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The optimisation of extraction of antioxidants from potato peel by pressurised liquids

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ABSTRACT

Response Surface Methodology was used to optimise the solid–liquid extraction and Pressurised Liquid Extraction of polyphenols from industrially generated potato peel. Efficiency of extraction was optimised by measuring antioxidant activity, phenol content and the level of caffeic acid. Conditions for optimal antioxidant activity as measured by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay were 75% ethanol, 80 °C and 22 min with solid–liquid extraction, resulting in an optimum activity of 352 mg Trolox Equivalents/100 g DW potato peel. In comparison, the use of Pressurised Liquid Extraction resulted in an optimum activity of 339 mg Trolox Equivalents/100 g DW potato peel at 70% ethanol and 125 °C. Therefore the use of Pressurised Liquid Extraction did not enhance extraction in comparison to solid–liquid extracts, but using aqueous ethanol as extraction solvent recovered a higher level of polyphenols than when using 100% methanol.

1. Introduction

By-products of food processing, such as peels and pomace, represent an abundant source of bioactive compounds. In many cases these by-products are not used to their potential and diverted to landfill. In addition, dealing with waste and by-products in a sustainable and environmentally friendly way is becoming a highly important issue in the food industry. Due to the European Landfill Directive, the food industry is forced to reduce the percentage of waste and by-products going to landfill by 2020 (Kosseva, 2009). Potatoes are a major world crop and over the last years, the consumption of processed potatoes has increased (Schieber & Saldaña, 2009). Potatoes are generally peeled when processed. Research to valorise and upgrade potato peel waste is therefore essential.

Potato peel waste has been proposed as dietary fibre for baking products (Arora & Camire, 1994), but also as a source of natural antioxidants. Polyphenols, an important group of antioxidants present in the potato, are largely concentrated in the peel, since they have a role in the defence mechanism against phytopathogens (Friedman, 1997). Potato peels have therefore been subject of study in lipid oxidation studies. Ethanolic extracts from potato peel retarded lipid peroxidation in radiated processed lamb meat (Kanatt, Chander, Radhakrishna, & Sharma, 2005). In addition, lyophilised aqueous extracts derived from potato peel waste showed similar antioxidant activity in sunflower oil as the synthetic antioxidant butylated hydroxyanisole (BHA) (Sotillo, Hadley, & Holm, 1994). A possible limitation of these extracts for the use as food ingredients would be the presence of glycoalkaloids. Glycoalkaloids are generally considered as toxic, but depending on their concentration present, can also have advantageous effects. They are also mainly located in the peel (Friedman, 2006).

Recently, interest in novel and green techniques to valorise by-products has increased. One technique of interest is Pressurised Liquid Extraction (PLE). PLE is a technique in which pressure is applied during the extraction, allowing the use of temperatures above the boiling point of solvents. The use of higher temperatures increases mass transfer and extraction rates and PLE generally involves shorter extraction times and a lower consumption of organic solvents than conventional techniques (Mendiola, Herrero, Cifuentes, & Ibanez, 2007). To date PLE has been mainly used to optimise analytical preparation procedures (Alonso-Salces et al., 2001; Luthria, 2008). Only recently, the technique has gained interest as a green extraction method to obtain bioactive compounds from by-products, such as grape pomace (Monrad, Howard, King, Srinivas, & Mauromoustakos, 2010; Ju & Howard, 2005).

In this study the extraction of antioxidants from industrial potato peel waste is optimised with regards to ethanol concentration, temperature and time using both solid–liquid extraction and PLE. For PLE ethanol concentration and temperatures were varied. Both techniques were optimised by Response Surface Methodology. In addition to antioxidant activity, phenol level and the level of caffeic

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acid, the level of glycoalkaloids was taken into consideration. The ethanolic extractions were compared with conventional extractions.

2. Materials and methods

2.1. Chemicals

Caffeic acid, +-catechin, α-chaconine, chlorogenic acid, 2,2-diphenyl-1-picrylhydrazyl (DPPH), epicatechin, ferulic acid, Folin–Ciocalteu Reagent (FCR), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox), p-coumaric acid, sinapic acid, α-solanine, syringic acid, trans-4-hydroxy-3-methoxy cinnamic acid, were purchased from Sigma–Aldrich Chemical Co. (St. Louis, USA).

2.2. Preparation of materials

Potato peel waste was provided by Largo Foods Ltd. (Ashbourne, Ireland). The peel waste was from standard crisp production, from the potato variety *Lady Claire*. On arrival the samples were vacuum packed to prevent oxidation and fermentation and stored at −20 °C for at least 24 h. Following this, samples were removed from the vacuum pack and lyophilised for a minimum of 5 days in an A6/14 freeze dryer (Frozen in Time Ltd., York, UK). The lyophilised samples were then vacuum packed and stored at −20 °C until required for analysis.

2.3. Solid–liquid extraction

On the day of extraction, lyophilised samples were milled to a fine powder using a blender (BL440001, Kenwood limited, Hampshire, UK). The particle size distribution of the potato peel powder was as follows: 2.2% > 1.4 mm; 17.5% > 850 μm and < 1.4 mm; 24.4% > 600 μm and < 850 μm; 56.0% < 600 μm. The moisture content of the potato peel powder was 13.6%. After adding 15 mL of X_1 concentration ethanol to 0.25 g sample powder, the samples were homogenised for 30 s at 10,000 rpm and 60 s at 20,000 rpm using a multi sample homogeniser (Omni-International, Marietta, USA). Following this the volume of the samples was added up to 25 mL with ethanol of concentration X_1 and heated at X_2 °C for X_3 min. The samples were then cooled to room temperature and more solvent was added if necessary to bring the final volume back to 25 mL. The samples were then vortexed with a V400 Multituve Vortexer (Alpha laboratories, North York, Canada) for 20 min at 1050 rpm and centrifuged for 10 min at 995*g* (MSE Mistral 3000i, Sanyo Gallenkamp, Leicestershire, UK). Ten millilitres of the supernatant was filtered through 0.45 μm PVDF syringe filters (Pall Gelman Laboratory, Portsmouth, UK). The extracts were stored at −20 °C.

2.4. PLE procedure

Potato peel powder was generated as described in Section 2.3. To extract the potato peel powder by PLE an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, CA) was used. To avoid clogging 0.40 g of potato peel powder was added between two layers of diatomaceous earth in the 22 mL extraction cell. A cellulose filter was used in the bottom of the cell. Different temperature ranges and ethanol:water concentrations were used in order to identify optimal conditions for antioxidant and polyphenol extraction by RSM. A standard stepwise PLE extraction protocol was used for all extractions. (1) The PLE cell was loaded into the extraction compartment and heated up to the temperature specified by the RSM design (X_1 °C). (2) The cell was filled with ethanol and water concentration at the specified concentration (X_2 %) until a pressure of 10.3 MPa was reached. (3) A static extraction of 5 min when pressure and temperatures were reached was then maintained. A preliminary study indicated that a static heating time of 5 min was optimal, which was in agreement with the advice of the manufacturer. (4) The cell was rinsed by passing an additional 60% of the volume of the solvent mixture which had already crossed the cell. Extracts were collected in 60 mL glass vials (Dionex, Sunnyvale, CA) and their volume was measured. In all methods described below the final volume and therefore concentration of potato peel was taken into account in calculations. Prior to analysis the samples were centrifuged for 15 min at 2238 g (MSE Mistral 3000i, Sanyo Gallenkamp, Leicestershire, England). Ten millilitres of the supernatant was filtered through 0.45 μm PVDF syringe filters (Pall Gelman Laboratory, Portsmouth, England). The extracts were stored at −20 °C.

2.5. Conventional extraction procedures

Previous studies indicated 100% methanol was optimal for the extraction of polyphenols and antioxidants from apple pomace (Wijngaard & Brunton, 2009, 2010). Therefore a conventional extraction with 100% methanol was carried out to assess optimum antioxidant activity, phenol content and caffeic acid level of potato peel. Twenty-five millilitres of methanol was added to 0.25 g freezedried potato peel. This sample was not heated, but directly vortexed, centrifuged and filtered after homogenisation. For standard extraction of glycoalkaloids an extraction solution following the extraction method of Knuthsen, Jensen, Schmidt, and Larsen (2009) was used. An aqueous extraction solution (water/acetic acid/sodium hydrogen sulphite solution, 100/5/0.5, v/v/w), was added to freezedried potato peel (0.05 g/L). As with the methanolic extracts the samples were not heated during extraction and directly vortexed and centrifuged after homogenisation.

2.6. Measurement of in vitro antioxidant activity

A modified version of the diphenyl picrylhydrazyl (DPPH) assay using Trolox as a standard was used to measure *in vitro* antioxidant activity (Goupy, Hugues, Boivin, & Amiot, 1999). Standard samples were prepared by diluting a methanolic Trolox stock solution (0.2 mM). The Trolox standard samples and blanks were used for the calibration curve. The results are expressed in mg Trolox equivalent/100 g dry weight (mg TE/100 g DW). A working DPPH solution (0.048 mg/mL) was prepared by making a 1 in 5 dilution of the methanolic DPPH stock solution (2.38 mg/mL). Prior to analysis, serial dilutions of the ethanolic extracts were prepared. Diluted ethanolic extract (500 μL) was added to 500 μL of the DPPH working solution in micro-centrifuge tubes. After vortexing, the tubes were left in the dark for 30 min at room temperature. The absorbance was then measured against ethanol at 515 nm in 1 mL propylene cuvettes using a spectrophotometer (UV-1700 Pharma Spec, Shimadzu, Milton Keynes). The decrease in absorbance of a sample was calculated in comparison to a blank sample and corrected for the absorbance of the sample extract itself. The relative decrease in absorbance (PI) was then calculated as follows: PI (%) = $1 - (A_e/A_b)$, with A_e the absorbance of sample extract and A_b the absorbance of blank. The PIs used to calculate the related antioxidant activity were superior (PI_1) and inferior (PI_2) to the value estimated at 50%. The antioxidant activity was defined as the concentration of sample extract necessary to obtain an activity of 50% (IC_{50}). In all experiments the IC_{50} of Trolox was determined as well. The final results for antioxidant activity were determined using the following equation: antioxidant activity = $(IC_{50Trolox}/IC_{50Sample}) \times 10^5$. The antioxidant activity was expressed in mg Trolox equivalent (TE) per 100 g dry weight sample (mg TE/100 g DW).