Journal of Food Engineering xxx (2017) 1–8

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Sustainable extraction and encapsulation of pink pepper oil

Kátia S. Andrade [a], Denis Poncelet [b], Sandra R.S. Ferreira [a,*]

[a] Chemical and Food Engineering Department, Federal University of Santa Catarina, EQA/UFSC – C.P. 476, CEP 88040-900, Florianópolis, SC, Brazil
[b] Génie des Procédés Environnement et Agroalimentaire, GEPEA/ONIRIS, Rue de la Géraudière, B.P. 82225-44332 Nantes Cedex 3, France

ARTICLE INFO

Article history:
Received 25 October 2016
Received in revised form
11 January 2017
Accepted 19 February 2017
Available online xxx

Keywords:
Pink pepper
Antioxidant activity
Supercritical fluid
Encapsulation

ABSTRACT

Pink pepper (*Schinus terebinthifolius R.*) is a native tree from Brazilian coast and presents important biological activities, such as antitumor, anti-inflammatory, antioxidant, among others. The objective of this work was to explore the use of the supercritical fluid extraction (SFE) for pink pepper fruits, a sustainable method for a novelty material, comparing with different techniques in terms of process yield, total phenolic content (TPC), and antioxidant activity of the recovered extracts. The SFE was performed at pressures from 150 to 300 bar and temperatures of 40, 50 and 60 °C, with CO_2 as solvent. Pink pepper extracts were also obtained by Soxhlet (SOX) and by Ultrasound accelerated extraction (UE) using hexane, ethanol (EtOH), and ethyl acetate (EtOAc) as solvents. The extracts were evaluated as antioxidant potential (ABTS and DPPH methods), total phenolic content (TPC) and chemical profile (GC-MS). The encapsulation process was evaluated using the extract obtained at 300 bar and 60 °C, through the emulsification and solvent extraction technique, using PLA as encapsulating agent. The best extraction yields were obtained by SOX-EtOH and UE-EtOH (44 ± 1% and 21 ± 2%, respectively), followed by SFE at 300 bar and 60 °C (5.9 ± 0.3%). Pink pepper extracts obtained by SOX-EtOH and SFE 300 bar/60 °C presented the best DPPH value. The major compounds identified in the pink pepper extracts were germacrene D, sabinene, β and α-phellandrene. The microencapsulation by the emulsification and solvent extraction technique led the formation of micrometer-sized particles with spherical shape and morphology of the microspheres. The encapsulation efficiency of pink pepper extract in polylactic acid (PLA) ranged from 34.3% to 74.1%. The results from this work suggest the importance of this raw material as a potential for generating high value products with therapeutic applications.

1. Introduction

Schinus terebinthifolius Raddi (Anacardiaceae) is a perennial tree native to the Brazilian coast and spread to other regions of South America, Central America, Europe, Asia and Africa. The use of the fruits from *Schinus terebinthifolius* R. as food seasoning in homely and industrial products is rather extensive. The pink pepper has been used as a substitute for black pepper and, according to chemical analysis reported in the literature, there are similarities in chemical composition between both species (Cláudio et al., 2007).

Different therapeutic properties are attributed to pink pepper, such as antioxidant, antitumor and antimicrobial. Brazilian's folk medicine uses it as anti-inflammatory, astringent, tonic and stimulant. These properties have been related to the presence of polyphenols such as apigenin, ellagic acid, and naringin. In addition, antimicrobial activity have been associated to substances like terebinthona, hidroximasticadienoic acid, terebinthifolic acid and ursolic acid, present in the plant extract. The main monoterpenes found in ripe fruits extracts are α-pinene, β-phellandrene and *trans*-ocimene, followed by the sesquiterpene germacrene-D (Bendaoud et al., 2010; Bertoldi, 2006; Santos et al., 2007).

The quality of natural extracts, related to composition and biological activity, is strongly associated to the extraction process, the solvent used, the characteristics of the vegetal matrix, its storage condition and pre-treatment applied. The extraction techniques and the solvents used must be carefully chosen to optimize the balance between maximizing yields and selectivity (Azmir et al., 2013; Louli et al., 2004; Moure et al., 2001).

Several studies involving the extraction of pink pepper leaves are reported in the literature, and very few works with pink pepper fruits. However, the methods employed are basically hydrodistillation and Soxhlet extraction with ethanol (Bendaoud et al., 2010; Bertoldi, 2006; Lloyd et al., 1977; Santana et al., 2012).

* Corresponding author.
E-mail address: s.ferreira@ufsc.br (S.R.S. Ferreira).

http://dx.doi.org/10.1016/j.jfoodeng.2017.02.020
0260-8774/© 2017 Elsevier Ltd. All rights reserved.

The supercritical fluid extraction (SFE) is an alternative extraction method which enables the solvating power modulation by controlling the process temperature and pressure, with consequent selectivity adjustment. Besides, SFE employs green solvents, like carbon dioxide, and not requires a step for solvent removal. Then, SFE is a viable alternative for extraction and fractionation of natural products, especially for food and pharmaceutical industries (Michielin et al., 2009; Reverchon and De Marco, 2006).

The use of high quality natural extracts, obtained by environment friendly technologies, is the focus of countless studies in different fields of research. Furthermore, it is also important to preserve the integrity of these compounds against degradation, for instance by means of encapsulation in biopolymers by equally friendly methods. The encapsulation process provides protective effect of the core material, preventing losses of volatile compounds, masking undesirable flavors and odors and enhances the solubility of hydrophobic compounds in a aqueous media that increases its range of application (Gomes et al., 2011). The microencapsulation by solvent extraction technique is widely used in pharmaceutical industries and consists of four steps: *(a)* dissolution or dispersion of the bioactive compound in an organic solvent containing the polymer; *(b)* emulsification of this organic phase in a second continuous phase immiscible with the first one; *(c)* extraction of the organic solvent from the dispersed phase by the continuous phase, in order to transforming the droplets into solid microspheres; *(d)* harvesting and drying of the microspheres.

In this method, a careful selection of the encapsulation conditions and the materials used aid the control of the particle size, within *nano*metric to *micrometer* range (Freitas et al., 2005; Li et al., 2008). Polylactic acid (PLA), widely used in encapsulation process, is an aliphatic polyester with adjusted hydrolyzability, approved by the Food and Drug Administration (FDA) and by European regulatory authorities, and is *Generally Recognized As Safe* (GRAS) (Costa Lima et al., 2012).

Studies related to biological activities and encapsulation process of SFE from *Schinus terebinthifolius* fruits are new and suggest a distinct valorization of this unique raw material. Therefore, the objective of the present work aimed to compare different extraction methods and solvents to obtain pink pepper fruit extracts, for encapsulation in biopolymers to extend its use by means of green processes. The results from this work are presented comparing the extraction yields, and also evaluating the extracts quality in terms of total phenolic content, antioxidant activity and chemical profile. With this research, different method to obtain and protect bioactive extracts from pink pepper fruit were investigated to aid the development of therapeutic formulations.

2. Materials and methods

2.1. Raw material and sample preparation

Pink pepper samples (*Schinus terebinthifolius* R.) were collected in the campus of the Federal University of Santa Catarina. The plant was identified and a voucher specimen (number 54104) was deposited at “Herbário Flor” of the Federal University of Santa Catarina. After harvest, the samples were cleaned to remove leaves, branches, debris, dust and other undesired materials. The pepper grains were then stored in transparent polyethylene bags at 2 °C until the drying process. The raw material presented 20.8 ± 0.4% (w/w) of moisture and volatile content, determined according to the 950.46B method of AOAC (Latimer, 2012). After the drying process, the pepper grains were ground in a domestic blender and the grounded material was stored at − 18 °C until the extractions were performed. All solvents used in the experiments were of analytical grade (P. A.) purchased from Lafan Química Fina LTDA. Carbon dioxide (99.9% purity) was purchased from White Martins S/A (São Paulo, Brazil) and delivered at pressure up to 60 bar. NaturePlast (France) kindly provided the PLA pellets (PLE 003).

2.2. Extraction methods

2.2.1. Soxhlet (SOX)

The SOX extraction was performed according to 920.39C method of AOAC (Latimer, 2012). Three different solvents were used: hexane (Hx), ethyl acetate (EtOAc) and ethanol (EtOH), with ascending polarity of 0, 4.4 and 5.2, respectively (Ritchie, 2000). The residual solvent from all extracts (SOX and UE with three solvents) was eliminate in a rotatory evaporator (Fisatom, 802, Brazil), supplied with cooling and vacuum control. Next, the extracts were stored in amber glass flasks at −18 °C. The extraction yields of all method/solvent systems were determined by the ratio between the mass of extract obtained and the mass of raw material (wet basis) and the results are presented by average ± standard deviation.

2.2.2. Ultrasound-assisted extraction (UE)

The ultrasound-assisted extractions were carried out in an ultrasonic cleaner bath, which operates at a frequency of 55 kHz and potency of 100 W (Vinatoru, 2001). The method consisted of placing 7 g of raw material and 210 mL of solvent inside a covered glass balloon. The extractions were performed in duplicate at room temperature for 45 min using the same solvents described in Section 2.2.1.

2.2.3. Supercritical fluid extraction (SFE)

A high-pressure unit, previously described by Zetzl et al. (2007), was used for the SFE with CO_2 as solvent by following the extraction procedure from Michielin et al. (2005) to obtain the pink pepper extracts. Briefly, the extraction consisted of placing a fixed mass of 15 g of the dried raw material (grounded pink pepper) inside the extractor cell to form the fixed bed of particles, followed by the control of the process variables (temperature and pressure). The extraction was then performed and the solute collected in amber flasks and weighed on an analytical balance (OHAUS, Model AS200S, NJ, USA). The SFE with CO_2 was conducted at temperatures of 40, 50 and 60 °C and pressures of 150, 200 and 300 bar, at constant solvent flow rate of 8 ± 2 g/min. The extraction time was set at 3 h according to the kinetic extraction curve performed at 200 bar, 50 °C (intermediary conditions of extraction) and 8 ± 2 g CO_2/min. The solvent density values were obtained according to Angus et al. (1976). The results were expressed in terms of extraction yield (X_0).

2.3. Determination of total phenolic content (TPC)

The TPC was determined according to the Folin-Ciocalteu spectrophotometric method (Singleton and Rossi, 1965). Briefly, the reaction mixture was composed by 0.1 mL of extract (concentration of 1667 mg/L), 7.9 mL of distilled water, 0.5 mL of Folin–Ciocalteu reagent (a mixture of phosphomolybdate and phosphotungstate) and 1.5 mL of 20% sodium carbonate, placed in opaque flasks. The flasks were agitated and allowed to rest for 2 h, then the absorbance measured at 765 nm in a spectrophotometer (Femto, 800XI, Brazil). The TPC value was calculated according to a standard curve ($y = 0.0011x + 0.0352$; $R^2 = 0.9951$), prepared previously with gallic acid as standard (galic acid equivalent: GAE). The analysis was performed in triplicate and the results expressed as mg GAE/g extract as mean ± standard deviation.

Please cite this article in press as: Andrade, K.S., et al., Sustainable extraction and encapsulation of pink pepper oil, Journal of Food Engineering (2017), http://dx.doi.org/10.1016/j.jfoodeng.2017.02.020