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Selective extraction of saponins from *Ilex paraguariensis* St.-Hil. unripe fruits

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ABSTRACT

The unripe fruits of mate tree are an abundant source of saponins, known natural surfactants. The aim of this work was to evaluate non-conventional extraction techniques for the selective extraction of saponins from unripe fruits of yerba mate. Different ultrasound power (282–565 $W\,cm^{-2}$) and electric field (25–50 $V\,cm^{-1}$) intensities were assayed, as well as different solvent flow rates ($1.67–2.78 \times 10^{-4}$ $kg\,s^{-1}$) for pressurized liquid extraction applied to the fruits. In this study, the pressurized liquid extraction was more selective for saponins than ultrasound and electric field. At optimal conditions, the extraction using ultrasound and electric field resulted in yields of 6.42% and 6.83% of saponin equivalent per gram of extract, respectively. Although pressurized liquid extraction showed low brute extracts yields, it was highly selective for saponins, yielding up to 10.09%. Mathematical models, suitable for each extraction technique, were used to model the experimental data.

1. Introduction

Ilex paraguariensis St.-Hil. is a native South American tree from the Aquifoliaceae family. Its leaves, popularly known as “mate”, are widely used as tea-like beverage prepared as infusion. Brazil is the largest producer of mate green leaves, producing 860 thousand ton per year (SEAB – Secretaria de Estado da Agricultura e do Abastecimento, 2014). An adult plant produces around 150 kg of leaves and 20 kg of fruits (Fernandes et al., 2016). However, the fruits are considered an undesired byproduct of the mate manufacturing processes. These fruits consist of a non-negligible amount raw material that is usually discarded, causing an environmental problem. Nevertheless, it can be an alternative to develop new products and to add value to food industry.

Studies shown that the unripe mate fruits are rich in triterpenoids saponins (Pavei et al., 2007; Treter et al., 2010), known as natural surfactants, used due to their emulsifier and pharmacological properties (Sparg et al., 2004; Lee et al., 2015). Due to increase preference for natural as opposed to synthetic substances by the consumer, saponins have been studied and used in foods as natural surfactant and preservative in controlling microbial spoilage of food (Cheok et al., 2014).

The extraction techniques of saponins most often used are conventional ones, and few studies have been made about the extraction processes. Conventional extraction processes (e.g. maceration, Soxhlet and percolation) usually present low selectivity and efficiency, demanding long times of solid–solvent contact to reach equilibrium and high temperatures. These factors can impact on the quality of the extracts, changing their therapeutic, nutritional and sensorial properties (Cheok et al., 2014). The development of alternative technologies to replace conventional extraction methods with higher extraction efficiency and lesser environmental impact is particularly important for the recovery of valuable natural bioactive compounds. An ideal extraction method should have some characteristics: be swift, produce yield significant recovery rates and avoid or reduce degradation; moreover, the extracts should be easily separated from the solvent.

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Nomenclature

C_{calc}	Concentration of triterpenoid saponins μg_{ilex} mL^{-1}
C_{∞}	Amount of solute transferred in infinit time g
C_t	Amount of solute transferred in a given time g
a_0	Specific area for a spherical particle m^{-1}
k_f	Mass transfer coefficient for fluid phase $m\,s^{-1}$
k_s	Mass transfer coefficient for solid phase $m\,s^{-1}$
$\dot{q}$	Specific flow rate of solvent s^{-1}
q_m	Specific amount of solvent at the beginning of extraction in the interior of particles
q_n	Specific amount of solvent at the end of the extraction of easily accessible solute
q_n	Non-zero roots of Eq. (3)
x_0	Overall initial concentration related to solute-free solid phase
x_{1E}	Coded electric field
x_{1F}	Coded solvent flow rate
x_{1P}	Coded ultrasound power
x_2	Coded temperature
x_k	Inaccessible oil concentration inside the solid phase particles
y_r	Solubility
z_w	Dimensionless coordinate of the boundary between fast and slow extraction
E	Electric field $V\,cm^{-1}$
F	Solvent flow rate $10^{-4}\,kg\,s^{-1}$
P	Ultrasound power $W\,cm^{-2}$
S	Total saponin in extracts % $g_{ilex}g^{-1}{}_{extract}$
t	Extraction time s
T	Temperature °C
D	Mass diffusivity of the solute inside the particle $m^2\,s^{-1}$
K	Partition coefficient
N	Mass of the solute-free solid phase kg
Q	Mass of solvent kg
V	Volume of solution mL
W	Parameter of slow-extraction period
Z	Parameter of fast extraction period
d	Diameter of one fruit m
e	Mass of extract relative to N
q	$\left(=\frac{Q}{N}\right)$ dimensionless amount of solvent
r	Radius of one fruit m
u	Superficial solvent velocity $m\,s^{-1}$
y	Experimental design response

Greek letters

$\propto$	Ratio of the volumes of the solution and plant
β_0	Constant
β_j	Linear coefficients
β_{ij}	Interaction coefficient
β_{jj}	Coefficient of the quadractic term
ε	Bed porosity
ρ	Density of solvent $kg\,m^{-3}$
ρ_s	Density of solid phase $kg\,m^{-3}$

Electric fields with intensities lower than $1000\,V\,cm^{-1}$ are usually classified as moderate electric fields (MEF). Its use have shown interesting influences on the permeability and diffusion across cell membranes through electroporation phenomenon (Loghavi et al., 2009; Sensoy and Sastry, 2004). Some authors attributed to this phenomenon the potential applicability of moderated electric fields on bioactive compounds extraction from food (Oliveira et al., 2015). Although no studies were found about electric field applied to unripe mate fruits for saponin extraction, reports of the use of pulsed electric field in ginseng indicated its applicability for saponin extraction (Hou et al., 2010).

Ultrasound (US) is the most popular non-conventional extraction technology used for saponin extraction. It is a low-cost, efficient, and simple technique offers high reproducibility and requires low energy input. Several researches focused on the isolation of specific saponins and evaluation of its pharmaceutical properties relies on ultrasonic baths (Borges et al., 2013; Avula et al., 2011; Wang et al., 2012). However, few studies emphasize the extractions conditions. Wu et al. (2001) evaluated the use of ultrasound on the extraction of ginsenosides from ginseng roots, comparing ultrasound bath and probe extraction to Soxhlet and report that extractions assisted by ultrasound are faster than conventional methods and can be used to avoid thermal degradations of unstable compounds.

Compressed fluid-based techniques (e.g., supercritical fluid extraction and pressurized liquid extraction) provide several operational advantages that overcome many limitations of conventional extraction methods. Due to their low viscosity and relatively high diffusivity, supercritical fluids have enhanced transport properties than liquids, can diffuse easily through solid materials, and can therefore give faster extraction rates. Other advantage, compared to other extraction techniques, is the use of solvents generally recognized as safe (GRAS), being carbon dioxide the solvent more usually used. However, the extraction using pure supercritical carbon dioxide is restricted to apolar and low polarity substances. One alternative for the extraction of more polar compounds such as saponins is the use of pressurized liquid extraction (PLE), also called accelerated solvent extraction (ASE). The use of solvents below their critical points, in liquid state, at high pressure and temperature conditions improve the extraction process mass-transfer kinetics. Pressurized liquid extraction has been extensively applied to extract bioactive compounds, although few studies concerned the extraction of saponins from plant materials (Cheok et al., 2014; Herrero et al., 2013). Fernandes et al. (2017) evaluated the properties of extracts of *I. paraguariensis* ripe fruits obtained from supercritical CO_2 and compressed propane extraction. However, to the best of our knowledge, there have been no reports highlighting the extraction of saponins from aerial parts of *I. paraguariensis* with the technique until now.

Another important aspect for engineering process is the mathematical modeling of kinetic data. This procedure is a valuable tool for the design and improvement of industrial processes. There is no generic model that can be applied to any mass transfer phenomenon, since factors such as type of product, raw material, solvent and extractor vessel geometry can influence the extraction curve. For that reason, several models with different approaches have been developed and used in the description of extractive processes. Diffusive models deduced from the Fick's second law are widely used to model the mass transport phenomenon on diffusive processes affected by electric fields (Barba et al., 2015; Kusnadi and Sastry, 2012; Sarang and Sastry, 2007).

For pressurized liquid extraction, mathematical models based on the differential mass balance for the fluid and solid phases inside an extraction bed are suitable, because they are consistent with the physical situation. In this category of models we can mention those proposed by Reverchon (1996) and Sovová (1994) that have been widely used in the modeling of extraction curves for different raw materials and operating conditions (Mezzomo et al., 2009; Nuñez et al., 2015; Rossa et al., 2018; Scopel et al. 2014; Leitão et al. 2013; Reis-Vasco et al. 2000).

The preeminence of saponins pharmaceutical properties and its applicability in food products has motivated the research of new extraction techniques such as electric field, ultrasound and pressurized liquid extraction in order to supply the current demand. This study focused on these three techniques, specifically on the use of moderated electric field, ultrasound probe, and a mixture of ethanol and pressurized carbon dioxide. The best operational conditions within a pre-set group of process variables for the extraction techniques were identified for each technique.