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Optimization of phytochemicals production from potato peel using subcritical water: Experimental and dynamic modeling

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ABSTRACT

Phytochemicals were obtained from potato peel using conventional and subcritical water (sCW) extraction. The influence of process parameters on the removal of carbohydrates, phenolics and antioxidant compounds were optimized using Response Surface Factorial Design and the Taguchi method. Ethanol concentration (1–90%) and pH (3–10) were studied for the conventional extraction and static holding time (2–25 min), pressure (40–120 bar), temperature (140–260 °C), and pH (3–9) were studied for the sCW extraction. Higher amounts of phytochemicals were obtained with the sCW extraction than with the conventional extraction. The highest total carbohydrates (610 mg GE g^{-1} potato peel), total phenolics (20 mg GAE g^{-1} potato peel), and total antioxidant activity (42 mg $FeSO_4$ g^{-1} potato peel) with low browning color of the extracts were obtained at 40 bar, 190 °C, and 9 min of static holding time using a flow rate of 3 mL min^{-1}. The proposed dynamic mass transfer-reaction model fitted well the experimental data with a mean square error of 0.4 and predicted well the potato peel residual mass.

1. Introduction

Obtaining phytochemicals of biomass has motivated further development of new technologies, such as subcritical fluid (sCF) processing with water (sCW, subcritical water), with aqueous methanol (sCAM, subcritical aqueous methanol) or with aqueous ethanol (sCAE, subcritical aqueous ethanol). The sCF process relies on the decrease of fluid polarity by increasing the temperature under pressure to maintain the fluid in the liquid state. Depending on the temperature and fluid polarity, the sCF can extract selectively polar or non-polar organic compounds of different biomass matrices. In particular, the sCW has been used for the extraction of phenolics of potato peel [1,2], Damnacanthal from roots of *Morinda citrifolia* [3], and flavor compounds from *Rosmarinus officinalis* [4].

By-products resulting from agriculture and food processing industry are abundant biomass, such as potato peel that is a by-product from the peeling process, and represent non traditional sources of phytochemicals. Studies on extraction of phenolics from potato peel using sCF technology have been conducted using different experimental designs at various temperatures and a constant pressure. For example, Singh and Saldaña [1] removed total phenolics with methanol solid–liquid (S–L) batch extraction (0.83 mg g^{-1} dry potato peel) and with sCW extraction (1.48 mg g^{-1} dry potato peel). Wijngaard et al. [2] reported similar total phenolics extraction with both aqueous ethanol S–L batch extraction (3.94 mg g^{-1} dry potato peel) and with sCAE extraction (3.68 mg g^{-1} dry potato peel). Despite a number of studies on phenolics removal using sCFs, few studies are available for the removal of carbohydrates. Yang et al. [5] reported 25% yield of carbohydrates removal from *Grifola frondosa* at 210 °C, 44 min, 26:1 (water:solid) and a pressure over 50 bar in a batch reaction system. Reducing sugars were also obtained from the hydrolysis of ginger bagasse starch using sCW and CO_2 at 200 °C [6] for further fermentation. Then, the removal of carbohydrates from potato peel could find potential applications in the biofuel or pharmaceutical industry.

Experimental designs have been used to determine the effect and optimal conditions of one or more factors (variables) upon one response. The one factor at a time (OFAT) design evaluates one variable at a time while maintaining the other variables constant but lacks to evaluate interactions among the variables studied. Response surface methodology (RSM) has been commonly used to determine optimum conditions for one response using the significant variables with a polynomial fitting on the response. But, the RSM accuracy is affected by limitations on the number of data points, data noise (errors not normally distributed), and inadequacy of the quadratic fitting model [7]. The data noise can increase with highly sensitive responses, such as temperature for the sCF extraction, thus requiring the use of replicates in the experimental

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Nomenclature

FRAP	ferric reducing/antioxidant power
GAE	gallic acid equivalent
GE	glucose equivalent
mse	mean square error
OFAT	one factor at a time
RI	refraction index
RSM	response surface methodology
sCF	subcritical fluid
sCW	subcritical water
sCAE	subcritical aqueous ethanol
SHT	static holding time

Symbols

A_{420}	absorbance at 420 nm
C_{ie}	concentration of the phytochemical *i* in equilibrium ($mg\,mL^{-1}$)
C_i	concentration of the phytochemical *i* in the bulk liquid ($mg\,mL^{-1}$)
C_{i0}	concentration of the phytochemical *i* inside the potato peel ($mg\,mL^{-1}$)
dC_S/dt	variation of the concentration of the substrate as a function of time ($mg\,mL^{-1}\,min^{-1}$)
dN/dt	mass transfer rate of the phytochemical *i* ($mg\,min^{-1}$)
K	convective mass transfer coefficient in the substrate (min^{-1})
k_LA/V	convective mass transfer coefficient in the fluid (min^{-1})
k_p, k_c	reaction rate constants (min^{-1}) for phenolics and carbohydrates, respectively
P	pressure (bar)
pp	dry potato peel
r_P	rate of production of phenolics ($mg\,mL^{-1}\,min^{-1}$)
r_C	rate of production of carbohydrates ($mg\,mL^{-1}\,min^{-1}$)
T	temperature (K)
TC	total carbohydrates ($mg\,GE\,g^{-1}$ pp)
TP	total phenolics ($mg\,GAE\,g^{-1}$ pp)

Greek letters

κ	conductivity ($mS\,cm^{-1}$)
η	internal effective factor (adimensional)

design. These limitations explain the variability of results reported by Wijngaard et al. [2], who obtained slightly higher extraction of phenolics using the solid–liquid (S–L) batch extraction than with the sCF extraction. An alternative experimental design is the Taguchi method [7] that determines the optimal conditions of the factors without the use of a fitting model, considering the variation of the experiment. In a multiresponse experiment, such as the sCF extraction of phytochemicals, measurements of various responses are obtained for each setting of parameters. Also, optimum conditions for a multiresponse experiment are not global because conditions that are optimal for one response may be far from the optimal for the other responses. However, the desirability function approach is the most widely used method in the industry to calculate the optimum conditions of multiresponse experiments [7]. Despite the increase on experimental data using sCF extraction, the mathematical representation of the physical phenomena to optimize operating conditions and simulate the process still lacks attention.

Extraction of phytochemicals from the matrix by sCFs, includes the dissolution of phytochemicals with the solvent, reaction, its diffusion through the matrix and its transportation by the sCF. The removal of phytochemicals and their transportation can be described by kinetic and mass transfer models, respectively. A good correlation of the kinetic data of the sCW extraction of Damnacanthal from roots of *Morinda. citrifolia* was obtained by Anekpankul et al. [3] with an external mass transfer resistance model. But, this model lacks to consider the material balance of the extracted phytochemicals throughout the process. Therefore, the main objective of this study was to evaluate the effect of various processing conditions on the production of phytochemicals from potato peel, and to propose a dynamic kinetic-mass transfer model that also predicts the residual mass. For the S–L batch extraction, the pH and ethanol concentration were optimized using the RSM. For the sCW semi-continuous extraction, the OFAT and the Taguchi method were used to optimize the pressure, temperature, flow rate and static holding time (SHT).

2. Materials and methods

2.1. Materials and sample preparation

The water used was degasified distilled water with pH of 6.7. Phenolics and carbohydrates standards, with purity ≥96%, were obtained from Sigma Aldrich (St. Louis, MO) and Fisher Scientific (Fair Lawn, NJ), respectively. Potato, variety Red, was obtained from a local supermarket Superstore (Edmonton, AB, Canada). Potato peel was freeze dried for 3 days using a Vertis freeze drier (Gardiner, NY) and milled in a Fritsch mill model no.14-4050 (Idar-Oberstein, Rhineland-Palatinate, Germany) using four different sieves (20, 30, 40 and 50 mesh) with a final average particle size of 0.43 mm. Potato peel was stored inside Uline ziploc bags at −20 °C.

2.2. Characterization of extracts

2.2.1. Refraction index, pH and conductivity measurements

Refraction index was measured using an automatic refractometer Mettler-Toledo RE50 (Tokyo, Tokyo, Japan) with a resolution of $\pm10^{-5}$, an uncertainty in the experimental measurements of $\pm2\times10^{-5}$, and an uncertainty in the temperatures of ±0.01 °C. The pH and conductivity were measured using the Fisher Scientific Accumet instrument (Ottawa, ON, Canada) with a resolution of $\pm10^{-2}$, an uncertainty in the experimental measurements of $\pm2\times10^{-2}$ and an uncertainty in the temperatures of ±0.1 °C.

2.2.2. UV–VIS spectrophotometric analysis of extracts

The Folin–Ciocalteu method was used to determine total phenolics content, following the methodology proposed by Singleton and Rossi [8]. A sample aliquot of 40 μL was mixed with 3.1 mL of water and Folin–Ciocalteu reagent (200 μL) added to withstand for 7 min. Then, sodium carbonate (20% w/v; 600 μL) was added and after shaking, the mixture was incubated for 90 min in dark. The absorbance was measured at 765 nm. The final results were expressed as milligrams of gallic acid equivalents per gram of dried potato peel ($mg\,GAE\,g^{-1}$ pp).

The methodology of Dubois et al. [9] was used to determine total carbohydrates content. Then, 0.5 mL of phenol and 2.5 mL of sulfuric acid (96%) were added to an aliquot of 1000 μL of the diluted extract. The absorbance was measured at 490 nm using a Jenway Genova spectrophotometer. The final results were expressed as milligrams of glucose equivalents per gram of dried potato peel ($mg\,GE\,g^{-1}$ pp).

The ferric reducing/antioxidant power (FRAP) was used to estimate the antioxidant activity of the extracts. FRAP analysis was performed according to the methodology reported by Benzie and