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# Converting potato peel waste into bioactive extracts: reduction of pesticides by traditional and novel pretreatment technologies

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Potato peel, a primary component of potato processing waste, is rich in bioactive phenolic compounds. Nevertheless, it often contains elevated levels of pesticide residues that require reduction before further processing. This study aimed to diminish pesticide content in potato peel using water immersion (WI), ultrasound (US), liquid nitrogen immersion (LNI), and pulsed electric field (PEF) pretreatment processes while preserving its bioactive value. Specific pesticide compounds, including Chlorpropham, Spirotetramat, Azoxystrobin, Propiconazole, and Captan, were diluted in water and spiked onto potato peel samples. The spiked samples underwent WI (1:4 sample-to-water ratio), US (acoustic energy density:  $592.46 \pm 3.59 \text{ W L}^{-1}$ , 1 to 5 min duration, 1:4 sample-to-water ratio), PEF ( $3 \text{ kV cm}^{-1}$ , 12 to 50 pulses, 1:4 sample-to-water ratio), and LNI (2 min-immersion-thawing cycles: 1 to 4). Changes in total phenolic content, chlorogenic acid, hardness, color, and water electrical conductivity, along with light microscopy images, were evaluated before and after pretreatments to assess their impact on potato peel. Ultrasound treatment proved to be the most effective in reducing pesticide content, achieving a 100% reduction for Captan, followed by PEF (up to 80%) and LNI (20%). Removal of pesticides from potato peel using WI, with or without intensification processes, correlated well with the octanol–water partition coefficient of individual pesticide compounds. Furthermore, the retention of total phenolic content exceeded 90% for LNI, while for the US, it surpassed PEF (88% and 54%, respectively). Results of potato peel hardness, color, water electrical conductivity, and microscopic tissue images led to a plausible explanation of the differing polyphenol content. Overall, ultrasound pretreatment exhibited excellent potential for reducing hydrophilic pesticides in potato peel while preserving a significant amount of phenolic compounds.

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## Sustainability spotlight

This study addresses the challenge of potato peel waste, focusing on its impact on environmental sustainability and resource utilization. The innovative use of pre-treatment techniques such as water immersion, ultrasound, pulsed electric field, and liquid nitrogen immersion aims to enhance the quality and safety of potato peel waste. By reducing pesticide residues and preserving bioactive compounds, these methods align with the principles of responsible consumption and production (Goal 12) and industry innovation (Goal 9) set by the United Nations' Sustainable Development Goals. This work contributes to sustainable practices in the agri-food sector, promoting efficient resource use and minimizing environmental impacts.

## 1. Introduction

Canadian exports of potatoes and potato products reached an estimated value of \$2.6 billion in 2021–2022, with frozen and processed potatoes accounting for 73% of the total.<sup>1</sup> Potato peel waste represents a significant proportion of the processing

operations, ranging from 15 to 40% of the potato weight depending on the peeling process.<sup>2</sup> The enormous magnitude of potato waste poses economic challenges and environmental concerns. Thus, developing an environmentally friendly solution for potato peel waste is imperative, particularly within the context of organic waste decomposition and environmental pollution.<sup>3</sup>

The conversion of fruit and vegetable waste from agri-food by-products into valuable products has lately gained significant attention, particularly in extracting polyphenols and other antioxidants (e.g., fiber, vitamin E, lycopene, etc.) done by converting these extracts into stable powders.<sup>4,5</sup> In the case of potato waste, dried peel extracts have been reported to contain

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phenolic compounds with antioxidant and antiviral activities.<sup>3,6</sup> The predominant phenolic compound in potato peel is chlorogenic acid, constituting approximately 80% of the total phenolic acids and contributing to its potent antioxidant activity.<sup>7</sup>

Potato waste tends to contain high amounts of pesticide residues predominantly concentrated in the outer parts of plants such as the peel.<sup>8</sup> Since potato waste primarily consists of peel, which is the focus of this study, it is crucial to address pesticide residue issues and their elimination through pretreatment methods before further waste transformation. Previous studies have demonstrated that washing and peeling can reduce pesticide residues to different extents. For example, peeling resulted in a reported 98% reduction in Captan residues in apples.<sup>9</sup> Conventional washing methods could be moderately effective in removing residual pesticides from fruits and vegetables, especially in the case of pesticides with higher water solubility.<sup>10</sup> Wu *et al.* (2019) reported removal rates of less than 35% and 32% for pesticides applied on cucumber and spinach, respectively, when washed with tap water.<sup>11</sup> Heshmati *et al.* (2020) found that washing grapes with tap water for 15 minutes resulted in removal rates of only 20.3%, 18.5%, 37.5%, 15.2%, and 16.6% for Penconazole, Hexaconazole, Diazinon, Ethion, and Phosalone, respectively.<sup>12</sup> Similarly, washing cabbage leaves with tap water showed low effectiveness, with only 17.6%, 17.1%, 19.1%, and 15.2% reduction in Chlorpyrifos, *p,p*-DDT, Cypermethrin, and Chlorothalonil residues, respectively.<sup>13</sup> Water immersion is especially effective in eliminating hydrophilic pesticide compounds with lower log *P* values (octanol–water partition coefficient).<sup>14</sup> For instance, washing kumquat fruits with tap water, removal rates of Dimethoate, Chlorpyrifos, Malathion, Methidathion, and Triazophos were 23.0%, 8.0%, 19.0%, 16.0%, and 10.0%, respectively, depending on their log *P* values, where lower log *P* values correlated with greater removal of residues.<sup>15</sup> In addition, in the case of potatoes, organochlorine residues exhibited less reduction compared to organophosphorus residues after washing with tap water.<sup>16</sup>

Ultrasound has been used to intensify the reduction of pesticide residues during washing. For instance, Zhang *et al.* (2010) demonstrated the effectiveness of ultrasonic treatment at  $T = 15 \pm 2$  °C and 25 kHz in degrading diazinon in apple juice, with the degradation percentage depending on the initial concentration and ultrasonic power. Higher initial pesticide concentrations resulted in decreased degradation percentages, and the treatment at 500 W was 2.7 times more effective than at 100 W.<sup>17</sup> Similarly, Chen *et al.* (2009) observed that the degradation of Methamidophos and Chlorpyrifos in apple juice after pulsed electric field pretreatment increased as the electric field strength was augmented from 8 kV cm<sup>-1</sup> to 20 kV cm<sup>-1</sup>. This increase in voltage induced the vibration and rotation of polar molecules, facilitating the degradation of these pesticides.<sup>18</sup> However, no studies have explored the application of ultrasound and PEF for reducing pesticides on potato peel waste.

Cyclic liquid nitrogen immersion has been used to accelerate drying processes by utilizing the freeze-cracking effects on the waxy layer of fruits such as blueberries.<sup>19</sup> Additionally, studies have shown that this technique can effectively extract waxes

from the epidermis of plant materials such as grains<sup>20</sup> and straw.<sup>21</sup> Given that a significant portion of pesticides tends to reside in the waxy layer of the peel, it could be possible to reduce pesticide compounds through the application of liquid nitrogen immersion, since this technique targets the specific location where these compounds are predominantly found.

Although these previously described pretreatments present an interesting potential to diminish residual pesticides in foods, they may as well cause a negative impact on the retention of valuable bioactive compounds. For instance, US and PEF intensification processes have been found to decrease the retention of total antioxidant compounds (20.7%), polyphenolic content (63%), and vitamin C when used during the processing of blackberry (US pretreatment), orange peel (PEF-600 µs), and red bell pepper (US and PEF), respectively.<sup>22–24</sup>

Considering the above-mentioned issues related to pesticides and the final quality in potato waste, the objective of this study is to reduce pesticide residue content in potato peel waste using ultrasound (US), liquid nitrogen immersion (LNI), and pulsed electric field (PEF) pretreatment processes, with diverse operating variables such as time, immersion cycles, and pulse numbers, respectively. The effect of these pretreatment methods on phenolic compounds and quality characteristics was assessed as well.

## 2. Materials and methods

### 2.1. Raw materials

Pre-washed potatoes (Russet) purchased from a local grocery store were manually peeled using a knife. Samples were obtained by cutting rectangular slabs from the peel, measuring 10 mm in length, 20 mm in width, and  $1 \pm 0.1$  mm in thickness.

### 2.2. Pesticides and spiking method

In this study, specific pesticide compounds, commercial-grade, including Chlorpropham (98A, AG-Services Inc., Canada), Spirotetramat (Movento 240 SC, Bayer, Canada), Azoxystrobin (Quadris, Syngenta, Canada), Propiconazole (Tilt fungicide, Syngenta, Canada), and Captan (Captan fungicide, Southern Ag, USA), were selected based on their applicability to potato growing and storage protection, and on their varying affinities with water and other physicochemical properties. These commercial-grade pesticides were dissolved in water to create solutions following concentrations recommended by the manufacturer. Initial pesticide concentrations in the solutions were 1.25 g L<sup>-1</sup> for Azoxystrobin, Propiconazole, and Spirotetramat, and 1.5 g L<sup>-1</sup> for Chlorpropham, and Captan.

Spiking of pesticides was carried out following the method presented by Wu *et al.*<sup>11</sup> with modifications. Potato peel samples were immersed in the pesticide solutions at  $T = 20 \pm 2$  °C for 1 hour. After immersion, the spiked samples were drained using a sieve, and any excess solution was blotted with absorbent paper to remove surface moisture. The samples were then placed in a closed container at  $T = 20 \pm 2$  °C for 1 hour to facilitate pesticide penetration. Two types of spiking solutions were employed: individual compound solutions, where single



pesticide solutions were used to spike each sample, and mixed compound solutions, where a mixture of all five pesticides was used.

### 2.3. Pesticide standards and chemical reagents

All chemical reagents used for GC determinations were of analytical reagent grade, and solvents were of HPLC grade. Standards for Chlorpropham, Spirotetramat, Azoxystrobin, Propiconazole, and Captan were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions ( $100 \text{ mg kg}^{-1}$ ) of each pesticide were prepared in acetonitrile (MeCN) and stored at  $-20^\circ\text{C}$ . Methanol (MeOH) and MeCN, magnesium sulfate ( $\text{MgSO}_4$ ), and sodium chloride (NaCl) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

### 2.4. Pretreatment experiments

The pretreatment experiment protocol is illustrated in Fig. 1. Pretreatment conditions were selected from preliminary experiments. Initially, potato peel samples (prepared as described in the previous section) were spiked with pesticides following the spiking procedure explained earlier. Subsequently, the potato samples were subjected to different pretreatment methods: liquid nitrogen immersion (LNI), water immersion (WI, used as a control), ultrasound (US), and pulsed electric field (PEF).

Pesticide concentration and various physicochemical evaluations, including total phenolics (TPC) and chlorogenic acid (CGA) contents, microscopy tissue observation, hardness and color of potato peel, and water electrical conductivity, were carried out as a function of pretreatment conditions. These

evaluations were performed after the pretreatment procedures and compared to the initial values. Detailed information regarding all the operations involved and the technical methods employed in this protocol will be provided in the following sections. All experiments were carried out in triplicates.

**2.4.1 Liquid nitrogen immersion.** For the liquid nitrogen immersion pretreatment, a liquid nitrogen container (Thermo-Flask™, Thermo Scientific™, USA) was filled with liquid nitrogen at a temperature of  $-196^\circ\text{C}$ . Spiked potato peel samples weighing 50 g were placed in a stainless-steel basket and subsequently immersed in the flask. The LNI pretreatment was performed using freezing-thawing 2 min cycles (1 min LNI immersion followed by 1 min thawing at room temperature,  $T = 20 \pm 2^\circ\text{C}$ ). Different numbers of immersion-thawing cycles (1 to 4) were used to assess the effect of pesticide reduction.

**2.4.2 Water immersion.** Water immersion pretreatment was used as a control. Spiked potato samples weighing 50 g were immersed in a beaker filled with water (sample-to-water ratio of 1 : 4 w/w) without agitation, for different durations (1, 2, 3, 4, and 5 minutes) at  $20 \pm 2^\circ\text{C}$ .

**2.4.3 Ultrasound.** Ultrasound pretreatment was conducted using a UP400 St ultrasonic processor (Hielscher Ultrasonics GmbH, Oderstrasse 53, D-14513 Teltow, Germany) equipped with a 22 mm sonotrode. Spiked potato peel samples weighing 50 g, were immersed in a jacketed beaker filled with water at a sample-to-water ratio of 1 : 4 (w/w). The samples were processed at a constant frequency of 24 kHz for different durations: 1, 2, 3, 4, and 5 minutes. Ultrasound treatments were performed under a continuous mode. Temperature ( $25 \pm 2^\circ\text{C}$ ) during the treatment was maintained through a cooling circulation system connected to the jacketed beaker.

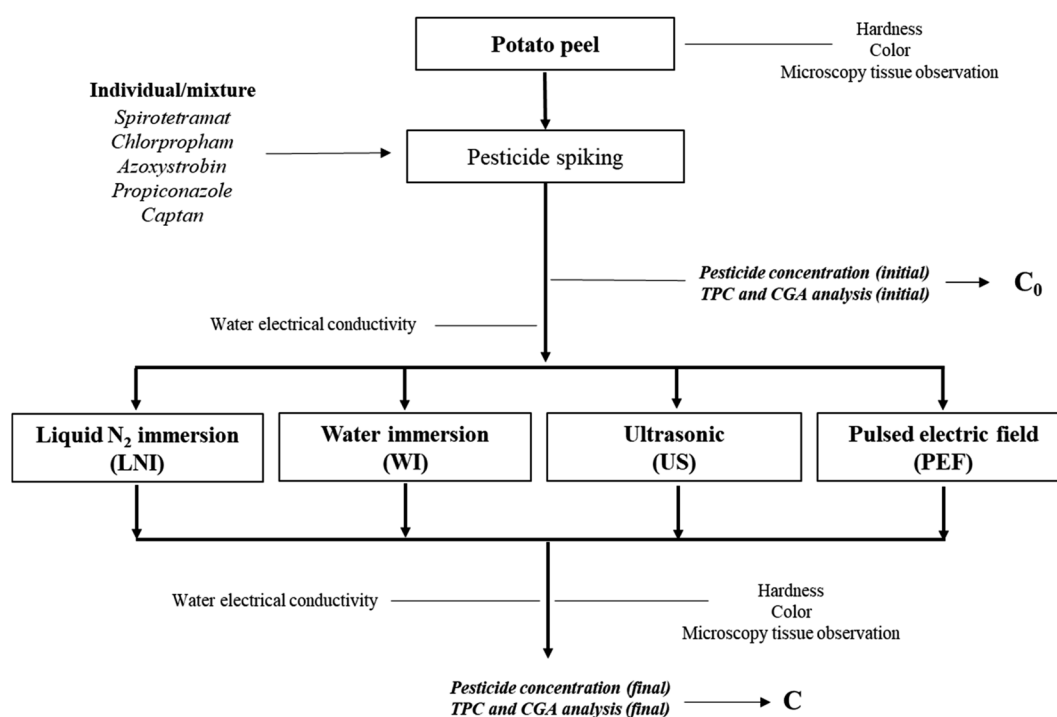


Fig. 1 Experimental protocol of the pretreatment studies for potato peel pesticide reduction and quality impact.



The actual power dissipated was determined using the calorimetric method.<sup>25</sup> For this purpose, temperature increase in 200 mL water, being sonicated without sample nor cooling circulation, was recorded using a thermocouple. From the temperature *versus* time data, the initial temperature increase rate  $dT/dt$  was obtained through linear regression. Ultrasound power was then calculated using the following equation:

$$P = mC_p \frac{dT}{dt}$$

Experiments were done in triplicate. The acoustic energy density (AED) was then calculated by dividing the measured power by the volume of water. The AED value for the applied amplitude levels was  $592.46 \pm 3.59 \text{ W L}^{-1}$ .

**2.4.4 Pulsed electric field.** For pulsed electric field (PEF) pretreatment, batch-type PEF equipment (Cellcrack III, DIL, ELEA, Quakenbrück, Osnabrück, Germany) was used. The voltage was set at 30 kV, and the distance between two parallel stainless-steel electrodes was adjusted to 10 cm, resulting in an electric field strength of  $3 \text{ kV cm}^{-1}$ . The pulse frequency was 2 Hz. Spiked potato peel samples weighing 150 g were immersed in the PEF treatment chamber filled with water ( $20 \pm 2^\circ\text{C}$ ) at a ratio of 1 : 4 (w/w).

The samples were subjected to different pulse numbers, namely 12, 25, and 50, to evaluate the effects of varying pulse numbers on pesticide reduction. Water temperature after PEF treatment was also measured ( $24 \pm 1^\circ\text{C}$ ).

## 2.5. Physicochemical analysis

**2.5.1 Residual pesticides.** To analyze residual pesticides, the samples were homogenized and extracted using the QuEChERS (Quick Easy Cheap Effective Rugged and Safe) method for pesticides, as described by Anastassiades *et al.* (2003),<sup>26</sup> with slight modifications. Potato peel samples were homogenized by Ultra-Turrax® homogenizer (T25 basic IKA®, Werke GmbH & Co.KG, Staufen, Germany) at a speed of 13 500 rpm for 3 minutes (in an ice bath). Then, 10 g of the homogenized sample was transferred into a 50 mL Falcon centrifuge tube. Acetonitrile (10 mL) was added to the tube, and the mixture was vigorously shaken for 1 minute using a Vortex Vortex (Scientific Industries G560 Vortex-Genie® 2 Shaker) at maximum speed (3200 rpm). Anhydrous  $\text{MgSO}_4$  (4 g) and NaCl (1 g) were added to the tube, followed by another 1 min mixing on the Vortex mixer. The resulting mixture was then centrifuged for 6 min at 6000 rpm. The supernatant was filtered through a  $0.2 \mu\text{m}$  PTFE filter and transferred to a 2 mL vial for GC-FID analysis.

Pesticide residue analysis was performed using a gas chromatograph (HP 6890 series) equipped with a flame ionization detector (FID). An RTX®-65TG (Restek, Bellefonte, PA, USA) column ( $30 \text{ m} \times 0.25 \text{ mm}$ ,  $0.10 \mu\text{m}$  film thickness) was used for compound separation. Ultra-high purity hydrogen was used as the carrier gas at a flow rate of  $1.1 \text{ mL min}^{-1}$ . The column temperature was initially set at  $80^\circ\text{C}$  with a hold time of 0.6 minutes, then ramped to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . It was

further increased to  $280^\circ\text{C}$  at a rate of  $20^\circ\text{C min}^{-1}$  and held for 5 minutes. The injector and detector temperatures were maintained at  $250^\circ\text{C}$  and  $280^\circ\text{C}$ , respectively. The injector was operated in split mode, and  $1 \mu\text{L}$  of the sample was injected using an autosampler.

Calibration curves (*i.e.* pic area as a function of concentration) were conducted for each pesticide standard. Thus, initial pesticide concentration in potato peel ( $C_o$ ) was estimated by comparing, for each pesticide compound, the GC elution areas of spiked potato peel samples with individual pesticide standard areas from calibration curves.

Pesticide retention values were reported as the percentage ratio between final (after pretreatment) concentration ( $C$ ) and initial concentration:

$$R(\%) = \frac{C}{C_o} \times 100 \quad (1)$$

**2.5.2 Total phenolic content (TPC).** For the analysis of phenolic compounds, potato peel samples were frozen in a Sanyo medical freezer (MDF 235, Gunma, Japan) at  $-40^\circ\text{C}$  for 24 hours. The frozen samples were then lyophilized for 24 hours using a Freezemobile 25 EL (VirTis, The Virtis Company, Inc., Gardiner, NY, USA) with a heating plate temperature of  $20^\circ\text{C}$ , a condenser temperature of  $-85^\circ\text{C}$ , and a vacuum level of less than 14 Pa. The freeze-dried samples were stored in desiccators with desiccant Drierite® (gypsum (calcium sulphate)) for further analysis.

The total phenolic content was determined using the Folin-Ciocalteu method as described by Al-Weshahy et Venket Rao<sup>2</sup> with slight modifications. Freeze-dried samples (500 mg) were mixed with 5 mL of methanol, followed by centrifugation (6000 rpm, 10 min). Then, a 200  $\mu\text{L}$  aliquot of the phenolic extract was mixed with 100  $\mu\text{L}$  of Folin-Ciocalteu reagent, and 700  $\mu\text{L}$  of saturated  $\text{Na}_2\text{CO}_3$  solution was added. After incubation in the dark at room temperature ( $T = 20 \pm 2^\circ\text{C}$ ) for 2 h, the absorbance was measured at 765 nm using a microplate spectrophotometer (xMark, Bio-Rad Laboratories, Hercules, CA, USA). Gallic acid (Sigma-Aldrich, Oakville, Ontario, Canada) was used as the standard, and the total phenolic content was expressed as mg of gallic acid equivalent per g dry matter (mg GAE/g matter). TPC retention values were reported using eqn (1).

**2.5.3 Chlorogenic acid (CGA).** The chlorogenic acid content was determined using the sodium nitrite method with slight adjustments as detailed in Griffiths *et al.*<sup>27</sup> 100 mg of the lyophilized sample was added to a 2 mL aqueous solution containing urea (0.17 M) and acetic acid (0.10 M). Then, 1 mL of water was added, and the mixture was vortexed for 15 s. Next, 1 mL of sodium nitrite (0.14 M) was added, followed by 1 mL of sodium hydroxide (0.5 M). The suspension was centrifuged at 2250 g for 10 min, and an aliquot of the supernatant was taken. The absorbance was measured at 510 nm using a microplate spectrophotometer (xMark Bio-Rad Laboratories, Hercules, CA, USA). A standard curve was prepared using different concentrations of chlorogenic acid (Sigma-Aldrich, Saint Louis, MO 63103, USA), and the results were expressed as milligrams of





chlorogenic acid per gram dry weight (mg per g dry matter). CGA retention values were reported using eqn (1).

**2.5.4 Water electrical conductivity.** Water electrical conductivity test was performed using an electrical conductivity meter (CyberScan PC 300, Eutech Instruments, Singapore).

**2.5.5 Hardness.** Hardness was measured by using a Texture Analyzer (EZ Text, Shimadzu Co., Kyoto, Japan) with a lower compression plate (118 mm diameter) and piercing needle jig (3 mm diameter). The test speed was 1 mm s<sup>-1</sup>, the trigger force was set to 100 g and 15 mm distance. The maximum force value (yield point) (N) was related to the hardness of potato peel samples.

**2.5.6 Color analysis.** Peel and flesh sides of potato peel samples were inspected visually and with a colorimeter Minolta CR-300 Colorimeter (Minolta Co., Osaka, Japan). The instrument was calibrated with a standard white reflector plate and the system selected was CIE L\* a\* b\*. The results were reported in L\* (lightness to darkness), a\* (redness to greenness), and b\* (yellowness to blueness) values. A fresh potato peel sample was taken as a control.

The total color difference ( $\Delta E$ ) was then determined using the following equation:

$$\Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (2)$$

The subscript "0" refers to the fresh potato peel sample (control).

In addition, hue angle ( $h$ ), and chroma ( $C^*$ ) were calculated using the following equations:

$$h = \tan^{-1} \left( \frac{b^*}{a^*} \right) \quad (3)$$

$$C^* = \sqrt{(a^{*2} + b^{*2})} \quad (4)$$

**2.5.7 Light microscopy observation.** For light microscopy observation, fresh and pretreated potato peel samples were cross-sectioned using a microtome (Leica Jung CM 3000, Nussloch, Germany). The cross-sectioned samples were then stained with alcian blue and mounted on microscope slides for examination. Light microscopy observation was conducted using an Olympus BX51 microscope (Olympus Optical Co., Ltd., Tokyo, Japan) equipped with a 20X objective lens. Images were captured using the digital camera provided with the microscope.

ImageJ 1.53k software program<sup>28</sup> was used to estimate inner cell surface area, epidermal cell surface area, and epidermal cell thickness from image data. The measurements were done in triplicate.

## 2.6. Statistical analysis

The data were expressed as the mean  $\pm$  SD of triplicate experiments ( $n = 3$ ) and analyzed using one-way analysis of variance (ANOVA) with Minitab 16.0 software (Minitab Inc., USA). The significant difference between means was evaluated using the

Tukey test for means comparison. A  $p$ -value of less than 0.05 was considered statistically significant.

## 3. Results and discussion

### 3.1. Pesticide chromatographic determination

Fig. 2 shows the GC chromatogram for Chlorpropharm (a), Captan (b), Propiconazole (c), Spirotetramat (d), and Azoxystrobin (e) chemical standards together with that for potato peel sample after spiking with pesticides of commercial grade (f), which provides the initial pesticide concentrations. From Fig. 2, it can be observed that elution times for different pesticides were 7.7 min (Chlorpropharm), 12.8 min (Captan), 13.9 min (Propiconazole), 16.1 min (Spirotetramat), and 18.8 min (Azoxystrobin) (Fig. 2-a-e, respectively). As well, Fig. 2-f shows the presence of the corresponding different spiked commercial pesticides in the potato peel sample at similar times, together with other compounds coming from additives of commercial pesticides and natural wax compounds from the potato peel.<sup>21</sup>

Initial pesticide concentrations ( $C_0$ ) of potato peel were found to be  $476 \pm 7$  mg L<sup>-1</sup>,  $866 \pm 36$  mg L<sup>-1</sup>,  $786 \pm 47$  mg L<sup>-1</sup>,  $1016 \pm 100$  mg L<sup>-1</sup>, and  $1197 \pm 71$  mg L<sup>-1</sup> for Spirotetramat, Chlorpropharm, Azoxystrobin, Propiconazole, and Captan, respectively.

### 3.2. Effect of pretreatments on pesticide residues

The retention of spiked pesticides in potato peel after diverse pretreatments is presented in Fig. 3 for individually spiked samples. All the pretreatments had a positive impact in decreasing pesticides but to different extents. The effect of each pretreatment will be described separately in the following paragraphs.

As shown in Fig. 3-a, pesticide residues on potato peel after LNI pretreatment were just slightly reduced, decreasing linearly along with the number of immersion-thawing cycles. Results showed a significant decrease ( $p < 0.05$ ) of pesticide residues (Azoxystrobin, Captan, Spirotetramat, and Propiconazole) on potato peel between 1 and 4 cycles of LNI pretreatment. No clear differential behavior of individual pesticide retention values was observed (Fig. 3-a). After four (4) cycles of pretreatment, two pesticides exhibited similar reductions (approximately 23.0% and 21.5% for Azoxystrobin and Captan, respectively). In contrast, Spirotetramat and Propiconazole showed slightly lower reductions of 14.8% and 14.6% while Chlorpropharm exhibited the smallest reduction at only 10%, and no significant difference ( $p < 0.05$ ) between the number of cycles pretreatment. These results could be explained by the impact of liquid nitrogen immersion on the modification of epidermal waxes from plant-based materials<sup>49</sup> and by the distribution of compounds in intracuticular and extracuticular waxes.<sup>29</sup> Ketata *et al.* found that after three liquid nitrogen immersion-thawing cycles, the cuticle thickness of highbush blueberries was reduced by up to 80%, while for lowbush blueberry species, it decreased by up to 55%.<sup>19</sup> Other authors also reported that vegetal waxes from rice, sorghum, wheat,<sup>20</sup> wheat, and flax



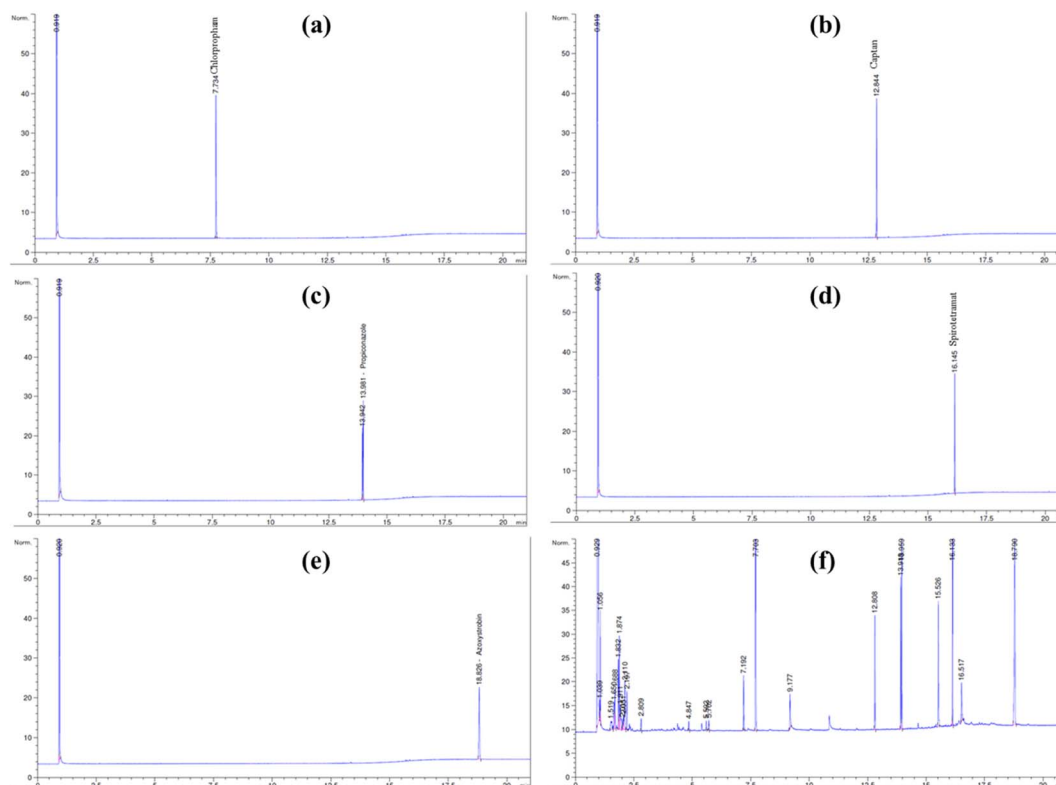


Fig. 2 An example of GC chromatograms of pesticide chemical standards (a–e) and untreated potato peel, spiked with a mixture of 5 pesticides (f).

straw<sup>21</sup> were effectively extracted by immersion cycles in liquid nitrogen. As indicated by Angioni *et al.*,<sup>30</sup> pesticides are mainly present in the plant epidermis, although they could be distributed in epicuticular or intra-cuticular waxes depending on their affinity to different compounds. Therefore, this could explain the slight impact of LNI pretreatment on decreasing pesticide residues from potato peel (around 20%) merely accompanying the wax disappearance due to freeze-cracking of superficial waxes by liquid nitrogen immersions, and additionally, indicating that Chlorpropham could be located internally (intracuticular waxes) rather than at the surface of the potato peel (epicuticular waxes) making its removal more difficult by LNI.

The results of water immersion (WI) pretreatment on pesticide residues indicate a significant reduction ( $p < 0.05$ ) of applied pesticides between 1 to 5 minutes of pretreatment time (Fig. 3-b). These curves show an initial rapid decrease in pesticide retention followed by a “plateau”, from which the equilibrium retention value could be determined. Also, from Fig. 3-c, pesticide residues are significantly reduced by intensification of water immersion with US ( $p < 0.05$ ), with reduction increasing with pretreatment duration. During the ultrasonic process, alternative pressure changes cause the creation, expansion, and implosive collapse of microbubbles in ultrasonically irradiated liquids, which is known as “acoustic cavitation”, striking the surface of sample.<sup>31</sup> This phenomenon accelerates external mass transfer happening during WI and eases the removal of pesticide compounds from the potato peel matrix. For instance,

the removal of pesticide residues from Bok choy (pakchoi cabbage) leaves using ultrasonic treatment was more efficient compared to deionized water soaking, which was attributed to the powerful cavitation effect on the surface of the leaves.<sup>32</sup> Similarly, Lozowicka *et al.* observed that ultrasonic treatment resulted in a greater reduction of 16 pesticide residues from strawberries compared to tap water soaking alone, explained by the formation of cavitation bubbles, which generate mechanical energy in the form of shockwaves and cause agitation within the small pores on the uneven surfaces of strawberries.<sup>33</sup> To end, PEF pretreatment (Fig. 3-d) showed a positive impact in decreasing final pesticide retention compared to WI, however, this reduction is less important than the one observed for US pretreatment. The reduction of pesticide residues was no significant difference ( $p < 0.05$ ) between 25 and 50 pulses of PEF pretreatment, except for Propiconazole residue. Thus, the number of PEF pulses further than 25 does not seem to increase further the reduction of residual pesticides, which could be a good consideration for reducing energy consumption associated with this pretreatment method. To improve PEF performance, a higher electric field strength could be a good venue to test.

As expected, Fig. 3-b–d show that the reduction of pesticides exhibited two different behaviors for WI, US, and PEF pretreatments depending on the type of pesticide: Chlorpropham and Propiconazole presented significantly smaller reductions compared to the group consisting of Spirotetramat, Azoxystrobin, and Captan (Fig. 3-b–d). For instance, the



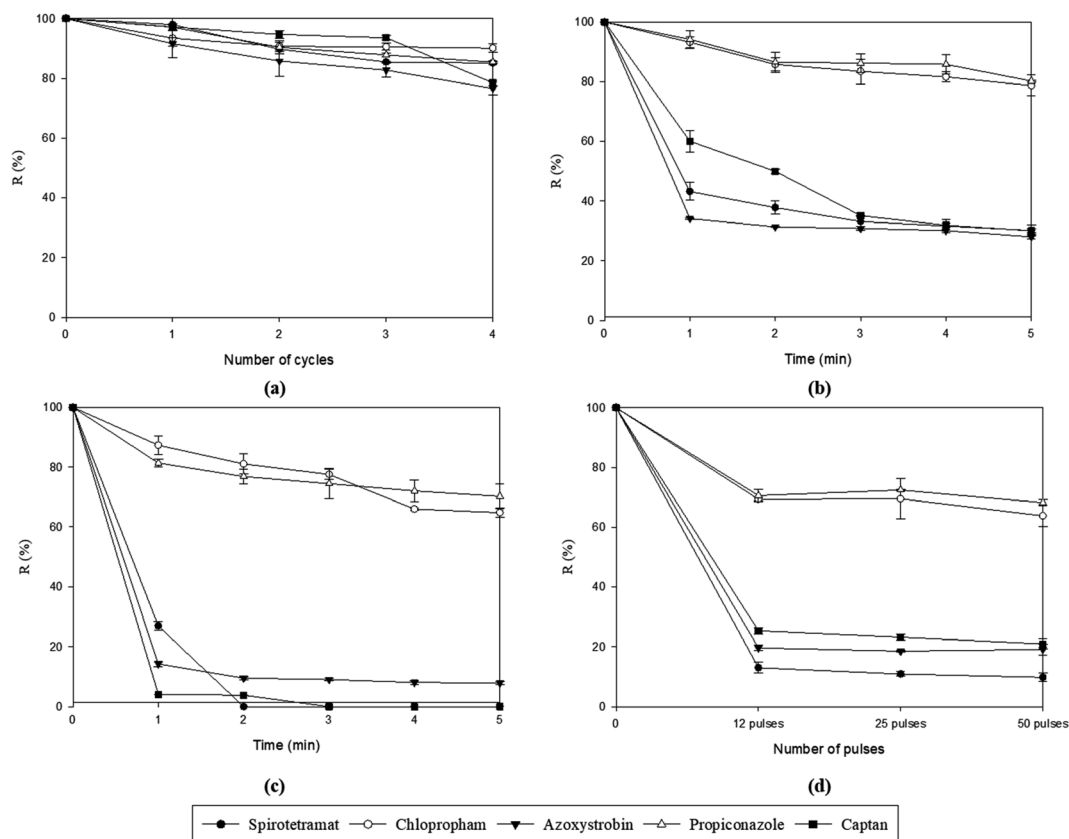


Fig. 3 Pesticides retention after different pretreatments: LNI (a), WI (b), US (c), and PEF (d) for potato peel samples.

retention amount of Chlorpropham and Propiconazole after 5 minutes of US pretreatment reached 64.8%, and 70.2%, respectively (Fig. 3-b), but Spirotetramat, Captan, and Azoxystrobin residues decreased to 0%, 0% and 7.9%, respectively. For PEF pretreatment (Fig. 3-d), the retention of Chlorpropham and Propiconazole at 50 pulses was reduced to 63.8% and 68.2%, respectively, while the retention of Spirotetramat, Captan, and Azoxystrobin was 9.8%, 20.9%, and 19.1%, respectively. These results demonstrate an effective reduction of pesticide retention of potato peel waste through PEF and US pretreatments, particularly for the US regarding the latter group of pesticides. This difference in reduction behavior depending on the type of pesticides can be attributed to variations in  $\log P$  values, which aligns with the results of previous authors.<sup>11,15,33</sup> Discussion about the relationship between pesticide retention and their physicochemical properties will be presented later.

The behavior of pesticides, both individually spiked (Fig. 3-b-d) and mixture spiked (not shown), exhibited similar trends. The differential pesticide retention behavior observed previously was also found to happen for potato peel spiked with a mixture of pesticides. For instance, after 5 minutes of US pretreatment, the retention percentages of Chlorpropham and Propiconazole in potato peel spiked with pesticide mixture were 45.2% and 46.9%, respectively, which were higher than those of Spirotetramat, Azoxystrobin, and Captan (12.4%, 11.8%, and 0.0%, respectively). Retentions of Chlorpropham and Propiconazole residues in a mixture of spiked potato peel for US and

PEF pretreatments were found to be somewhat lower than those for individually spiked ones, while the retention of Spirotetramat, and Azoxystrobin residues were slightly higher. This could be explained by the interaction occurring of the pesticides in the mixture.<sup>34–36</sup>

Fig. 3-a shows that LNI pretreatment is the least effective in reducing pesticide compounds compared to WI, US, or PEF pretreatments (Fig. 3-b-d).

**3.2.1 Equilibrium retention values and  $\log P$ .** To understand better the difference in retention behavior of pesticide compounds after pretreatments, equilibrium retention values for each pesticide are presented in Table 1 together with the octanol–water partition coefficient ( $\log P$ ) representing the lipophilicity of a compound.<sup>10</sup> This property affects various aspects of pesticide behavior, including absorption, transport, persistence, and bioaccumulation.<sup>10</sup> Pesticides with higher  $\log P$  values are generally more hydrophobic, indicating a greater affinity with nonpolar solvents like lipids and organic matter. From Table 1, it can be observed that Chlorpropham and Propiconazole have higher  $\log P$  values (3.76 and 3.72, respectively) compared to Spirotetramat, Azoxystrobin, and Captan (2.51, 2.50, and 2.50, respectively). Additionally, retention values at equilibrium also presented in Table 1 show that the reduction of these pesticides during pretreatment correlates positively with  $\log P$  values, as found previously by other authors.<sup>11,15,33</sup> For instance, in a study by Wu *et al.*, Chlorpyrifos and Bifenthrin pesticides applied on cucumber, exhibited retention rates of



Table 1 Equilibrium pesticide retention (%) after pretreatments of individual spiked potato peel samples<sup>a</sup>

| Pesticides    | log <i>P</i> <sup>57</sup> (at pH 7, 20 °C) | Equilibrium pesticide retention <i>R</i> <sub>eq</sub> (%) |                           |                           |                           |
|---------------|---|--|---------------------------|---------------------------|---------------------------|
|               |   | LNI  | WI                        | US                        | PEF                       |
| Spirotetramat | 2.51  | 85.13 ± 0.46 <sup>a</sup>                                  | 30.04 ± 1.33 <sup>b</sup> | Not detected              | 9.79 ± 1.50 <sup>c</sup>  |
| Chlorpropham  | 3.76  | 90.10 ± 1.37 <sup>a</sup>                                  | 90.01 ± 0.74 <sup>a</sup> | 64.78 ± 1.60 <sup>b</sup> | 61.78 ± 0.26 <sup>c</sup> |
| Azoxystrobin  | 2.50  | 77.09 ± 2.82 <sup>a</sup>                                  | 28.99 ± 0.78 <sup>b</sup> | 7.89 ± 0.47 <sup>d</sup>  | 19.09 ± 1.78 <sup>c</sup> |
| Propiconazole | 3.72  | 85.41 ± 0.34 <sup>a</sup>                                  | 79.93 ± 2.07 <sup>b</sup> | 70.23 ± 4.25 <sup>c</sup> | 68.20 ± 1.08 <sup>c</sup> |
| Captan        | 2.50  | 78.52 ± 0.98 <sup>a</sup>                                  | 24.96 ± 0.57 <sup>b</sup> | Not detected              | 20.93 ± 1.59 <sup>c</sup> |

<sup>a</sup> Values are mean ± SD of triplicates (*n* = 3). Means in the same row (pesticide) with different lowercase superscripts are significantly different (*p* < 0.05).

76% and 85%, respectively, after a 5 minutes washing with tap water. These retention rates presented a positive correlation with their respective log *P* values of 4.7 and 6.6.<sup>11</sup> Another study focused on kumquat fruits, found that Dimethoate and Triazophos residues showed removal rates (inverse of retention rate) of 23% and 10%, respectively, after a 5 minutes washing with tap water. These rates also depended on their log *P* values of 0.75 and 3.55.<sup>15</sup> Furthermore, Lozowicka *et al.* (2016) reported that Acetamiprid (log *P* = 0.8) and Deltamethrin (log *P* = 4.6) spiked on strawberries exhibited removal rates of 56% and 27%, respectively, following a 5 minutes washing with tap water.<sup>33</sup> In the case of potatoes, where the applied pesticides are located on the surface of the potato peel containing epicuticular waxes, those pesticides with higher log *P* values tend to remain attached to the waxes and epidermis and are more difficult to remove, which correlates adequately with our results. This can be explained by the different bonding behaviors of the spiked pesticide molecules on the waxy layer (lipid) of the potato peel.<sup>10,37</sup>

Comparing all the pretreatment methods used in this study, the US was found to be the most effective in decreasing the retention of pesticides, especially for hydrophilic compounds having a weak bonding with epidermal waxes. As discussed previously, pesticide compounds are attached to different extents to the waxy epidermis and US intensification acts mainly on the surface of potato peel easing the removal of hydrophilic compounds.

### 3.3. Effect of pretreatments on quality parameters

**3.3.1 Polyphenol content.** The effect of pretreatments (WI, US, PEF, and LNI) on the average retention of total phenolic compounds (TPC) and chlorogenic acid (CGA) contents is shown in Fig. 4-a and b, respectively. In Fig. 4, average results were presented (instead of results as a function of pretreatment operation variables such as time or pulse number) since no significant difference was found (*p* < 0.05) between them. This could be due to the material-to-solvent ratio used for the experiments (1 : 4), which is higher than most ratios used in the literature,<sup>38–42</sup> hampering the polyphenol removal by quickly saturating the solvent phase. In the literature, the extraction yield of phenolic compounds is influenced by the material-to-solvent ratio used during the extraction process, a higher ratio leads to a reduced mixture density, which affects the efficiency

of extraction.<sup>43</sup> For example, previous studies used various lower material-to-solvent ratios, such as 1 : 20 (w/v, g mL<sup>−1</sup>) for grape pomace,<sup>38</sup> 1 : 10.5 (w/v, g mL<sup>−1</sup>) for fresh blackberries,<sup>22</sup> 1 : 16.7 (w/v, g mL<sup>−1</sup>) for mulberry leaves,<sup>39</sup> and 1 : 24 (w/v, g mL<sup>−1</sup>) for freeze-dried apples<sup>40</sup> treatments. Razola-Díaz *et al.* (2021)<sup>41</sup> also reported the successful extraction of phenolic compounds from orange by-products using a solid-to-solvent ratio of 1 : 24 (w/v, g mL<sup>−1</sup>).

From Fig. 4-a, a slight decrease in polyphenol content (less than 9%) from fresh potato peel was observed in samples pretreated with LNI, WI, and US (not significantly different between pretreatments, *p* < 0.05). In contrast, the retention of TPC in samples pretreated with PEF was significantly lower compared to the other pretreatments, with a retention rate of only 55.9%. Similarly, a 10% decrease in CGA content was observed in samples pretreated with LNI, while decreases of 19% and 23% were observed in samples pretreated with WI and US, respectively. On the other hand, the retention of CGA in samples pretreated with PEF was significantly lower compared to the other pretreatments, with a retention rate of only 54.6%.

In the research conducted by Peiro *et al.*, it was found that the total phenolic content (TPC) extracted from lemon peels significantly increased by 1.6 times when the peels were pretreated with PEF at 7 kV cm<sup>−1</sup> for 30 pulses, compared to untreated samples.<sup>42</sup> Similarly, Luengo, Álvarez, & and Raso reported a remarkable 2.3-fold increase in TPC yield from orange peel extracts when treated with PEF at 3 kV cm<sup>−1</sup> and 20 pulses. This increase was attributed to the permeabilization effect of PEF on the cell membranes of the orange peel, which facilitated the release of polyphenols from inside the cells.<sup>44</sup> However, in the study conducted by Roselló-Soto *et al.*, no significant differences (*p* < 0.05) were observed in the amount of total phenolic compounds extracted from olive kernels with water extraction assisted by PEF and US<sup>45</sup> operated at similar specific powers from 18 to 109 kJ kg<sup>−1</sup>. This different result could be due to the olive kernel matrix structure and composition (different from plant cellular structures), equivalent to a hardwood with cellulose and lignin predominating, or because the solid/liquid ratio used for extraction (1/10) was smaller than in our study (1/4).

Results in Fig. 4 suggest that while there is a slight reduction in both TPC and CGA after certain pretreatments, the differences in TPC were not significant for LNI, WI, and US. However,





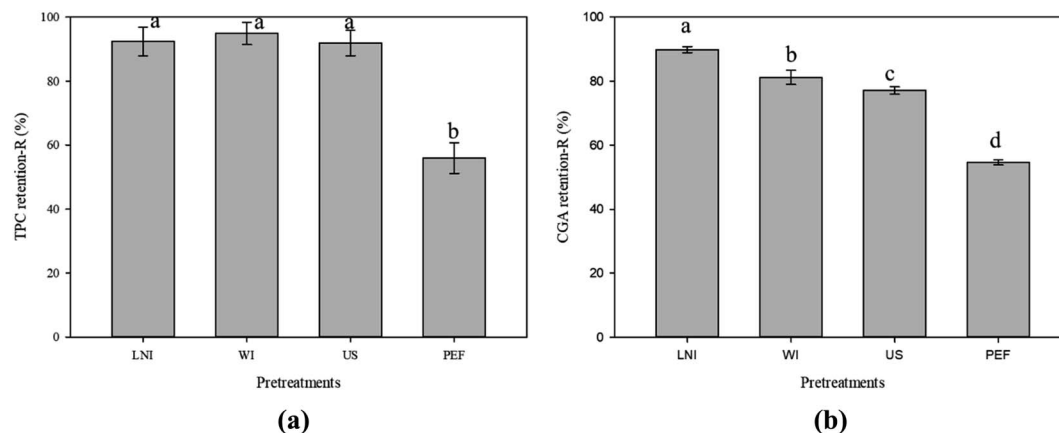


Fig. 4 Average values of total phenolics (a) and chlorogenic acid (b) content retention (R%) of potato peel waste after pretreatments.

it was found that PEF pretreatment has a significant negative impact on the retention of both TPC and CGA in potato peel samples, which could be explained by the different mechanisms of US and PEF pretreatments on the potato peel samples. In the case of US, cavitation bubbles near the material surface during a compression cycle collapsed, leading to the formation of microjets directed towards the epidermal layer of the peel.<sup>22</sup> This phenomenon facilitates the removal of pesticide residues and other contaminants present on the surface of the peel, while causing minimal or negligible changes in the internal cellular structure where polyphenols are located, slowing down their removal, consistent with the findings of Wiktor *et al.* (2021).<sup>46</sup> On the other hand, when PEF was applied to potato peel samples, short intense electric pulses were employed causing electroporation of the internal cell membranes.<sup>47</sup> This electroporation phenomena could lead to the formation of temporary pores in the cell walls, allowing for the release of intracellular compounds, including phenolic compounds and other bioactive substances. It is worth noting that phenolic compounds are mainly located in the vacuoles of plant cells,<sup>48</sup> and the electroporation process during PEF treatment could ease their release.

**3.3.2 Hardness.** Fig. 5-b illustrates the changes in potato peel texture (hardness) following different pretreatments (WI, US, and PEF) at end values of operational variables (time and pulse numbers, respectively). Hardness changes, represented by the ratio of pretreated-to-fresh sample hardness ( $H/H_0$ ) for both WI and US pretreated potato peel samples, were around 1.0. Indicates that the texture of potato peel was minimally affected by WI and US pretreatments, with no significant differences observed between the two processes ( $p < 0.05$ ). On the other hand, PEF pretreatment significantly affected the texture of potato peel, resulting in a lower hardness ratio ( $H/H_0$ ) of 0.65 ( $p < 0.05$ ). These findings align with a study by Lammerskitten *et al.*, which revealed that PEF application reduced apple hardness by 53.8% to 63.1% compared to control samples.<sup>40</sup> In addition, the texture of plant tissue can also be related to cellular disintegration values, as shown in the research by Zongo *et al.*, where PEF (1 kV cm<sup>-1</sup>, 30 pulses) led to a 56% increase in mango sample disintegration values.<sup>49</sup> These results

indicate that PEF pretreatment alters the mechanical properties of potato peel tissue, leading to increased softness and reduced rigidity, corroborating previous results on TPC and CGA lower retention values. This effect can be attributed to the disturbance of cell membrane continuity caused by electrical forces, ultimately resulting in a change in the natural texture, as reported by Wiktor *et al.*<sup>50</sup>

**3.3.3 Color.** The color parameters ( $L^*$ ,  $a^*$ , and  $b^*$ ) of both the peel and flesh sides of potato peel from fresh and pretreated samples were measured to assess the impact of various pretreatments (WI, US, and PEF), as presented in Table 2. Compared to fresh potato peel, there were no significant differences ( $p < 0.05$ ) in the  $L^*$  values among pretreatment samples. However, the US pretreatment sample exhibited a significant decrease ( $p < 0.05$ ) in the  $b^*$  parameter, hue angle ( $h$ ) degree, and chroma value ( $C^*$ ) for the peel side. Conversely, the  $L^*$  values decreased significantly ( $p < 0.05$ ) in the PEF pretreatment, while the  $a^*$  value increased significantly ( $p < 0.05$ ) for the flesh side of potato peel. Specifically, the increase in chroma value was significantly different ( $p < 0.05$ ) for PEF pretreated peel samples compared to fresh potato samples.

Consequently, Fig. 5 presents the color changes ( $\Delta E$ ) in both the peel and flesh sides of potato peel, respectively, following various pretreatments (WI, US, and PEF) at end values of operational variables (time and pulse numbers, respectively). Regarding the peel side (Fig. 5-c), remarkable color changes were observed from the control sample to the pretreated samples, with  $\Delta E$  values of 9.1, 10.9, and 16.1 for WI, PEF, and US pretreated samples, respectively. There was no significant difference in color change between WI and PEF pretreated samples. However, a distinct difference was observed for the US-pretreated sample, which became lighter in color after pretreatment. This can be attributed to the intensity of the US waves on the surface of the sample leading to a more rapid superficial compound dissolution (such as residual dust or dirt left after pre-washing), subsequently causing lightening of the peel surface and an increase in  $\Delta E$  value. These findings are consistent with previously published data regarding the impact of washing methods on the residual presence of these compounds.<sup>51</sup>



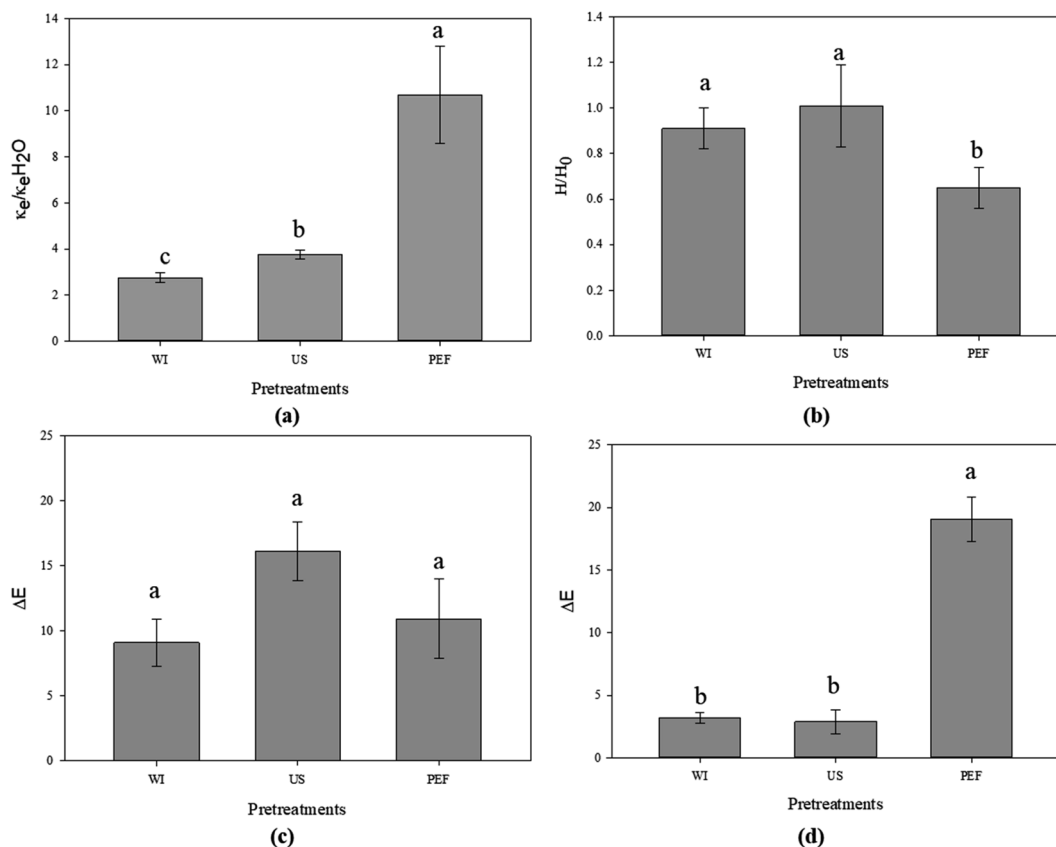


Fig. 5 Changes of water electrical conductivity (a), hardness (b), and color of peel (c) and flesh (d) parts of the potato peel under different pretreatments (results for WI and US are for 5 min, while for PEF, for 50 pulses).

Table 2 Color parameters of fresh and pretreated potato peel at maximum operational variable values<sup>a</sup>

| Samples    |       | Fresh              | US                    | WI                     | PEF                    |
|------------|-------|--------------------|-----------------------|------------------------|------------------------|
| Peel part  | $L^*$ | $49.66 \pm 7.33^a$ | $47.87 \pm 10.27^a$   | $48.93 \pm 7.25^a$     | $42.53 \pm 2.68^a$     |
|            | $a^*$ | $2.86 \pm 2.18^a$  | $8.05 \pm 5.85^a$     | $6.37 \pm 5.71^a$      | $6.37 \pm 5.76^a$      |
|            | $b^*$ | $28.90 \pm 0.81^a$ | $16.38 \pm 7.92^b$    | $30.16 \pm 9.64^{ab}$  | $26.19 \pm 7.62^{ab}$  |
|            | $h$   | $84.43 \pm 4.12^a$ | $65.50 \pm 6.39^b$    | $76.19 \pm 14.44^{ab}$ | $74.59 \pm 15.91^{ab}$ |
|            | $C^*$ | $29.07 \pm 1.02^a$ | $18.30 \pm 9.67^b$    | $31.30 \pm 8.13^{ab}$  | $27.47 \pm 5.93^{ab}$  |
| Flesh part | $L^*$ | $64.07 \pm 5.81^a$ | $61.78 \pm 5.25^a$    | $65.18 \pm 2.48^a$     | $46.93 \pm 3.05^b$     |
|            | $a^*$ | $0.03 \pm 1.33^b$  | $-1.09 \pm 0.08^b$    | $-1.23 \pm 0.49^b$     | $7.38 \pm 4.93^a$      |
|            | $b^*$ | $19.86 \pm 0.74^a$ | $21.02 \pm 0.65^a$    | $19.46 \pm 0.99^a$     | $23.34 \pm 5.45^a$     |
|            | $h$   | $89.84 \pm 3.84^a$ | $92.97 \pm 0.11^a$    | $93.65 \pm 1.61^a$     | $71.36 \pm 14.83^b$    |
|            | $C^*$ | $19.88 \pm 0.73^a$ | $21.04 \pm 0.65^{ab}$ | $19.51 \pm 0.96^a$     | $24.89 \pm 3.65^b$     |

<sup>a</sup> Values are mean  $\pm$  SD. Means in the same row (color parameter) with different lowercase superscripts are significantly different ( $p < 0.05$ ).

Slight color changes were observed on the flesh side of the potato peel (Fig. 5-d) for WI and US pretreated samples, with no significant differences between them ( $p < 0.05$ ). However, in the case of PEF pretreatment, the  $\Delta E$  value for the flesh side was 19.0, which was significantly higher than for WI and US pretreatments. After PEF pretreatment, the flesh side of the samples was darker, which was indicated by lower  $L^*$  values, and higher chroma ( $C^*$ ) values.

Polyphenol oxidase (PPO) activity plays a crucial role in the browning reaction that occurs in minimally processed potatoes. It oxidizes phenolic compounds present in potatoes, converting them into quinones, which further polymerize to form melanin pigments.<sup>52</sup> In addition, chlorogenic acid, constituting 80% of total phenolic acids,<sup>7</sup> significantly contributes to the browning of fresh-cut potatoes. These oxidation processes lead to the development of undesirable colors and texture in the potatoes, ultimately reducing the nutritional and economic value of the



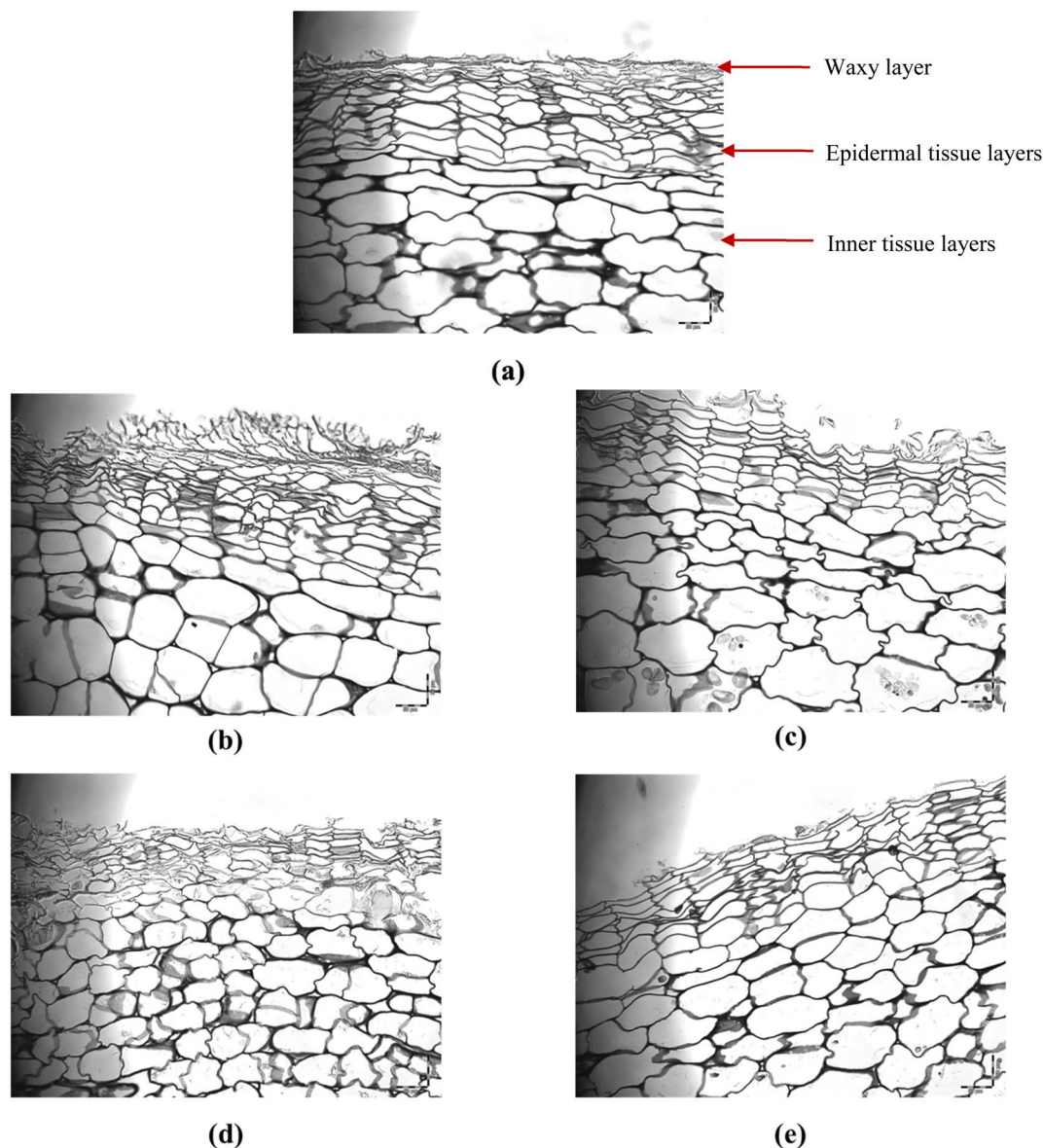


Fig. 6 Microscopy observation of the cross-section through the potato peel under different pretreatments. (a) Fresh potato peel (untreated), (b) WI, (c) US, (d) PEF, and (e) LNI.

Table 3 Values of microstructural changes of fresh and pretreated potato peel<sup>a</sup>

| Sample | Inner cell surface area ( $\mu\text{m}^2$ ) | Epidermal cell surface area ( $\mu\text{m}^2$ ) | Epidermal cell layer thickness ( $\mu\text{m}$ ) |
|--------|---|---|--|
| Fresh  | 4614 $\pm$ 2236 <sup>a</sup>                | 805 $\pm$ 484 <sup>a</sup>                      | 160 $\pm$ 15 <sup>a</sup>                        |
| WI     | 5173 $\pm$ 1977 <sup>a</sup>                | 834 $\pm$ 318 <sup>a</sup>                      | 154 $\pm$ 36 <sup>ab</sup>                       |
| US     | 5099 $\pm$ 2505 <sup>a</sup>                | 881 $\pm$ 396 <sup>a</sup>                      | 130 $\pm$ 8 <sup>bc</sup>                        |
| PEF    | 2015 $\pm$ 793 <sup>c</sup>                 | 461 $\pm$ 187 <sup>b</sup>                      | 92 $\pm$ 28 <sup>d</sup>                         |
| LNI    | 3490 $\pm$ 1467 <sup>b</sup>                | 905 $\pm$ 323 <sup>a</sup>                      | 122 $\pm$ 26 <sup>cd</sup>                       |

<sup>a</sup> Values are mean  $\pm$  SD. Means in the same column with different lowercase superscripts are significantly different ( $p < 0.05$ ).

food. This points out that PEF-treated potato peel samples may have experienced a higher deterioration in the intracellular space of the flesh side, resulting in browning and corroborating

previous results on TPC and CGA lower retention values, while US pretreatment under the conditions used in this study is more promising in terms of final product visual quality.

### 3.3.4 Cellular tissue structure and integrity

**3.3.4.1 Water electrical conductivity.** Water electrical conductivity measurement of the immersion media, before and after the pretreatment processes that use water immersion (WI, US, PEF), allowed for the monitoring of electrolytes or small molecule leakage from the cell tissue and intracellular compartments, which can provide valuable insights of the cellular integrity and permeability of the potato peel samples. The impact of pretreatments on changes in water electrical conductivity is shown in Fig. 5-a at maximum end values of operational variables. The water used for WI and US pretreatments on potato peel exhibited moderate increases of 2.8-fold



and 3.7-fold in water electrical conductivity, respectively. In contrast, PEF pretreatment led to a significant 10-fold surge in water electrical conductivity. Similarly, the results obtained by Wiktor *et al.* (2015) showed that PEF application ( $5 \text{ kV cm}^{-1}$ , 50 pulses) on apple and carrot samples resulted in water electrical conductivity increases of 6-fold and 8-fold, respectively.<sup>53</sup> This substantial increase in electrical conductivity with PEF can be attributed to the phenomenon of electroporation, resulting in the release of intracellular compounds, whereas, the impact of US and WI seems to affect less the internal tissue, as previously discussed. Results of water electrical conductivity corroborate previous results regarding TPC and CGA retention rates, hardness, and color of pretreated potato peel samples.

**3.3.4.2 Light microscopy images.** Fig. 6 shows light microscopic images of the cross-section of potato peel for a fresh sample (Fig. 6-a) along with those after WI, US, PEF, and LNI pretreatments (Fig. 6-b-e) at their respective maximum operational variable values (time, pulse numbers, and cycles). Fig. 6-a offers a clear observation of the distinct layers of potato peel: a thin layer of epicuticular waxes on the surface, a layer of epidermal cells, and another layer of inner tissue cells. The fresh sample (Fig. 6-a) exhibited a microstructure characterized by an intact, compact, and uniform waxy layer and uniform distribution (in cell size and shape) of epidermal and inner tissue layers. Cells in the epidermal layer are distributed densely compared to the inner tissue layer, with a smaller size. Their shape is rectangular. For inner tissue cells, the size is superior, and their shape is oval. For WI pretreated samples (Fig. 6-b), the waxy layer seems stretched compared to fresh peel (Fig. 6-a), which could be because of water flux exchange between water and the sample. The inner tissue cells are round, likely due to water sorption during immersion pretreatment. Conversely, the US pretreated sample (Fig. 6-c) displayed surface damage and loss of the epicuticular waxy layer. The inner tissue cells showed shrinkage, attributable to water flux to the surface where cavitation and accelerated mass transfer occur.<sup>54</sup> The microscopic image of the PEF-treated sample (Fig. 6-d) exhibited as well, a destroyed and absent waxy layer, but significantly smaller inner tissue cells compared to the fresh sample (Fig. 6-a), accompanied by signs of high cellular damage. This phenomenon can be attributed to PEF-caused disintegration of cellular membranes, followed by the release of water and vacuole compounds,<sup>55</sup> resulting in a reduction in vacuole size and shape.<sup>56</sup> As expected, LNI pretreated samples revealed the disappearance of some epicuticular waxes of potato peel surfaces (Fig. 6-e). Although similar in shape, smaller inner tissue cell size was observed compared to initial samples (Fig. 6-a), which could be attributed to the freeze-cracking impact caused by LNI immersion freeze-thawing cycles.<sup>21</sup>

Table 3 provides estimated values for inner cell surface area, epidermal cell surface area, and epidermal cell layer thickness, further highlighting significant reductions in these parameters for PEF and LNI pretreated samples ( $p < 0.05$ ) as found previously from Fig. 6. In the case of PEF pretreatment, the average inner cell surface area was reduced by 56.3%, while epidermal cell surface area and thickness together decreased by 42.7%, and 42.5% compared to untreated samples, respectively.

Additionally, LNI pretreatment resulted in a 24.4% reduction in the average inner cell surface area and a 23.8% reduction in epidermal cell layer thickness. These results corroborate the visual image observations described previously.

Microscopic image results support previous findings of increased water electrical conductivity post-PEF pretreatment, along with lower retention values for TPC and CGA, lower hardness, and darker color of potato peel samples.

## 4. Conclusions

This study focused on innovative pretreatment techniques (WI, US, PEF, and LNI) to enhance the safety of potato peel, a by-product of potato production, by removing residual pesticides while maintaining an interesting bioactive quality before further processing. US and PEF pretreatments emerged as effective strategies for reducing pesticide residues. The elimination of pesticides from potato peel, whether through water immersion independently or with US/PEF intensification processes, was influenced by the compounds' affinity to lipids/water ( $\log P$ ). A higher solid/solvent ratio used in most of the pretreatments together with the impact of ultrasounds mainly on potato peel surface, led to superior retention of phenolic compounds of US pretreated samples, compared to PEF samples for which cell electroporation was predominant. The observed changes in hardness, water electrical conductivity, color, and microstructure after pretreatments corroborated the mechanisms by which these intensification processes worked on pesticide reduction and polyphenol preservation. Thus, using a higher material-to-solvent ratio (1/4) combined with ultrasound pretreatment presented an interesting advantage for preserving bioactive compounds while effectively reducing pesticide residues on potato peel, enhancing the value of such waste towards the application of circular economy in potato transformation industries.

The implementation of these results at the industrial level requires the scale-up of innovative pretreatment techniques, which may pose challenges and considerations. While ultrasound (US) and pulsed electric field (PEF) pretreatments show efficacy in reducing pesticide residues in potato peel on a lab scale, transitioning these methods to large-scale production requires careful evaluation. Scaling up these novel technologies, in addition to the cost and skills required by the industry, necessitates addressing factors such as the need for consistent and reliable power sources, optimization of treatment parameters, and the integration of these technologies into existing production processes. Furthermore, addressing the environmental impact of pesticide residues in wastewater is another important consideration.

## List of abbreviations

|     |                           |
|-----|---------------------------|
| WI  | Water immersion           |
| US  | Ultrasound                |
| PEF | Pulse electric field      |
| LNI | Liquid nitrogen immersion |





|                |                                       |
|----------------|---------------------------------------|
| TPC            | Total phenolic content                |
| CGA            | Chlorogenic acid                      |
| R              | Pesticide retention                   |
| C <sub>0</sub> | Initial concentration                 |
| C              | Final concentration                   |
| log P          | Octanol-water partition coefficient   |
| P              | Power                                 |
| m              | Mass of water                         |
| C <sub>p</sub> | Heat capacity of water                |
| dT/dt          | The initial temperature increase rate |
| AED            | Acoustic energy density               |
| GC             | Gas chromatography                    |
| FID            | Flame ionization detector             |
| κ <sub>e</sub> | Electrical conductivity               |
| H              | Hardness                              |
| L*             | Lightness to darkness                 |
| a*             | Redness to greenness                  |
| b*             | Yellowness to blueness                |
| ΔE             | Total color difference                |
| h              | Hue angle                             |
| C*             | Chroma                                |

## Conflicts of interest

There are no conflicts to declare.

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