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Subcritical water extraction of bioactive compounds from waste onion skin

M.T. Munir [a], Hamid Kheirkhah [b], Saeid Baroutian [a, *], Siew Young Quek [b], Brent R. Young [a]

[a] Department of Chemical & Materials Engineering, Faculty of Engineering, The University of Auckland, Auckland, 1023, New Zealand
[b] School of Chemical Sciences, Faculty of Science, The University of Auckland 1010, Auckland, New Zealand

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ABSTRACT

Subcritical water extraction (SCWE) is a modern extraction technique that provides a number of advantages compared with traditional solvent extraction methods. The use of water rather than solvents is particularly advantageous when extracting medically and commercially important phenolic compounds from food and food-processing by-products. In this study, SCWE was used to recover bioactive phenolic compounds from onion skins. The efficiency of extraction using the SCWE process was affected by extraction temperature, particle size and pH. Extraction temperature was found a key factor affecting total phenolic content (TPC) and maximum TPC values were obtained at lower temperature. The antioxidant activity and total flavonoid content (TFC) of the extracts were mainly affected by the pH. Maximum antioxidant activity and TFC were obtained at higher pH during SCWE. Comparison of SCWE with conventional solvent extraction using ethanol also showed that subcritical water can be an excellent substitution for organic solvent when extracting bioactive compounds from onion skin.

1. Introduction

Onion (*Allium cepa* L.) is cultivated around the world and is the second most grown horticultural crop after tomatoes (Griffiths et al., 2002). Global onion production was estimated at 89 million tonnes in 2014 with an increase in production of more than 25% over the past decade. As a result, more than 550,000 tonnes of onion skin bio-waste is produced annually (Choi et al., 2015). This quantity of onion skin waste has become an environmental problem because this waste is not suitable as animal food and so is usually sent to landfill. However, onion skin waste is rich in bioactive compounds such as phenolics and flavonoids (Choi et al., 2015; Gawlik-Dziki et al., 2015). Bioactive compounds are extra-nutritional constituents believed to provide nutrition and health benefits such as anti-inflammation and anti-cancer effects (Nowacka et al., 2018). Processes suitable for producing quality extracts in high quantities need to be investigated.

Organic solvents are commonly used in many industrial extraction processes but some are toxic and environmentally damaging. Therefore, stringent solvent removal procedures are required whenever products or extracts are prepared for food or medical uses. Furthermore, the solvents themselves can be costly to obtain at high purity and often cannot be easily disposed of, taking both time and money. Consequently there is a need for extraction techniques and/or solvents that are non-toxic.

Recently, several techniques have been reported in the literature to extract bioactive compounds from onion skin. These include solvent extraction (Suh et al., 1999; Wach et al., 2007), microwave-assisted extraction (Routray and Orsat, 2012; Zill e et al., 2011), and ultrasound-assisted extraction (Jang et al., 2013; Jin et al., 2011). However, these techniques are time-consuming (approximately five times of subcritical water extraction) and inefficient. For example, a large amount of solvent (approximately 50 mL per 1 g of dried onion skins) is consumed during conventional solvent extraction (Choi et al., 2015), microwave-assisted extraction involves a long extraction time and little information is available on conditions suitable for extracting bioactive compounds (Kala et al., 2016), while ultrasound-assisted extraction has to be undertaken carefully as it can quickly degrade bioactive compounds (Veggi et al., 2014; Zhao et al., 2006).

Subcritical water extraction (SCWE) is an environmentally friendly process that is increasingly used as an alternative to traditional extraction methods such as solvent extraction (Cheigh et al., 2012; Todd and Baroutian, 2017). For example, SCWE uses

* Corresponding author.
E-mail address: s.baroutian@auckland.ac.nz (S. Baroutian).

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no organic solvent and produces higher yields than traditional methods (Plaza et al., 2010). During SCWE, feedstock is heated in the aqueous phase at a sub-critical temperature (~150–320 °C) and pressure (~20–150 bar) (Getachew and Chun, 2017; Munir et al., 2017). This level of pressure is used to maintain the water in its liquid state (Zhang et al., 2017). Under these conditions, the dielectric properties of water change (Abdelmoez et al., 2014). For example, the dielectric constant of water is approximately 80 at room temperature. However, this value decreases to 27 at 250 °C, which lies between that of methanol and ethanol at 25 °C (33 and 24 respectively) (Wiboonsirikul and Adachi, 2008). The dielectric constant of water is a measure of its polarity or ability to insulate charges (i.e., ions) from each other. Under elevated temperature, the reduced dielectric constant of water enhances its dissolution properties (Speight, 2005). The exact properties can be altered by adjusting the extraction conditions. Thus, increasing the temperature of the pressurised water lowers its polarity by a known amount, which results in non-polar substances being more water soluble (Kronholm et al., 2007). The mass transfer rate also increases due to the reduced viscosity and surface tension of the water as well as its increased diffusivity (Asl and Khajenoori, 2013). This simple principle allows extraction and fractionation of a wide range of compounds to be achieved with a high degree of specificity (Cacace and Mazza, 2006; Güçlü-Üstündağ et al., 2007).

Subcritical water extraction has been used to extract value-added products (e.g., bioactive phenolic compounds) from plant materials such as wheat straw (Abdelmoez et al., 2014), satsuma mandarin (Ko et al., 2016), grape marc (Todd and Baroutian, 2017), and red ginseng (Lee et al., 2018). However, limited studies were found about the use of subcritical water to extract bioactive phenolic compounds from onion skin. Furthermore, there was a 'poor' understanding of the effect of extracting process parameters on the quality of bioactive phenolic compounds.

The aim of this study was to investigate the effect of SCWE process variables on the quality and quantity of phenolic and flavonoid bioactive compounds extracted from waste onion skins. The results of SCWE were compared with those obtained from traditional organic solvent extraction using ethanol. Extraction experiments were designed using a face-centred central composite design (FC–CCD) of response surface methodology (RSM) to study the effect of three process variables (reaction temperature, onion skin sample particle size and suspension pH) on the concentration and quality of extracts. Total phenolic content (TPC) and total flavonoid content (TFC) were measured, and 2,2-diphenyl-1-picrylhydrazyl (DPPH) antioxidant activity (radical scavenging activity assays) was determined. The effects of the three process variables studied on TPC, TFC and DPPH were then modelled using an RSM technique. Analysis of variance (ANOVA) was also used in this study to investigate the fit and significance of the developed models. Flavonols were identified using high-performance liquid chromatography (HPLC) analysis. The results from SCWE were also compared with those obtained by organic solvent extraction.

2. Materials and methods

2.1. Materials

New Zealand grown dry Pukekohe Longkeeper brown onion skins were obtained from a local onion processing company and were crushed using a coffee bean grinder. A Retsch AS200–vibratory sieve shaker with adjustable amplitude, 1.8 mm was used to separate the material into three different particle size fractions: 100–200 μm (S1); 200–500 μm (S2); and 500–850 μm (S3). Each fraction was mixed with deionized water using a magnetic stirrer to make an aqueous mixture with 2 wt % total solids.

All standard reference materials including kaempferol, gallic acid, quercetin, Folin–Ciocalteu's phenol reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), and trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) were purchased from Sigma-Aldrich (New Zealand). Sodium carbonate, sodium nitrite, sodium hydroxide, aluminium chloride and HPLC-grade solvents, including ethanol and methanol, were also purchased from the same supplier.

2.2. Subcritical water extraction (SCWE)

Subcritical water extraction was carried out in a 1 L Parr Reactor (Series 4540 high-pressure reactor; Parr Instrument Company, USA) using a face-centred central composite experimental design (explained in Section 2.7). The extraction vessel was filled with 600 mL of sample suspension for each run. Sulphuric acid (10 wt %) and sodium hydroxide (10 wt %) were used to adjust suspension pH to the desired value within the range of 2–10. The extraction vessel was then purged with N_2 to remove air then additional N_2 was used to pressurise the vessel to 30 bar. A mixing speed of 400 rpm and total extraction time of 30 min were used for all extractions but the temperature was varied within a range of 170–230 °C. The selected conditions of SCWE were based on optimal conditions determined from preliminary experiments. Time zero (untreated) samples were prepared by adding 2 wt % onion skin samples (three size fractions) into deionized water. A mixture of liquid product and solid was obtained after the SCWE and was filtered off the liquid using glass microfiber filters, 0.7 μm. Filtered liquid product was further used as samples for analysis such as TPC, TFC, and DPPH.

2.3. Solvent extraction

Duplicate solvent extractions were carried out using 70% (v/v) ethanol at 60 °C, for 3 h, with moderate shaking (150 rpm) using samples of each particle size fraction at a concentration of 2% (w/v). The selected conditions of solvent extraction were based on optimal conditions determined from previous studies (Jin et al., 2011; Ko et al., 2011; Lee et al., 2014).

2.4. Determination of total phenolic content (TPC)

The TPC of each sample (filtered extract liquid product) was determined according to an improved version of the procedure explained by Singleton and Rossi (1965) and the method suggested by Tang et al. (2015). Triplicate 25 μL aliquots of gallic acid standards and samples were transferred into separate wells of a 96-well plate and mixed with 125 μL of 10-fold freshly diluted Folin–Ciocalteu's phenol reagent by gentle shaking. After 10 min, 125 μL of 7.5% sodium carbonate (w/v) was added. Plates were incubated in the dark for 60 min at room temperature (~23 °C), and the absorbance was measured at 765 nm using an ultraviolet–visible (UV–Vis) microplate reader (PerkinElmer 2300 EnSpire Multimode Reader, USA) against a reagent blank. The total phenolics content in each extract was determined using a standard curve prepared for gallic acid, and the results were expressed as mg of gallic acid equivalents per gram of dry onion skin (mg gallic acid equivalent/g DW).

2.5. Determination of total flavonoid content (TFC)

The TFC of each sample (filtered extract liquid product) was measured according to the aluminium chloride colorimetric assay of (Albishi et al., 2013). Briefly, 1 mL aliquots of samples or quercetin standards were mixed with 4 mL of Milli-Q water and 0.3 mL of aqueous 5% $NaNO_2$. Then 0.3 mL 10% $AlCl_3$ and 2 mL 1 M NaOH