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Comparative kinetic analysis of isothermal extraction of caffeine from guarana seed under conventional and microwave heating

Borivoj Adnadjevic[a,*], *Biljana Koturevic*[b], *Jelena Jovanovic*[a]

[a] *Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12–16, Belgrade 11001, Serbia*
[b] *The Academy of Criminalistic and Police Studies, Cara Dusana 196, 11080 Belgrade, Zemun, Serbia*

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ABSTRACT

The kinetics of the isothermal extraction of caffeine from the guarana seed powder with water under conventional (CH) and microwave heating (MWH) were investigated. By applying the isoconversional method, it was established that the kinetics of the caffeine extraction under CH and also under MWH is an elementary kinetic process. The model fitting method was used to determine the kinetics model of caffeine extraction. It was found that the kinetics of the caffeine extraction for both heating modes can be described by the Jander's equation. The rate of the extraction of caffeine under MWH is ~2 times higher than under CH. The values of kinetics parameters (E_a and lnA) of the extraction process under MWH are lower than for CH. The established influence of MWH on the kinetics of caffeine extraction is explained with a specific activation mechanism of water molecules and with an increase in the energy of the ground vibration level of resonant oscillator of N_3–CH_3 band of caffeine molecule ($\nu = 317\ cm^{-1}$) which is caused by the absorption of microwave energy.

1. Introduction

Caffeine (1,3,5-trimethylxanthine) is an alkaloid with widespread occurrence in a variety of plants, such as: coffee, tea, mate, cola nuts, cocoa and guarana. Caffeine is a valuable substance for pharmaceutical, food and cosmetics industries, which acts as stimulant for the heart, respiratory and the central nervous system, and is a vasodilator and a diuretic (Jun, 2009). The amount of caffeine found in plants varies, with the highest amounts found in guarana (*Paullinia cupana*, Sapindaceae), that can be up to 7.5% (Beck, 2005), which makes guarana a useful raw material for the extraction of caffeine.

Extraction of caffeine from various plants was abundantly investigated, focusing mainly on conventional solvent extraction, using either pure solvents (water, methylene chloride, and chloroform) or water–organic solvent mixtures (Wang and Helliwell, 2000). These methods have some disadvantages since they are time-consuming and result in low extraction yields.

In recent years, more advanced extraction methods have been used as an alternative to conventional solvent extractions of caffeine. These methods include ultrasound-assisted extraction (Rostagno et al., 2011; Sereshti et al., 2013); supercritical fluid extraction (Mehr et al., 1996; Saldaña et al., 2002; Tello et al., 2011); solid-phase extraction (Jafari et al., 2011); dispersive liquid–liquid extraction (Sereshti and Samadi, 2014); pressure processing assisted extraction (Jun, 2009); extraction using battery type extractor (Senol and Aydin, 2006); and column-chromatography extraction (Wang et al., 2012). Among these advanced methods, considerable attention in recent years has been focused on microwave-assisted extraction (MAE).

* Corresponding author.
E-mail addresses: bora@ffh.bg.ac.rs, biljanakoturevic@gmail.com (B. Adnadjevic).
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MAE is a process that uses microwave energy and solvents to extract target compounds from various matrices (Spigno and De Faveri, 2009). When used for the extraction of biologically active compounds from plant materials, MAE has shown many advantages over the conventional extraction method featuring as it can reduce the time of isolation analyte, requires less volume of solvents and produces higher extraction yields (Kaufmann and Christen, 2002). The effect of microwave heating on the kinetics of chemical reaction and physicochemical processes is explained as combination of the thermal effect (overheating, hot spots and selective heating) and specific microwave effects (Hoz et al., 2005).

Many reports have been published on the application of MAE of various bioactive compounds from plants, such as: saponins, anthraquinones, flavonoids, and chlorogenic acid (Chen et al., 2007; Hemwimon et al., 2007; Xiao et al., 2008; Zhang et al., 2008). MAEs of caffeine have also been reported, from various teas (Rahim et al., 2014; Lou et al., 2012; Vuong et al., 2012; Wang et al., 2011; Pan et al., 2003) and from cacao (González-Nuñez and Cañizares-Macías, 2011).

Considering findings that the MAE can be effective at extracting bioactives from plant materials, in some papers a comparison of MAE has been made with conventional extraction systems. Pan et al. (2003) and Vuong et al. (2012), investigated the effect of non-isothermal microwave heating on the caffeine extraction from tea and find that microwave irradiation improved caffeine extraction compared to the conventional extraction.

Despite findings that microwave heating can improve extraction of caffeine, there is no literature data about investigations of the kinetics of the isothermal MAE of caffeine. However, the kinetics of the non-isothermal MAE of total phenols and caffeine from black tea powder was studied in the work of Spigno and De Faveri (2009). The effects of microwave power (450 W–900 W) and irradiation time (30 s–210 s) on the degree of extraction of total phenols using an ordinary household microwave oven were investigated.

The kinetics of conventional extraction of caffeine from various plants has been studied extensively. The kinetic model that is usually used for the interpretation of experimental extraction data is the steady state kinetic model, proposed by Spiro and Jago (1982). This model was used by Spiro et al. (1992) and Jaganyi and Price (1999) for describing the conventional extraction of caffeine from tea, and it was established that the concentration of caffeine with time follows first-order kinetics. Other approaches to model the extraction of various compounds from plants include second-order kinetic model (Pan et al., 2012; Rakotondramasy-Rabesiaka et al., 2007), and combined second-order-diffusional kinetics model (Linares et al., 2010). Besides these expressions, the kinetic models that are frequently used for the interpretation of extraction data are mathematically derived from Fick's second law, as was shown by Stapley (2002) and Ziaedini et al. (2010). Some simplified models derived from Fick's law like the film theory (Stanković et al., 1994), and unsteady state diffusion through plant material (Ponomaryov, 1976; Veličković et al., 2006; Stanisavljević et al., 2007) are also used. Furthermore, for modeling the extraction kinetics, empirical models like Peleg model (Peleg, 1988; Boussetta et al., 2011) and empirical equation of Ponomaryov (Veličković et al., 2006) were also proposed.

To the best of our knowledge, there is no report on the kinetics of the isothermal microwave-assisted extraction of caffeine nor its comparison with kinetics of the conventional extraction technique. Considering the fact that the kinetics of extraction under microwave heating was mainly investigated under non-isothermal conditions, the aim of this work was to impartially determine the influence of microwave heating on the kinetics of extraction. The objective of this work is to perform a comparative analysis of the kinetics of the isothermal extraction of caffeine from guarana seed powder with water under the conventional and microwave heating. The degree of kinetic complexity, kinetic model and kinetic parameters (activation energy (E_a) and pre-exponential factor (lnA)) for both extraction techniques were investigated. Based on the obtained results, formulation of model mechanism of the extraction of caffeine from solid particles of guarana under conventional and microwave conditions is suggested.

2. Materials and methods

2.1. *Materials and reagents*

Powdered guarana seeds (Moisture content 7.8%) with particle size (dp ≤ 250 μm) were purchased from a grocery store in Brazil.

Hydrochloric acid (36%) (p.a.) and sulphuric acid (98%) (p.a.) were supplied from Zorka Pharma (Šabac, Serbia). Lead acetate anhydrous (≥33% basic Pb as PbO) (p.a.) was supplied from Carlo Erba (Milano, Italy).

2.2. *Guarana extraction*

2.2.1. *Conventional extraction of caffeine from guarana*

In a typical experiment, 1 g of guarana seed powder was suspended in 80 mL of distilled water which was preheated to a predetermined temperature in a round-bottom flask. The suspension was stirred continuously with a magnetic stirrer at 410 rpm (IKA, RCT basic, Germany) maintaining constant temperature at 313 K, 323 K, 333 K, and 343 K (±1 K). At predominated time intervals, aliquots were taken from reaction mixture, quickly cooled down with an ice bath and filtered through Munktell No. 8 filter paper, (Munktell, Grycksbo, Sweden). All the extractions were performed in triplicate and average value has been reported in the figures.

2.2.2. *Microwave-assisted extraction of caffeine from guarana*

The microwave extraction was carried out in a commercially single-mode microwave device (Discover, CEM Corporation, Matthews, North Carolina, USA), operating at 2.45 GHz with adjustable microwave power output (from 0 to 300 W). Distilled water (80 mL) was placed in a borosilicate vessel (round-bottom flask, designed for microwave reactor) and guarana seed powder (1.0 g) was added.

The suspension was stirred continuously maintaining constant temperature at 313 K, 328 K, and 333 K in a microwave reactor. At predominated time intervals, aliquots were taken from the reaction mixture, and further treatment were carried out as described above.

The temperature of the extraction mixture was monitored using a calibrated thermometer (fiber-optic probe) inserted into the microwave device. The temperature, power and profiles were monitored using a commercially available software provided by the manufacturer of the microwave device. The used microwave device was modified to maintain automatically required temperature in the reaction system with rapid variations in input power and/or with a change in the flow of