Biljana Koturevic, Borivoj Adnadjevic* and Jelena Jovanovic

Isothermal green microwave-assisted extraction of caffeine from guarana: a kinetic study

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Abstract: The kinetics of isothermal green microwave-assisted extraction of caffeine from guarana seed powder with water at a temperature range from 40°C to 60°C was investigated. The caffeine concentration in the water extract was determined by UV-Vis spectrophotometry. By applying the isoconversional method, it was established that the kinetics of the caffeine extraction from the guarana seed powder with microwave heating is an elementary kinetic process. The model fitting method was used to determine the kinetic model of the caffeine extraction under microwave heating. It was found that the kinetics of the caffeine extraction can, under microwave heating, be modeled by the Jander's model of three dimensional diffusion. The kinetic parameters, activation energy and pre-exponential factor of the caffeine extraction were determined.

Keywords: caffeine; green microwave-assisted extraction; guarana; kinetics.

Symbols

E_a	[kJ mol ⁻¹]	activation energy
A	[min ⁻¹]	pre-exponential factor
R	[J mol ⁻¹ K ⁻¹]	gas constant (8.314)
C	[mg l ⁻¹]	concentration of caffeine in water extract
C_{max}	[mg l ⁻¹]	highest possible concentration of caffeine in water extract achieved during the extraction process
V_s	[l]	volume of water extract
C_{∞}	[g l ⁻¹]	equilibrium concentration of caffeine
α	–	degree of extraction
t	[min]	time
t_n	–	the normalized time
$t_{0.9}$	[min]	time at which the degree of extraction is 0.9

R^2	–	the correlation coefficient
T	[°C]	temperature
T^{-1}	[°C ⁻¹]	reciprocal temperature
k_s	[min ⁻¹]	observed first-order rate constant
k_M	[min ⁻¹]	model rate constant
n		number of reacting particles of guarana
R		radius of guarana seed particle
x		thickness of extraction residue layer on the guarana particle
π		mathematical constant
D		diffusion coefficient
k		constant dependent on the nature of the solid and liquid phases
ρ		density of the guarana seed particle

1 Introduction

Guarana (*Paullinia cupana*, Sapindaceae) is a shrubby, woody plant native to the Amazon rain forests [1]. This plant is generally recognized by its characteristic red colored capsulated fruit that contains one to four dark brown seeds [2]. Originally, guarana was only consumed internally by the Amazon population, but later it became accepted worldwide as a medicinal plant with therapeutic properties. Its popularization can also be attributed to numerous scientific reports that confirm the pharmacological benefits of guarana. Guarana has been shown to have antioxidant, antibacterial, antimicrobial, fat burning, cytoprotective, anticancer effects and many more [2]. Guarana seeds are the commercially useful part of the plant due to the fact that they consist of methylxanthines (caffeine, theophylline and theobromine), as well as polyphenols, tannins, catechins, saponins, polysaccharides, etc. [3]. The high caffeine level, which can reach up to 7.5% [4], makes this plant a useful raw material for the extraction of caffeine, a valuable substance for the pharmaceutical, food and cosmetics industries.

Caffeine extraction from various plants is usually carried out using either pure solvents (methylene chloride, chloroform) or water-organic solvent mixtures [5]. Most of the solvents used for caffeine extraction are known as possible human carcinogens, so in order to obtain the so-called “green coffee extract”, extraction is performed using water under conventional heating, or using more advanced extraction methods. These methods

*Corresponding author: Borivoj Adnadjevic, Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12–16, Belgrade 11001, Serbia, e-mail: bora@ffh.bg.ac.rs

Biljana Koturevic: The Academy of Criminalistic and Police Studies, Cara Dusana 196, 11080 Belgrade, Zemun, Serbia

Jelena Jovanovic: Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12–16, Belgrade 11001, Serbia

include ultrasound-assisted extraction [6, 7], supercritical fluid extraction [8], solid-phase extraction [9], dispersive liquid-liquid extraction [10], pressure processing assisted extraction [11], extraction using battery type extractor [12], and column-chromatography extraction [13].

In recent years, considerable attention has been given to microwave-assisted extraction (MAE). MAE is a process that uses microwave energy and solvents to extract target compounds from various matrices [14]. When used for the extraction of biologically active compounds from plant materials, the microwave energy penetrates the material and then the highly localized temperature and pressure can cause stretching and rupturing in the cell wall, which facilitates selective migration of the target compounds from the material to the extraction solvent [15]. MAE of biologically active compounds has many advantages over the conventional extraction method – it can reduce the time of isolation analyses, requires less volume of solvents and produces higher extraction yields [16]. The results of the effect of microwave irradiation in chemical reactions and physico-chemical processes cannot be explained by the effect of rapid heating alone. This effect is a combination of the thermal effect (overheating, hot spots and selective heating) and specific microwave effects [17]. Thermal effects arise from the different characteristics of microwave dielectric heating and conventional heating, while the issue of specific microwave effects is still a controversial matter [18].

Many reports have been published on the application of MAE of various bioactive compounds from plants [19–23]. MAEs of caffeine have also been reported [24–26].

The kinetics of conventional extraction of caffeine from various plants have been studied extensively. The kinetic model that is usually used for describing the extraction mechanism is the steady state kinetic model, proposed by Spiro and Jago [27]. Spiro et al. [28] found that the concentration of caffeine, with time, follow first-order kinetics. Jaganyi and Price [29] also found that the concentration of caffeine followed the first-order kinetics. Their results showed a much lower value of activation energy of caffeine in the water, which was determined to be 9.6 kJ mol^{-1} . Another kinetic model that is frequently used for the interpretation of extraction data is mathematically derived from Fick's second law [30]. Linares et al. [31] used a combined second-order-diffusional kinetics model for describing the aqueous extraction of the total water soluble solids from yerba mate leaves. They found that the second-order-diffusional kinetic model fits the experimental data more satisfactorily than the pseudo first-order kinetic model. The calculated activation energy in the first-order kinetic model is $14.26 \text{ kJ mol}^{-1}$, while the

one calculated through second-order-diffusional kinetic model is 9.7 kJ mol^{-1} .

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 [14] using an ordinary household microwave oven. The effects of microwave power of an ordinary household microwave oven (450–900 W) and irradiation duration (30–210 s) on the degree of extraction of total phenols and on their kinetics of extraction were investigated.

To the best of our knowledge, there is no report on the kinetics of the isothermal microwave extraction of caffeine in general or from guarana seed powder. The aim of this work is to examine the kinetics of the isothermal green microwave extraction of caffeine from guarana seed powder with water. The kinetic complexity, kinetic model and kinetic parameters (activation energy $[E_a]$ and pre-exponential factor $[\ln A]$) were investigated.

2 Materials and methods

2.1 Materials and reagents

Powdered guarana seeds (moisture content 7.8%) with particle size ($dp \leq 250 \mu\text{m}$) were purchased from a grocery store in Brazil.

Hydrochloric acid (36%) (p.a.) and sulfuric acid (98%) (p.a.) were supplied from Zorka Pharma (Šabac, Serbia). Lead acetate anhydrous ($\geq 33\%$ basic Pb as PbO) (p.a.) was supplied from Carlo Erba (Milano, Italy). Caffeine, laboratory grade, was purchased from Fisher Scientific (Loughborough, Leicestershire, UK).

2.2 Determination of total concentration of caffeine in guarana seed

The total concentration of caffeine in guarana seed was determined spectrophotometrically according to method of Wanyika et al. [32] for determination of the total concentration of caffeine in tea and coffee. In short, the method was as follows: 2 g of guarana seed powder was weighted and put into a 250 ml beaker. Some 160 ml of boiling distilled water was added and let stand for 5 min with stirring [at 410 rpm (IKA, RCT basic, Germany)], then the solution was cooled and filtered into a flask.

2.3 Microwave extraction of guarana

The microwave extraction was carried out in a commercially single-mode microwave device (Discover, CEM Corporation; Matthews, NC, USA), operating at 2.45 GHz with adjustable microwave power output (from 0 W 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 a constant temperature at 40°C, 55°C, and 60°C in a microwave reactor. At predetermined time intervals, aliquots were taken from the reaction mixture, quickly cooled down in an ice bath and filtered through Munktell no. 8 filter paper, (Munktell, Grycksbo, Sweden). The temperature of the extraction mixture was monitored using a calibrated thermometer fiber – the optic probe was inserted into the microwave device. The temperature, power and profiles were monitored using commercially available software provided by the manufacturer of the microwave device. The used microwave device was modified to maintain the automatically required temperature in the reaction system with rapid variations in input power and/or with a change in the flow of cooled N₂ through the heat exchanger immersed in the reactor. When the sensor of the instrument detects a decrease in the temperature of the reaction system related to it, the input power of the microwave field is automatically increased and N₂ flow is decreased, i.e. in contrary, when the increases in temperature of the reacting system happen, the input power of the microwave field is automatically decreased and N₂ flow is increased in order to achieve the desired temperature of the reacting system.

As can be seen from Figure 1, after the first 60 s, the temperature in the reactor was maintained at a constant value of 55 ± 1°C, which indicates that the satisfactory conditions for studying the isothermal extraction of caffeine were achieved.

2.4 Determination of caffeine concentration in water extract

Based on available literature data, seeds of guarana have been found to contain methylxanthines, mainly caffeine (3–10%), and theophylline, plus theobromine in smaller quantities (less than 1%), as well as polyphenols (nonhydrolyzable tannins (12%) such as catechin (5.98%) and epicatechin (3.78%), and condensed tannins such as flavan-3-ol and procyanidins) [33–35].

In works by Yao et al. [36, 37] it was found that tannins hinder absorption of caffeine during the spectrophotometric determination of caffeine in water extract, so in these works, a method for precipitation of insoluble tannins was developed.

Following the proposed method, in order to remove the tannins, water extract (2 ml), HCl solution (0.01 mol l⁻¹; 1 ml) and Pb(CH₃COO)₂

solution (1.5 mol l⁻¹; 0.2 ml) were mixed and diluted to 25 ml with distilled water. The obtained solution was filtered through Munktell No. 8 filter paper. The filtrate (5 ml) and H₂SO₄ solution (4.5 mol l⁻¹; 0.02 ml) were combined and diluted to 10 ml with distilled water to eliminate excess lead and then filtered using the same type of filter paper.

2.5 Standard stock solution of caffeine in water

Caffeine stock solution (1000 mg l⁻¹) was prepared by weighting 100 mg of pure caffeine, transferring it into a 100 ml volumetric flask and making it to the mark with distilled water.

2.6 Calibration standards

Calibration solutions (10 mg l⁻¹, 20 mg l⁻¹, 40 mg l⁻¹, 60 mg l⁻¹, and 80 mg l⁻¹) were prepared by serial dilution of the standard stock solution in 25 ml flasks and making it to mark with distilled water.

The absorbance (Abs) of the calibration standards and samples were measured using a UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) at 274 nm.

The concentration of caffeine (*C* mg l⁻¹) was calculated using standard curve derived from the caffeine with the following equation:

$$C = \text{Abs} / 0.0516 + 0.004 \quad (R^2 = 0.999) \quad (1)$$

where *R*² is the correlation coefficient.

2.7 Determination of extraction degree

For each temperature, the degree of extraction (*α*) was determined by the equation:

$$\alpha = \frac{C}{C_{\max}} \quad (2)$$

where *C* (mg l⁻¹) is the caffeine concentration in water extract in the time interval *t* and *C*_{max} is the highest possible concentration of caffeine in water extract. The total concentration of caffeine in the sample of guarana seed used was determined to be 4.78%, so *C*_{max} is calculated using following equation:

$$C_{\max} = \frac{1 \cdot 0.0478}{V_s} \quad (3)$$

where *V*_s (L) is volume of water extract.

2.8 Methods used to evaluate the kinetic model and kinetic parameters

2.8.1 Model fitting method: The kinetic models of the reactions in solid state and in the interface of the solid-solution are derived from a number of presumptions about the mechanisms of the process. The model fitting method is based on the fitting of obtained data into various known solid state reaction models. According to the model-fitting method, the kinetic reaction model is classified into five

Figure 1: Temperature variation in microwave reactor during extraction.

groups depending on the reaction mechanism: (1) power law reaction, (2) phase controlled reaction, (3) reaction order, (4) reaction described by the Avrami equation, and (5) diffusion controlled reactions.

The selection of the kinetic equation for fitting the experimental data was performed using the model fitting method proposed by Brown et al. [38]. In accordance with this method, the experimentally obtained curves that describe the dependence of the degree of extraction on time ($\alpha = f(t)$), was transformed into a normalized conversation curve $\alpha = f(t_n)$, where t_n is the normalized time, defined by equation:

$$t_n = \frac{t}{t_{0.9}} \quad (4)$$

where $t_{0.9}$ is obtained by calculating the time at which the degree of extraction (α) is 0.9. The kinetic model is determined by analytically comparing the normalized conversation curve with the experimentally obtained conversation curve. The chosen kinetic model for fitting the experimental data is the one for which the sum of squares was minimal.

2.8.2 Differential isoconversion method: The Friedman isoconversional method [39] was used to determine the kinetic parameters, activation energy (E_a) and pre-exponential factor ($\ln A$) of the investigated extraction process of caffeine from guarana for various extraction degrees. According to this method, the kinetic analysis of experimental data is based on the following rate equation:

$$\frac{d\alpha}{dt} = Af(\alpha) \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where $d\alpha/dt$ is the reaction rate, T is the temperature, A is the pre-exponential factor, E_a is the activation energy, $f(\alpha)$ is the general mathematical expression of the kinetic model and R is the gas constant. The logarithm form of Eq. (5) leads to:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + \ln f(\alpha) - \left(\frac{E_a}{RT}\right) \quad (6)$$

Accepting that the reaction rate constant is an extent of conversion and only a function of temperature (isoconversional principle of Friedman), Eq. (6) can be written as:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[A_\alpha \cdot f(\alpha)] - \left(\frac{E_a, \alpha}{RT}\right) \quad (7)$$

The plot ($\ln d\alpha/dt$) versus reciprocal temperature (T^{-1}) should be a straight line, the slope of which allows the evaluation of the activation energy for a particular degree of extraction (α).

3 Results and discussion

The obtained isothermal kinetic curves of the caffeine extraction (dependence of C vs. time), and dependence of extraction degree on time at different temperatures under microwave heating are shown in Figure 2A and B.

The extraction kinetic curves at all of the investigated temperatures have the same shape. It is easy to distinguish three characteristic shapes of changes in the increase of the concentration of extracted caffeine over extraction time: linear, convex and plateau. Initially, the concentration of the caffeine increases rapidly, almost linearly, with time. Further increase of the extraction time leads to a convex-like increase in the concentration of the caffeine which is subsequently followed by the plateau. With increasing temperature of extraction the duration of linear changes and time required to reach the plateau are decreased. Extraction degree of 80% has been reached at 60°C (Figure 2B).

The Friedman's isoconversional method was applied to determine the dependability of the activation energy on the degree of extraction. Figure 3 presents the dependences of $\ln(d\alpha/dt)$ on T^{-1} for different degrees of caffeine extraction.

As can be seen from the results presented in Figure 3, the dependences of the $\ln(d\alpha/dt)$ versus T^{-1} for all degrees of caffeine extraction are linear. From the slopes and

Figure 2: (A) The isothermal kinetic curves of the extracted caffeine from a guarana seed under microwave heating at 40°C (■), 55°C (●) and 60°C (▲). (B) Dependence of extraction degree (α) on time under microwave heating at 40°C (■), 55°C (●) and 60°C (▲).

Figure 3: The dependences of $\ln d\alpha/dt$ on T^{-1} for different degrees of caffeine extraction at [0.1 (■), 0.2 (●), 0.3 (▲), 0.4 (▼), 0.5 (◆), 0.6 (◀), 0.7 (▶), 0.8 (●), 0.9 (*).]

Figure 4: The dependence of E_a , versus degree of caffeine extraction.

intercepts of these straight lines, the values of the kinetic parameters (E_a and $\ln A$) for different degrees of caffeine extraction were calculated. The dependence of E_a versus α is shown on Figure 4.

From the results presented in Figure 4, it can be seen that the value of activation energy ($E_a = 13 \text{ kJ mol}^{-1}$) is practically independent of the degree of caffeine extraction. Keeping in mind that the E_a is independent of the degree of caffeine extraction, we can claim with a high degree of certainty that the investigated extraction of caffeine presents a rate limiting step.

For the interpretation of experimental extraction data, there are several kinetic models that can be used: (a) pseudo first-order model proposed by Spiro and Jago

[27]; (b) solution of Fick's second law of diffusion [40]; (c) the Peleg equation [41]; and d) second-order kinetic model [42].

Bearing in mind the nature of the investigated extraction system, the possibility of using the Spiro's pseudo first-order kinetic model for modeling the extraction of caffeine from a guarana seed was investigated. This model is expressed by the equation:

$$\ln \left(\frac{C_\infty}{C_\infty - C} \right) = k_s \cdot t + \alpha \quad (8)$$

where C_∞ is equilibrium concentration of caffeine (g l^{-1}) at the highest temperature, and C is the concentration of caffeine at time t (min), k_s is observed first-order rate constant (min^{-1}), and α is an integration constant. In the case when kinetics of the extraction of the caffeine follow first-order behavior, plotting $\ln [C_\infty/(C_\infty - C)]$ versus time will give straight lines, the slope of which corresponds to the constant of the caffeine extraction rate. Figure 5 shows the isothermal dependence of $\ln (C_\infty/[C_\infty - C]) = f(t)$ at different temperatures.

According to the results presented in Figure 5, it is easy to conclude that the plots of $\ln (C_\infty/[C_\infty - C])$ on time do not give straight lines in the entire range of α , for all of the investigated temperatures. That directly proves that the kinetics of caffeine extraction in this temperature range cannot be modeled by the proposed Spiro's pseudo first-order kinetic model.

Bearing in mind the previously obtained results, to determine the real kinetic model of isothermal caffeine extraction, the model fitting method was applied. The experimental normalized conversion curves of caffeine

Figure 5: The isothermal dependence of $\ln [C_\infty/(C_\infty - C)]$ versus time at 40°C (■), 55°C (●) and 60°C (▲).

extraction under microwave heating at the investigated temperatures are shown on Figure 6. These curves have the same shape, so it was assumed that all of them can be described by the same kinetic model.

By using the model fitting method, with great degree of certainty (≥ 0.999), it was established that the kinetics of isothermal caffeine extraction under microwave heating can be described by the Jander theoretical kinetic model of three dimensional diffusion [43] which is given by the following equation:

$$[1 - (1 - \alpha)^{1/3}]^2 = k_M \cdot t \quad (9)$$

where, k_M is the model rate constant of caffeine extraction from the guarana seed.

If the kinetics of the microwave extraction of caffeine from the guarana seed can be described by the three dimensional diffusion kinetic model, then the dependences $[1 - (1 - \alpha)^{1/3}]^2$ on time should give straight lines. The isothermal dependences of $[1 - (1 - \alpha)^{1/3}]^2$ versus time of caffeine extraction are shown on Figure 7.

As can be seen from Figure 6, the dependences of $[1 - (1 - \alpha)^{1/3}]^2$ on the extraction time are linear during the entire duration of the caffeine extraction process and at all investigated temperatures, which confirms that the correct kinetic model was selected for describing caffeine extraction from the guarana seed.

The determined kinetics model of the extraction of caffeine indicated that the rate-limiting step of the extraction process is the diffusion of the water molecule through the extraction of the residue layer on the particle surface. This allows the calculation of the model rate constant (k_M), and

Figure 6: Experimental normalized conversion curves of the caffeine extraction under microwave heating at 40°C (■), 55°C (●) and 60°C (▲).

Figure 7: The isothermal dependences of $[1 - (1 - \alpha)^{1/3}]^2$ versus time at 40°C (■), 55°C (●) and 60°C (▲).

the kinetic parameters, namely, activation energy (E_a) and pre-exponential factor ($\ln A$) for the investigated extraction process. Since the model rate constant increases with temperature, the kinetic parameters for this kinetic model were determined by applying the Arrhenius equation. The effects of temperature of the microwave extraction on the k_M values and kinetic parameters (E_a and $\ln A$) are given in Table 1.

The calculated value of E_a for the studied temperature range is slightly high in comparison to the values of the activation energy reported by Spigno and De Faveri [14] for the total phenol extraction from black tea, which is found to be $14.63 \text{ kJ mol}^{-1}$ in the temperature range 55–90°C. Similar results of E_a were reported Linares et al. [31] for extracting total water soluble solids from yerba mate leaves in the temperature range 40–70°C, which was found to be $14.26 \text{ kJ mol}^{-1}$. Furthermore, the value of the calculated E_a in this work is slightly lower than the value of diffusion of caffeine in water found by Spiro et al. [28], which was 17.3 kJ mol^{-1} . The E_a value calculated in this work is also slightly lower than the measured value of activation energy for diffusion of water molecule ($E_a = 18.8 \text{ kJ mol}^{-1}$) [44], which indicates that the structure of the extraction residue layer on the guarana powder particle is very open

Table 1: The influence of temperature of the microwave extraction on the model rate constant and kinetic parameters E_a and $\ln A$.

T (°C)	k_M (min ⁻¹)	R	Kinetic parameters
40	0.094 ± 0.002	0.994	E_a (kJ mol ⁻¹) = 13.02 ± 0.10
55	0.117 ± 0.002	0.998	$\ln A$ (min ⁻¹) = 5.55 ± 0.77
60	0.126 ± 0.001	0.999	$R = 0.999$

and allows easy transport of water to caffeine molecules and also easy transport of the water extract of caffeine from the guarana particle.

Based on the established mathematical model of kinetic extraction, it is possible to assume the following model mechanism of the extraction of caffeine from solid particles of guarana using the selective solvent:

- The solid component (powder) consists of “ n ” equal spherical particles of the initial radius (R).
- Water very quickly forms the product layer (water extract) on the particle interface due to its small external diffusion resistance.
- It is well known that the formation of product layers on the surfaces of particles may limit the rate of reaction by hindering the diffusion of soluble reactants or products through this layer. However, the water does not form a tight layer of the extraction's product on the particle's surface, so the water extract diffuses very easily into solute.
- The extraction of the caffeine from the guarana powder particle is kinetically limited with volume diffusion of the water molecule through the extraction residue layer on the particle with the thickness value (x).
- The solvent diffusion coefficient of water does not change with time.
- The rate of layer thickness is proportional to the diffusion coefficient (D) of water and inversely proportional to the thickness of the layer:

$$\frac{dx}{dt} = k \frac{D}{x} \quad (10)$$

where k is a constant dependent on the nature of the solid and liquid phases and conditions.

By integrating Eq. (10) with boundaries for x from $x=0$ to $x=x$ and for time from $t=0$ to $t=t$, we come to the Jander expression for the parabolic growth of residue layer:

$$x^2 = 2kDt \quad (11)$$

In that case, the degree of extraction (α) is given by the equation:

$$\alpha = \frac{\frac{4}{3}n\rho\pi R^3 - \frac{4}{3}n\rho\pi(R-x)^3}{\frac{4}{3}n\rho\pi R^3} \quad (12)$$

where n is the number of reacting particles, ρ is density of the guarana seed particle, and x is the thickness of the extraction residue layer. Eq. (12) can be easily transformed into:

$$\alpha = 1 - \left(\frac{R-x}{R} \right)^3 \quad (13)$$

The rearrangement of Eq. (13) leads to the definition of x :

$$x = R[1 - (1-\alpha)^{1/3}] \quad (14)$$

Bearing in mind that $x^2 = 2kDt$, substituting Eq. (11) into Eq. (14) gives:

$$R^2[1 - (1-\alpha)^{1/3}]^2 = 2kDt \quad (15)$$

or:

$$[1 - (1-\alpha)^{1/3}]^2 = \frac{2kD}{R^2} \cdot t = k_M \cdot t \quad (16)$$

where $k_M = 2kD/R^2$.

The mathematical identity of Eq. (16) with the integral form of the kinetic model indicates to: (a) the possible mechanism of extraction of caffeine from the guarana seed powder with water; (b) the assumption that the rate limiting step of the extraction process is three-dimensional diffusion of water molecules through the extraction of the residue layer on the particle surface; (c) the physical meaning of the model rate constant k_M , respectively the linear dependence of k_M on the diffusion coefficient D and inversely dependence on the R^2 ; (d) the possibility of enabling a much faster extraction process which we can accurately predict the duration of.

4 Conclusion

The isothermal MAE of caffeine from a guarana seed powder with water is an elementary kinetic process that takes place in a single elementary step. The kinetics of the isothermal MAE in the temperature range 40–60°C can be mathematically described by the equation:

$$[1 - (1-\alpha)^{1/3}]^2 = k_M \cdot t.$$

The rate limiting step of the extraction process at investigated temperatures is a three-dimensional diffusion of a water molecule through the extraction residue layer on the particle's surface. The determined activation energy is in correspondence with the energy of the diffusion of water through the pore space of porous media.

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References

- [1] Baumann TW, Schulthess BH, Hanni K. *Phytochemistry* 1995, 39, 1063–1070.
- [2] Schimpl FC, da Silva JF, de Carvalho Gonçalves JF, Mazzafera P. *J. Ethnopharmacol.* 2013, 150, 14–31.
- [3] Hamerski L, Somner GV, Tamaio N. *J. Med. Plants Res.* 2013, 7, 2221–2229.
- [4] Beck HT. In *The Cultural History of Plants*, Prance GT, Eds., Routledge: New York, 2005, p 173–190.
- [5] Wang H, Helliwell K. *Food Chem.* 2000, 70, 337–344.
- [6] Rostagno MA, Manchón N, D'Arrigo M, Guillamón E, Villares A, García-Lafuente A, Ramos A, Martínez JA. *Anal. Chim. Acta.* 2011, 685, 204–211.
- [7] Sereshti H, Samadi S, Jalali-Heravi M. *J. Chromatogr. A* 2013, 1280, 1–8.
- [8] Tello J, Viguera M, Calvo L. *J. Supercrit. Fluids* 2011, 59, 53–60.
- [9] Jafari MT, Rezaei B, Javaheri M. *Food Chem.* 2011, 126, 1964–1970.
- [10] Sereshti H, Samadi S. *Food Chem.* 2014, 158, 8–13.
- [11] Jun X. *J. Food Eng.* 2009, 94, 105–109.
- [12] Senol A, Aydin A. *J. Food Eng.* 2006, 75, 565–573.
- [13] Wang L, Gong LH, Chen C J, Han HB, Li HH. *Food Chem.* 2012, 131, 1539–1545.
- [14] Spigno G, De Faveri DM. *J. Food Eng.* 2009, 93, 210–217.
- [15] Mandal V, Mohan Y, Hemalatha S. *Pharmacogn. Rev.* 2007, 1, 7.
- [16] Kaufmann B, Christen P. *Phytochem. Anal.* 2002, 13, 105–113.
- [17] Hoz A, Diaz-Ortiz A, Moreno A. *Chem. Soc. Rev.* 2005, 34, 164–178.
- [18] Adnadjevic B, Jovanovic J. In *Advances in Induction and Microwave Heating of Mineral and Organic Materials*, Grundas S, Eds., Vena: Intech Open Access Publisher, 2011, p 391–422. (ISBN 978-953-307-522-8).
- [19] Chen Y, Xie MY, Gong XF. *J. Food Eng.* 2007, 81, 162–170.
- [20] Liao ZG, Wang GF, Liang XL, Zhao GW, Jiang QY. *Sep. Purif. Technol.* 2008, 63, 424–433.
- [21] Rostagno MA, Palma M, Barroso CG. *Anal. Chim. Acta* 2007, 588, 274–282.
- [22] Xiao W, Han L, Shi B. *Sep. Purif. Technol.* 2008, 62, 616–620.
- [23] Zhang B, Yang R, Liu CZ. *Sep. Purif. Technol.* 2008, 62, 480–483.
- [24] Rahim AA, Nofrizal S, Saad B. *Food Chem.* 2014, 147, 262–268.
- [25] Lou Z, Er C, Li J, Wang H, Zhu S, Sun J. *Anal. Chim. Acta* 2012, 716, 49–53.
- [26] Vuong QV, Tan SP, Stathopoulos CE, Roach PD. *J. Food Comp. Anal.* 2012, 27, 95–101.
- [27] Spiro M, Jago DS. *J. Chem. Soc., Faraday Trans. 1* 1982, 78, 295–305.
- [28] Spiro M, Jaganyi D, Broom MC. *Food Chem.* 1992, 45, 333–335.
- [29] Jaganyi D, Price RD. *Food Chem.* 1999, 64, 27–31.
- [30] Ziaedini A, Jafari A, Zakeri A. *Food Sci. Technol. Int.* 2010, 16, 505–510.
- [31] Linares AR, Hase SL, Vergara ML, Resnik SL. *J. Food Eng.* 2010, 97, 471–477.
- [32] Wanyika HN, Gatebe EG, Gitu LM, Ngumba EK, Maritim CW. *Afr. J. Food Sci.* 2010, 4, 353–358.
- [33] Ushirobira TMA, Yamaguti E, Uemura LM, Nakamura CV, Dias Filho BP, Mello JCP. *Acta Farm Bonaer.* 2007, 26, 5–9.
- [34] Pelozo MIDG, Cardoso MLC, Mello JCPD. *Braz. Arch. Biol. Technol.* 2008, 51, 447–451.
- [35] Roggia I, Ziegler S, Cruz IBM, Ourique AF, Gomeset P. *Int. J. Pharm. Sci. Res.* 2016, 7, 2334–2342.
- [36] Yao LH, Chen Y, Cheng C, Liu Y. *J. Food Ferment. Ind.* 1993, 19, 38–44, Chemical Abstract 120, 871–5335.
- [37] Yao L, Liu X, Jiang Y, Caffin N, D'Arcy B, Singanusong R, Datta N, Xu Y. *Food Chem.* 2006, 94, 115–122.
- [38] Brown ME, Dollimore D, Galway AK. In *Comprehensive Chemical Kinetics*, Bamford CH, Tipper CFH, Eds., Elsevier: Amsterdam, 1980, Vol. 22, p. 87–91.
- [39] Friedman HL. *J. Polym. Sci.* 1963, 6C, 183–195.
- [40] Herodež SŠ, Hadolin M, Škerget M, Knez Ž. *Food Chem.* 2003, 80, 275–282.
- [41] Peleg M. *J. Food Sci.* 1988, 53, 1216–1219.
- [42] Rakotondramasy-Rabesiaka L, Havet JL, Porte C, Fauduet H. *Sep. Purif. Technol.* 2007, 54, 253–261.
- [43] Jander W. Z. *Anorg. Allg. Chem.* 1927, 166, 31–52.
- [44] Eisenberg DS, Kauzmann W. *The Structure and Properties of Water*, Oxford University Press: USA, 2005.

Bionotes

Biljana Koturevic

Biljana Koturevic graduated in Chemistry-Biochemistry at the Faculty of Sciences, University of Novi Sad. She obtained her Master's degree from the Faculty of Physical Chemistry, University of Belgrade. Presently, she is a PhD student at the Faculty of Physical Chemistry, University of Belgrade. Her doctoral thesis and research interests deal with analysis of the kinetics of solid-liquid extraction under different heating conditions – conventional, microwave, and ultrasound; modeling kinetics of extraction; application of innovative extraction techniques on different plant materials; and green process of solvent extraction. She also works as a teaching assistant at the Forensics Department, Academy of Criminalistic and Police Studies, Serbia. She conducts laboratory courses in the area of chemical engineering in forensics.

Borivoj Adnadjevic

Borivoj Adnadjevic is a Full Professor of Solid State Chemistry and Colloid Chemistry at Faculty of Physical Chemistry, University of Belgrade. His research interest include areas of synthesis and

physico-chemical characterization of novel materials, the effects of microwave and ultrasonic fields and cavitation on the kinetics of various physico-chemical and chemical processes, kinetics of phase-transitions, mechanism and kinetics of hydrogel swelling. He is actively working on the development of novel technological processes. He has authored or co-authored more than 100 scientific papers and more than 10 patents. His technical solutions served as a ground for 12 industrial plant designs.

Jelena Jovanovic

Jelena Jovanovic is a principal researcher at the Faculty of Physical Chemistry, University of Belgrade. She obtained her PhD in Polymers Science at the Faculty of Chemistry, University of Belgrade. Her primary research areas include macromolecules, smart materials and hydrogels, introducing advanced methods of synthesis, mainly using microwave irradiation. Her current research is focused on understanding the effects of microwaves on reaction kinetics of various chemical and physico-chemical processes. Since 2008, she has actively served as an expert of the European Commission.