-1}$, respectively, which were higher than the values obtained in this work [16]. Another study reported the presence of chlorogenic acid and quercetin in mango peel extract at concentrations of 85.1 $\mu g \cdot g^{-1}$ and 429.2 $\mu g \cdot g^{-1}$, respectively, which were closer to the values achieved in this work [19]. Conversely, gallic acid, one of the most common phenolic compounds identified in mango peel, was not detected in this study. As mentioned previously, such differences may be related to the differing extraction conditions, the maturity of the fruit, or cultivation techniques which influence the composition of the peels. Furthermore, as seen in Table 3, most of the studies used a mixture of ethanol and water as the extraction solvent, which is more suitable for solubilizing a wider variety of compounds. Gallic acid is a polar compound due to the presence of a carboxyl group and thus is preferably extracted via water through hydrogen bonding [39]. One study evaluated the effect of ethanol concentration on the extraction of phenolic compounds from mango seed kernel and concluded that increasing the ethanol content from 75% to 100% resulted in a decrease in the recovery of gallic acid [40]. In this study, if water was added in a certain proportion, instead of using pure ethanol as solvent, gallic acid would probably be extracted.

### *3.2. Evaluation of the Solid Shampoo Formulations*

Samples from each batch of solid shampoo produced are displayed in Figure 2, corresponding to the compositions presented in Table 1. It can be observe that formulations $M_1$, $M_2$, and Mix exhibit a more intense yellowish colour compared to the remaining formulations, which is a result of the addition of the MP extract. All the shampoos display a smooth surface, without any visible cracks.

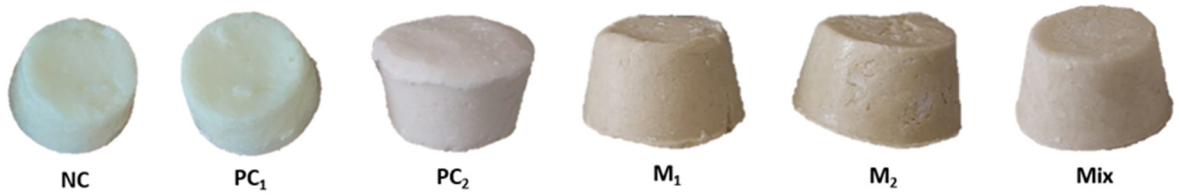


**Figure 2.** Samples of solid shampoo from each formulation produced. NC—solid shampoo without antioxidants (negative control); $PC_1$—solid shampoo with 1% of tocopherol; $PC_2$—solid shampoo with 0.5% of butylated hydroxytoluene; $M_1$—solid shampoo with 1% of MP extract; $M_2$—solid shampoo with 2% of MP extract; Mix—solid shampoo with 0.5% of tocopherol and 0.5% of MP extract.

#### 3.2.1. Determination of the Antioxidant Potential

The antioxidant capacity of the solid shampoos was assessed in order to determine the potential of the phenolic extracts from MP to act as antioxidants in the formulations developed according to Table 1. The methods used for the characterization of the MP extract were also applied to the solid shampoos, namely the DPPH and ABTS assays, and the results were given as the percentage of inhibition of each radical for each solid shampoo formulation. The TPC was also determined. The obtained results are displayed in Figure 3.

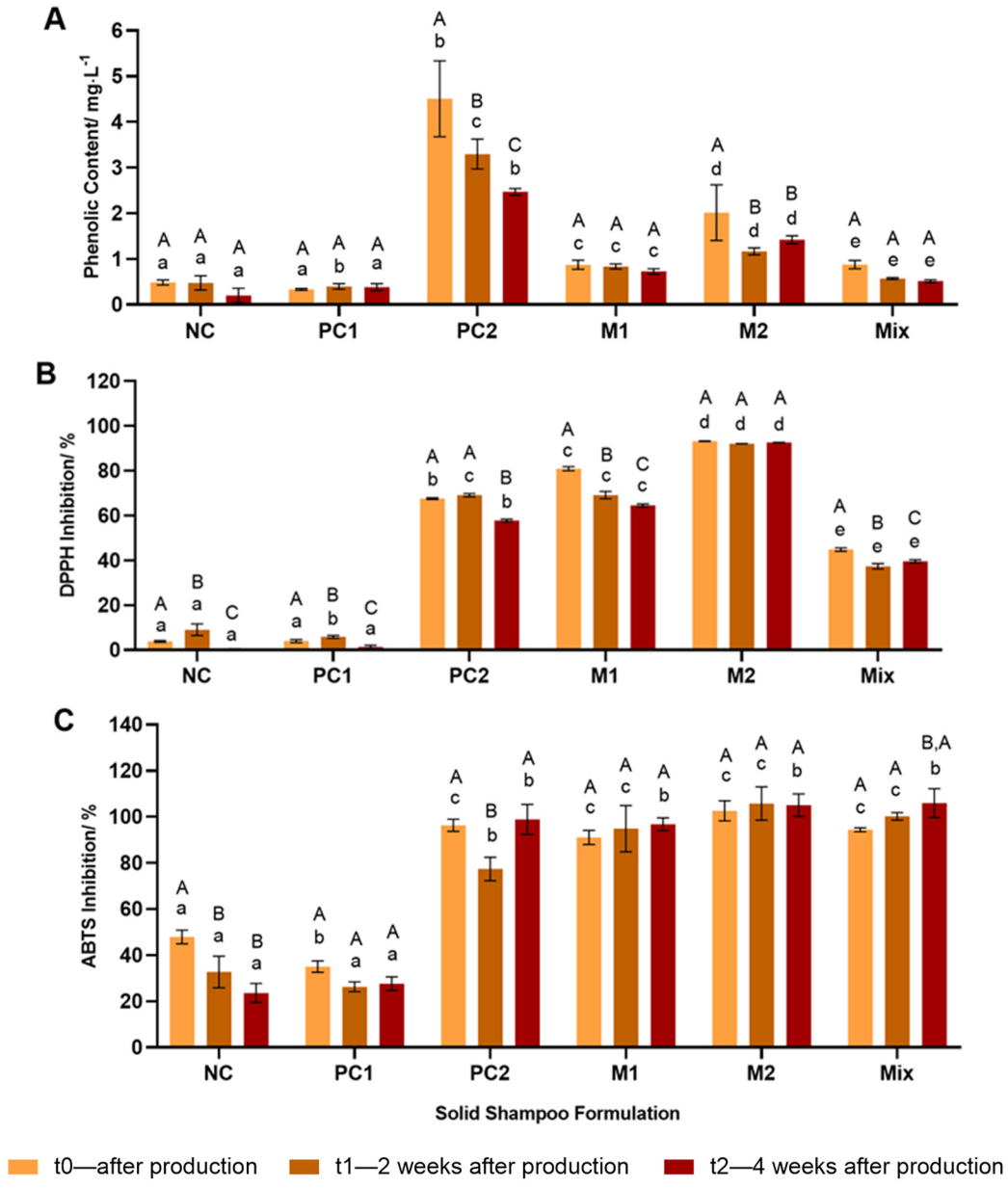


**Figure 3.** Antioxidant capacity of the solid shampoos obtained for the total phenolic content (**A**), DPPH (**B**), and ABTS (**C**) assays throughout the period of study. NC—solid shampoo with no antioxidants (negative control); $PC_1$—solid shampoo with 1% of tocopherol; $PC_2$—solid shampoo with 0.5% of butylated hydroxytoluene; $M_1$—solid shampoo with 1% of MP extract; $M_2$—solid shampoo with 2% of MP extract; Mix—solid shampoo with 0.5% of tocopherol and 0.5% of MP extract. The results are stated as means ± standard deviations of three independent measurements obtained from the same solid shampoo sample. The different lowercase letters (a–e) denote statistically different values ($p < 0.05$) for the same analysis time. The different capital letters (A–C) denote statistically different values ($p < 0.05$) for the same solid shampoo.

It is possible to observe in Figure 3 that the TPC tended to decrease throughout the study for all formulations of solid shampoos. These results were expected, since the phenolic compounds react with other species present in the formulation and degrade over time. All formulations of solid shampoos containing antioxidants exhibited higher antioxidant activity than the negative control, except for the formulation with tocopherol ($PC_1$). A possible explanation is that the tests performed were not the most adequate for the structure of tocopherol, resulting in no radical-scavenging capacity. According to the

literature, the cupric ion-reducing antioxidant capacity (CUPRAC) assay is more capable of measuring the antioxidant capacity of lipophilic antioxidants, including tocopherol, which is a natural-occurring form of Vitamin E [41]. Nonetheless, it is not the most appropriate for the type of extract analysed in this work, due to the nature and structure of the phenolic compounds.

The formulation with 2% of mango peel extract exhibited the highest antioxidant activity for both DPPH and ABTS assays, and it was always higher than the positive controls throughout the study. It was also the most stable during the study period. These results suggest that mango peel extract is a stable ingredient, with the capacity to replace commercial antioxidants in cosmetic formulations.

#### 3.2.2. Surface Tension and pH Value

The results of the surface tension and pH value of the solid shampoos are displayed in Figure 4. Regarding the surface tension, all the formulations of solid shampoo displayed equivalent results and the values obtained ranged between 33.0–34.5 $mN \cdot m^{-1}$ throughout the study period. The results are in accordance with a study performed on several commercial liquid shampoo brands, in which the surface tension ranged between 31.3–34.7 $mN \cdot m^{-1}$ [42]. According to that study, a good shampoo should be able to decrease the surface tension of water to at least 40 $mN \cdot m^{-1}$ for the efficient removal of the impurities present in the hair. It is observable in Figure 4 that all the solid shampoos decreased the surface tension of water below 40 $mN \cdot m^{-1}$.

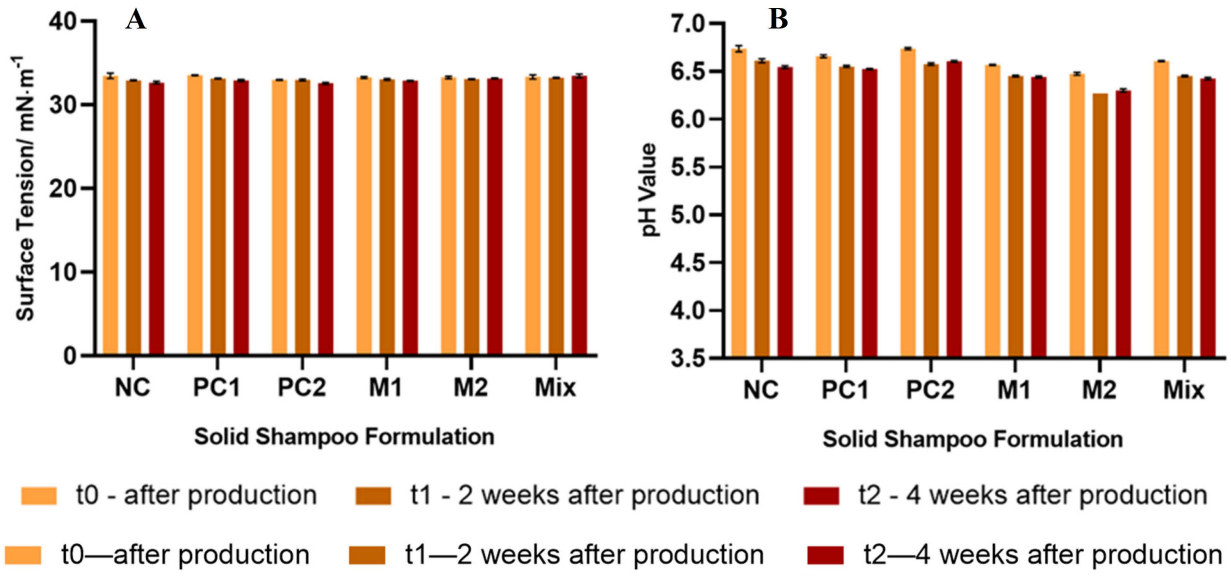


**Figure 4.** Results of the surface tension (**A**) and pH value (**B**) of the solid shampoos throughout the period of study. n = 3 measurements were performed for each sample. NC—solid shampoo with no antioxidants (negative control); $PC_1$—solid shampoo with 1% of tocopherol; $PC_2$—solid shampoo with 0.5% of butylated hydroxytoluene; $M_1$—solid shampoo with 1% of MP extract; $M_2$—solid shampoo with 2% of MP extract; Mix—solid shampoo with 0.5% of tocopherol and 0.5% of MP extract. The results are expressed as means ± standard deviations of three independent measurements obtained from the same solid shampoo sample.

The pH value of the scalp is around 5.5 and shampoos with a slightly acidic pH value are said to be gentler on the hair since the electrical charges are balanced, which seals the cuticles [43]. It is possible to observe in Figure 4 that the pH value was stable throughout the study and below 7 for all time periods, suggesting that the solid shampoo is gentle on the hair. It is also noticeable that the addition of the mango peel extract led to a slight decrease in the pH value, which is coherent with the relatively acidic nature of the phenolic

compounds. These results suggest that the incorporation of the MP extract did not affect these physicochemical properties.

#### 3.2.3. Dirt Dispersion Test

Figure 5 displays the results of the dirt dispersion test for some of the formulations of solid shampoo at the assessment point t0 (after the production of the shampoos). The results for the remaining formulations and assessment points are displayed in Figures S2–S4 of the Supplementary Materials. If the ink concentrates in the foam portion of the solution, it suggests that the shampoo is not effective in removing dirt and impurities from the hair, as they get redeposited on the hair and are not rinsed away with water during the washing process [32].

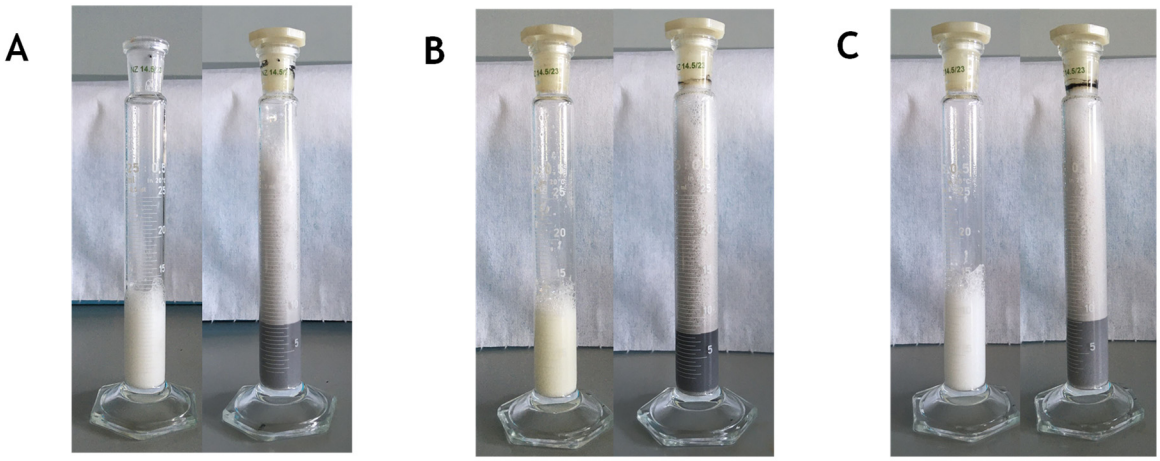


**Figure 5.** Results of the dirt dispersion test for t0 after the production of the solid shampoos. (**A**): formulation NC (without antioxidants); (**B**): formulation $M_1$ (1% of MP extract); (**C**): formulation $PC_2$ (0.5% BHT).

As seen in Figure 5, the ink concentrated in the water portion for all the formulations since the water acquired the colour of the ink and the foam remained almost completely clear. Hence, the results suggest that the solid shampoo is efficient in removing dirt from the hair and maintaining this physical property with the incorporation of the MP extract.

#### 3.2.4. Accelerated Thermal Stability Test

The results of the test to determine the thermal stability of the formulations of solid shampoo are displayed in Figure S1 of the Supplementary Materials. By observing the pictures, it is possible to conclude that the structure of all the solid shampoos remained unaffected throughout the study period. Additionally, no other changes were detected regarding the smell, texture, or colour for all formulations and time periods. It was possible to conclude that the incorporation of the MP extract did not affect the thermal stability of the solid shampoo.

#### 3.2.5. Oxidative Stability

To assess the oxidative stability of the solid shampoos, it was determined the peroxide value (PV). The PV indicates the extent of the primary oxidation of the lipids, fats, and oils present in a sample, which produces unpleasant effects, such as the generation of foul-smelling and changes in the colour and consistency of the cosmetic product [33]. The test results are presented in Figure 6.

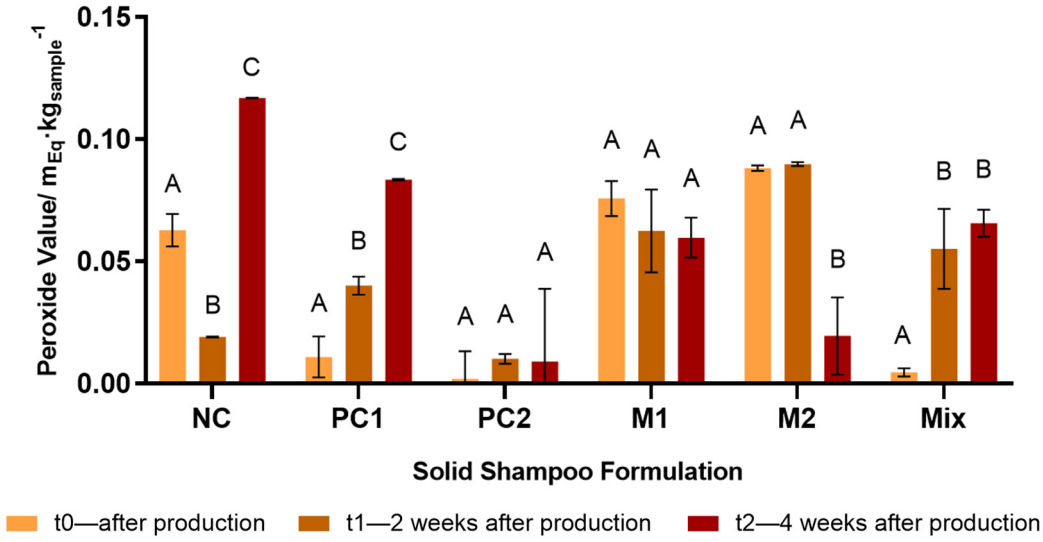


**Figure 6.** Variation of the peroxide value throughout the study period for the formulations of solid shampoo. The test was performed three times: t0—after production; t1—two weeks after production; t2—four weeks after production. NC—solid shampoo with no antioxidants (negative control); $PC_1$—solid shampoo with 1% of tocopherol; $PC_2$—solid shampoo with 0.5% of butylated hydroxytoluene; $M_1$—solid shampoo with 1% of MP extract; $M_2$—solid shampoo with 2% of MP extract; Mix—solid shampoo with 0.5% of tocopherol and 0.5% of MP extract. The results are stated as means ± standard deviations of two independent measurements obtained from the same sample. The different capital letters (A–C) denote statistically different values ($p < 0.05$) for the same solid shampoo.

From the results in Figure 6, it can be observed that all the formulations display a low oxidation state, according to the literature, since the PV was always inferior to 5 $m_{Eq} \cdot kg^{-1}$ [38]. However, it is possible to observe a tendency for the PV to continue to increase beyond the study period in formulations NC and $PC_1$, while in formulations $PC_2$, $M_1$, $M_2$, and Mix, the PV appears stable. It was expected that formulation NC would be more prone to oxidation since it is the negative control without any compounds with antioxidant capacity in its composition. Nonetheless, the formulation $PC_1$ containing tocopherol, a natural antioxidant added to cosmetics, exhibited a similar behaviour to the NC formulation in this test, which is in accordance with the results obtained in the antioxidant assays, which did not detect antioxidant activity in this formulation. The formulation $PC_2$ containing BHT demonstrated the lowest PV at all time points, and by the end of the study period, the formulations containing MP extract ($M_1$, $M_2$ and Mix) exhibited a lower PV value in comparison to NC and $PC_1$ formulations. These results suggest that the incorporation of the MP extract reduced the PV and increased the formulations' resistance to oxidation.

The low PVs of the solid shampoos obtained in this study do not necessarily indicate the absence of oxidation. Therefore, to obtain a more complete understanding of the extent of lipid oxidation in the formulations, an analysis of the secondary oxidation products could have been performed.

#### 3.2.6. Microscope Observation

To further evaluate the influence of the solid shampoo containing MP extract on the hair, two different samples of human hair were observed in the microscope before and after the wash with the $M_1$ formulation (containing 1% of MP extract). The main goal was to determine whether significant changes occurred in the hair structure after a wash. Figure 7 displays the results of the microscope observations.

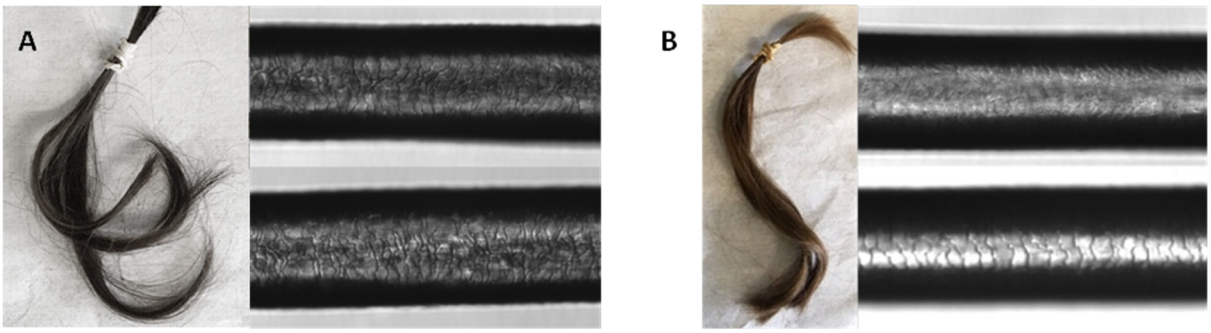


**Figure 7.** Results of the microscope observations before (top) and after (bottom) one wash with the formulation M1 of solid shampoo through a 40× objective lens. (**A**): sample of dark brown wavy hair; (**B**): sample of light brown straight hair.

Through this test, it was possible to observe the cuticle in detail for each human hair sample. A damaged cuticle means that the overlapping layers are detached from each other, causing the hair to look unhealthy. The more sealed the layers are, the healthier the hair is [44]. By observing Figure 7, the cuticle appears to have remained in its original structure after the wash with the solid shampoo for all hair samples. Additionally, no other changes seemed to have occurred in the structure and no residues or impurities were detected on the hair. These results suggest that the MP extract imposes no damage for the hair. Although the results of this test did not indicate any negative changes in the hair, further observations should be performed after repeated washing with the solid shampoo to obtain more accurate results.

## 4. Conclusions

The present work aimed to develop a sustainable solid shampoo formulation by preserving water, eliminating the use of plastic packaging, and reusing waste from the agricultural sector.

Mango peel extracts were obtained and characterized. The results revealed that MP extract exhibited strong antioxidant properties, presenting an $IC_{50}$ value of $51.5 \pm 2.0$ $mg_{extract} \cdot L^{-1}$ towards the DPPH radical. Additionally, the analysis of the extract in HPLC-DAD detected the presence of several phenolic compounds including catechin, quercetin, and chlorogenic acid. Subsequently, the extracts were incorporated into solid shampoo formulations in different concentrations to evaluate their antioxidant capacity and stability for a period of 4 weeks. The results of the antioxidant capacity assays revealed that the formulations containing MP extract exhibited higher capacity in inhibiting the DPPH and ABTS radicals in comparison to the formulations containing commercial antioxidants throughout the study period. Regarding the stability of the solid shampoos, it was concluded that the incorporation of the MP extract did not affect the physicochemical properties of the shampoo, more specifically the pH value, surface tension, and dirt dispersion, nor the thermal stability. Furthermore, the formulations containing the MP extract exhibited a lower oxidation state in comparison with the negative control. Additionally, the microscope observations suggested that the MP extract does not damage the hair cuticle. These results indicated that the MP extract is a stable ingredient and can potentially replace commercial antioxidants in cosmetic formulations, creating value-added products. It is also possible to conclude that the initial goal of developing a sustainable formulation of solid shampoo, without the need for water or plastics for the packaging, was achieved with satisfactory results. Nonetheless, future work should include toxicity assays to the MP extract to determine the presence of possible pesticides, synthetic fertilizers, and other substances resulting from the growing conditions.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cosmetics10050140/s1, Figure S1: Results of the accelerated thermal stability test to the solid shampoos throughout the study period, Figure S2: Results of the dirt

dispersion test for t0 after production of the solid shampoos, Figure S3: Results of the dirt dispersion test for t1, 2 weeks after production of the solid shampoos, Figure S4: Results of the dirt dispersion test for t2, 4 weeks after production of the solid shampoos.

**Author Contributions:** Conceptualization, I.B., S.M.F. and L.S.; methodology, I.B. and S.M.F.; software—not applicable; validation, I.B. and S.M.F.; formal analysis, I.B. and S.M.F.; investigation, I.B.; resources, L.S.; data curation, I.B. and S.M.F.; writing—original draft preparation, I.B.; writing—review and editing, S.M.F. and L.S.; visualization, I.B., S.M.F. and L.S.; supervision, L.S.; project administration, L.S.; funding acquisition, L.S. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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