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**Effect of cosolvents (ethyl lactate, ethyl acetate and ethanol)
on the supercritical CO₂ extraction of caffeine from green tea**

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Abstract

This paper reports experimental data to analyze the effect of different green cosolvents, namely ethyl lactate, ethyl acetate and ethanol, on the supercritical carbon dioxide (SCCO₂) extraction of caffeine from green tea leaves.

The experiments were carried out in a pilot-scale plant using two different approaches: a static procedure in which the cosolvent was introduced in the extraction cell soaking the vegetal material and then SCCO₂ was pumped, and a dynamic assay in which the cosolvent was pumped and mixed with SCCO₂ before introduction into the extraction cell. The overall caffeine recovery from plant matrix was determined for all experiments at the same extraction conditions (30 MPa and 343 K). Additionally, the overall extraction curves of the static experiments were determined at the same process conditions, and the mass transfer model of Sovová was utilized to adjust the kinetic data and to determine the mass transfer coefficients.

The highest caffeine yield was obtained with ethyl lactate in both static and dynamic extractions (13.0 and 14.2 mg/g of tea, respectively), followed by ethanol (10.8 mg/g with the static method and 8.8 mg/g with the dynamic method). The yield obtained with ethyl acetate in both extraction approaches was lower than 7 mg/g. These data reinforce previous results obtained by the authors regarding the competence of ethyl lactate in the extraction of caffeine from natural materials.

Keywords: Green Tea; Caffeine; Cosolvent; Ethyl Lactate; Supercritical Fluid Extraction.

1. Introduction

Green tea (*Camellia sinensis*) is one of the most popular beverages in the world [1] and contains around 2-5 % mass of caffeine (1,3,7-trimethylxanthine) in the dry leaves [2]. Some adverse effects derived from the excessive consumption of caffeine are well-known [3-5] and thus, the removal of caffeine is desired by several consumers.

Extraction using organic solvents is currently the most extended commercial method for decaffeinating green tea leaves. Despite the high selectivity towards caffeine, the use of solvents like chloroform or methylene chloride has progressively decline due to their high toxicity [6]. Another commercial solvent utilized is ethyl acetate which presents much lesser toxicity than chlorinated solvents.

Supercritical fluid extraction (SFE) with CO₂ is a viable alternative to organic solvents, offering many advantages such as non-toxicity, solvent-free products and high selectivity in caffeine removal. Several works about the use of supercritical CO₂ for decaffeination of different vegetal matrix, such as coffee beans [7], cocoa butter [8], guarana seeds [9] and mate tea leaves [10], have been reported. In fact, the extraction of caffeine with supercritical CO₂ is one of the most well-known commercial examples of SFE processes [11]. Many patents have been published about decaffeination of tea and coffee where extraction of caffeine is carried out by means of different layouts [12-15]. Moreover, in different countries, several large-scale plants have been designed for processing coffee, tea, and hops, and for spices and flavor extraction [16].

Regarding the extraction of caffeine from green tea leaves, in most cases, green tea was soaked previously with a liquid solvent, namely ethanol or water. For example, Park et al. [17, 18] studied the decaffeination of green tea using CO₂ and ethanol as cosolvent at 30 MPa and 343 K, attaining a recovery of caffeine around 92-96 %. In another contribution [19], the authors employed the same extraction conditions with pure CO₂

and water as cosolvent and caffeine recoveries were lower. Similarly, Kim et al. [20] attained a 59 % of caffeine recovery at 40 MPa, 323 K and using 7 % of water as cosolvent. Chang et al. [21] tested water, ethanol and different water/ethanol ratios at 31 MPa and 333 K, obtaining the best results with 70 % aqueous ethanol.

On the other side, Sun et al. [22] studied the supercritical extraction of caffeine also using ethanol and water, but the cosolvent was pumped and mixed with SCCO₂ in continuous flow (the vegetal material was not soaked previously). At 30 MPa and 333 K the recovery of caffeine using ethanol, 50 % aqueous ethanol and water was, respectively, 67.4 %, 92.8 %, 78.0 %.

Huang et al. [23] combined soaking and continuous CO₂+cosolvent pumping. Complete decaffeination was attained at 30 MPa and 353 K, but it should be taken into account the small content of caffeine (9.92 mg/g) contained in the green tea utilized in their experiments.

Thus, to the best of our knowledge, only water and ethanol have been studied as cosolvents in the supercritical extraction of caffeine from green tea leaves. In this work, the kinetic behaviour of the caffeine extraction when ethyl lactate and ethyl acetate are employed as cosolvents is presented for the first time. For comparison, also caffeine extraction using ethanol was analyzed and reported. Furthermore, the two most common approaches, i.e. previous soaking of the vegetal material and continuous CO₂ and cosolvent pumping, were investigated.

2. Material and methods

2.1. Samples and reagents

“Gunpowder” green tea (*Camellia sinensis*) leaves were acquired in a Spanish market. The green tea leaves were ground (particle size smaller than 500 μm) in a cooled knife mill (Grindomix GM 200. Retsch GmbH, Haan, Germany) using liquid nitrogen. Ethyl lactate ($\geq 98\%$ purity) and caffeine standard ($\geq 99\%$ purity) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ethyl acetate and acetonitrile (HPLC grade) were obtained from Lab-Scan analytical sciences (Gliwice, Polonia). Formic acid ($\geq 98\%$ purity) was obtained from Merck (Darmstadt, Alemania). Ethanol ($\geq 99\%$ purity) and sea sand were purchased from Panreac Química S.A.U. (Barcelona, España). CO_2 was provided by Air Products (Allentown, PA, USA). The total content of caffeine in the vegetal material was measured. For this purpose, 200 mg of green tea leaves were extracted at 343 K with 20 mL of an aqueous ethanol solution (30 % v/v) [17] in a Stuart Orbital S150 shaker apparatus (Bibby Scientific Limited Stone, UK) during 4 h. Then, the solvent was renewed and successive extraction cycles of 4 h were accomplished until the extraction yield in the corresponding cycle was lower than 2 % of total yield. The content of caffeine determined was 27 mg per g of green tea leaves.

2.2. Supercritical extraction method

Extractions were carried out in a pilot-scale supercritical fluid extractor (Thar Technology, Pittsburgh, PA, USA, model SF2000) comprising a 2 L cylinder extraction cell and two different separators (S1 and S2), each of 0.5 L capacity, with independent control of temperature and pressure. A detailed explanation of the experimental device can be found elsewhere [24].

The extractions were carried out using pure CO₂ and CO₂ with three different cosolvents, namely ethyl lactate (CO₂+EL), ethanol (CO₂+ETOH) and ethyl acetate (CO₂+EAC).

Based on the experimental information available in the literature [17, 18, 25, 26], the extraction pressure and temperature were selected to be 30 MPa and 343 K and were kept constant for all experimental assays. At these conditions high caffeine solubility in SCCO₂ is attained [25]. Furthermore, a supercritical procedure for the decaffeination of moistened green tea leaves has been early described at 293-353 K and pressure up to 30 MPa [26]. The extraction cell was loaded with 0.7 kg of green tea leaves and CO₂ flow rate was set to 9 kg/h. For the extractions using cosolvent, the cosolvent/CO₂ ratio (kg/kg) was 0.022 (around 2 % mass). These extractions were conducted in two different modes: static and dynamic modes. In the first case, green tea was soaked with the cosolvent and was loaded into the extraction cell. The soaked leaves were heated up to 343 K, then CO₂ was pumped until the extraction pressure was attained. The mixture was allowed to stand during 30 min and finally, CO₂ was pumped afterward during 3.5 h (210 min). In the dynamic mode, the dry grounded leaves were loaded into the extraction cell and heated up to 343 K, then CO₂ and the cosolvent were continuously pumped and mixed in the desired ratio previous to introduction into the cell.

Decompression of the extract up to ambient pressure was accomplished in a separator at 303 K. Extraction yield was calculated as the difference between the mass of green tea leaves loaded in the extraction cell and the mass of leaves remained in the cell after the extraction. Samples were collected at different intervals of time. Samples were stored at 253 K in the dark until analysis.

2.3 Identification and quantification of caffeine and catechins

Analysis was performed by HPLC-MS/MS with an Accela (Thermo Electron Corporation; San Jose, CA) equipped with an ACE 3 C18-AR column (150×4.6 mm, 3 µm particle size) (Advanced Chromatography Technologies, Aberdeen, UK) equipped with a DAD detector and triple quadrupole mass spectrometer (TSQ-Quantum, Thermo Electron Corporation, San Jose, CA) with an ESI (Electrospray Ionization) interface. Based on the method of Pelillo et al. [27] the composition of the mobile phase was (A) 0.5 % (v/v) formic acid in water (B) 0.3 % (v/v) formic acid in acetonitrile. The column temperature was maintained at 308 K, with a flow rate of 0.6 mL/min. The mobile phase gradient employed was as follows: initial 100 % A, 30 min 0 % A, 32 min 100 % A, 37 min 100 % A. Spray voltage and sheath gas pressure was set in 5000 and 35 psi respectively and the capillary temperature was 623 K. Mass analyzer was set simultaneously in full scan and SRM (Single Reaction Monitoring) modes. In this case, SRM experiments were done using 1 precursor ion and 1 daughter ion, operating in positive mode. Table 1 shows the SRM transitions selected automatically among the most abundant ions and the corresponding collision energy. The amount of caffeine and catechins in the different samples was calculated by triplicate from a calibration curve of standard.

3. Results and discussion

Table 2 shows the total extraction yield (g of extract / g of tea) and the caffeine yield (mg caffeine extracted / g tea) obtained for both extraction approaches (static and dynamic) and for each cosolvent studied.

The dynamic and static extractions with ethyl lactate were carried out by duplicate. The mean values of the total extraction yields are reported in Table 2 and the standard

deviations were, respectively, 0.3 and 0.2 %. Standard deviation obtained in the quantification of caffeine was lower than 0.1 mg/g.

Despite the extraction type, the effect of the cosolvent on the recovery of caffeine was as follows: ethyl lactate > ethanol > ethyl acetate. This behavior may be explained considering that hydrogen bonding would constitute one of the most important forces taking into account the chemical structure of the cosolvents and solute studied in this work [18, 22, 25, 28]. In this respect, ethyl lactate can develop hydrogen bonding owing to its hydroxyl and carbonyl group [29] while ethanol only possesses a hydroxyl group. On the other side, ethyl acetate is a polar aprotic solvent that do not possess donor hydrogen atoms and cannot form strong hydrogen bonds. Thus, in comparison with pure CO₂ (see Table 2) caffeine recovery was higher using ethanol or ethyl lactate cosolvents, but with ethyl acetate recoveries were similar and even lower (dynamic mode).

Additionally, solubility behaviour of caffeine in the liquid solvents also supports the observed behavior. The solubility of caffeine in ethyl lactate at 323 K is 5.1 % mass [30], while solubility in ethanol and ethyl acetate at the same temperature is, respectively, 2.3 % and 2.2 % mass [31].

The highest caffeine extraction yield was obtained with CO₂+EL and the recovery was slightly higher in the case of the dynamic approach (13.0 mg/g and 14.2 mg/g in the static and dynamic modes, respectively). Nevertheless, in the case of ethanol and ethyl acetate cosolvents, recoveries were considerably higher in the static mode.

Taking into account the total content of caffeine in the green tea leaves (27.0 mg/g), the recovery of caffeine (mass of caffeine in the extract / mass of caffeine in green tea leaves x 100) at 343 K, 30 MPa and 210 min of extraction were 48.3 % and 52.6 % using CO₂+EL in the static and dynamic modes respectively, while recoveries lower

than 40 % were obtained with the other cosolvents (see Tables 2 and 3). This result is in agreement with previous results reported by the authors [32] regarding the effectiveness of ethyl lactate in comparison with ethanol or ethyl acetate in the pressurized liquid extraction of caffeine from green coffee beans.

The selectivity of the cosolvents to extract caffeine was valued considering the concentration of caffeine in the extracts (see Table 2). As expected, pure CO₂ produced extracts with high content of caffeine (15.9 % mass) demonstrating high selectivity to extract this alkaloid, although recovery was the lowest (21.9 %). Among the cosolvents investigated, ethyl lactate produced the highest caffeine concentrations, with values similar (14.3 % mass in static mode) or even higher (18.2 % mass in dynamic mode) than pure CO₂ and the highest caffeine recoveries as mentioned previously.

Assessment of the co-extraction of substances other than caffeine is also important since these substances may affect the sensorial quality and/or bioactivity functions of green tea. In this respect, the content of catechins was determined by HPLC in the whole extract of the static assays, and resulted in values of 0.2, 0.8 and 6.7 mg catechins / g tea, respectively, for EA, EL and ETOH cosolvents. The caffeine/catechins selectivity can be pondered considering the ratio caffeine/catechins extracted per g of green tea leaves, which resulted 33 for EA, 16.3 for EL and 1.6 for ETOH. The cosolvent polarity is influencing the co-extraction of catechins and thus the caffeine/catechins selectivity.

Figure 1 shows the overall extraction curve (OEC) obtained using pure CO₂ and the three cosolvents in the static-SFE. The highest extraction rates of caffeine at the early extraction stages were obtained with CO₂+EL, while the lower extraction rates resulted with pure CO₂. The early extraction rate of caffeine were calculated on the basis of the first kinetic data collected (after 14 min of CO₂ flow) and were 0.063 mg/min in the case of pure CO₂, and 0.098 mg/min, 0.289 mg/min and 0.486 mg/min, respectively, for

CO₂+EAC, CO₂+ETOH and CO₂+EL. Then, ethyl lactate was the most efficient cosolvent and can produce a caffeine recovery enhancement close to 7 in comparison with pure CO₂.

The OECs of caffeine static-SFE are depicted in Figure 1 for the case of pure CO₂ (Figure 1a), CO₂+EAC (Figure 1b), CO₂+ETOH (Figure 1c) and CO₂+EL (Figure 1d).

The OECs were adjusted using the model of Sovová [33] which is based on assumption that X_p mass of solute is easy accessible to the supercritical solvent (due to cell wall disruption) while the rest (X_k) remains inside cell walls. Thus, three steps are considered in the SFE process: (i) the constant rate period, where only the easily accessible solute is removed and thus, is controlled by convection in the fluid phase; (ii) the falling rate period, where both convection and internal mass transfer are important; (iii) the internal diffusion controlled rate period, where the remaining solute is only inside the cell walls.

The corresponding model equations describing each extraction step are given in the Appendix.

Furthermore, it is considered that the supercritical solvent flows axially through a cylindrical extraction bed, the solvent is solute-free at the bed inlet and particle size distribution is homogeneous throughout the extraction cell.

The solid particle density (ρ_s) is 1046 kg/m³, bed porosity (ε) was determined on the basis of the corresponding apparent density (411.8 kg/m³) and resulted $\varepsilon = 0.6$, and CO₂ density (ρ) at 30 MPa and 343 K was determined from thermodynamic tables ($\rho = 788.6$ kg/m³) [34].

Due to the lack of experimental solubility data of caffeine in the CO₂+EL and CO₂+EAC supercritical solvents, the solubility (Y^*) was estimated as the slope of a theoretical linear behavior of the OEC between $t = 0$ and $t = 14$ min (Table 4). For comparison, the estimated caffeine solubility in pure CO₂ was 0.029 % mass, which is

quite in agreement with the experimental solubility measured at 343 K and 28.1 MPa (0.023 % mass) [35]. These estimated solubilities presume that, as in the case of the solubility of caffeine in the liquid solvents [30, 31], the solubility of caffeine in CO₂ with ethyl lactate cosolvent is higher than in the case of ethanol or ethyl acetate cosolvents.

Global caffeine yield (X_o) was assessed on the basis of the maximum yield attained in each OEC; 1% above the total amount of extract for each experiment as reported in Table 4. The extractable caffeine (X_p) was considered an adjustable parameter, but the same X_p/X_o ratio was considered for all OECs, since the same vegetal material (crushing and cell disruption) was employed and thus, it is presumed that the same percentage of caffeine is easy accessible in the constant rate period. Then, the X_p/X_o ratio and the mass transfer coefficients in the fluid and solid phase (k_{YA} and k_{XA}) were adjusted to reproduce the experimental OECs.

A suitable X_p/X_o ratio resulted to be 0.2 and the optimal k_{YA} and k_{XA} were adjusted to each kinetic data set. The values are given in Table 4 together with the average absolute relative deviation between calculated and experimental caffeine yield.

The optimal X_p/X_o ratio represents a X_k (amount of caffeine inside cell walls) around 4 times higher than X_p (readily accessible caffeine), denoting that caffeine is strongly bound in the vegetal matrix. Furthermore, this is in accordance with the fact that a very short constant extraction rate period was observed in the extraction curves (t_{CER} values were 0.96, 0.16 and 0.30 min, respectively, for EA, EL and ETOH) and thus, mass transport within the solid phase dominated extraction rate almost from the beginning of the process. In this respect, the solubility value (Y^*) calculated as the slope of a theoretical linear behavior up to 14 min of extraction should be considered as an estimated value.

The quality of the model regression can be observed in Figures 1a to 1d, in which the falling extraction rate period (FER) is depicted with dashed lines. A comparison of the OECs corresponding to the different supercritical fluids shows that if no cosolvents are employed the extraction entered the FER period at 54.5 min. Using the cosolvents, the caffeine extraction rate is considerably higher at the beginning of the extraction and thus, the FER period started at 23.6 min for CO₂+EAC, 11.3 min for CO₂+ETOH and 7.5 min for CO₂+EL.

The solid phase mass transfer coefficients (k_{XA}) resulted rather similar in the fitting of all OECs (see Table 4). In general, k_{XA} values were two orders of magnitude lower than k_{YA} values, indicating a strong limitation of caffeine mass transfer in the solid phase. This limitation become evident from the beginning of the extraction and thus, it is possible that the saturation of the supercritical phase was not attained. Furthermore, k_{XA} values resulted reasonably similar for all cosolvents used, representing similar mass transfer in the solid phase. Regarding fluid phase mass transfer coefficient (k_{YA}), values were 1.8 and 2.6 times higher for, respectively, CO₂+ETOH and CO₂+EL, with respect to pure CO₂ or CO₂+EA.

4. Conclusions

The SFE of green tea leaves was studied at 343 K and 30 MPa, using pure CO₂ and different green cosolvents for food processing. In comparison with ethyl acetate and ethanol cosolvents, ethyl lactate resulted in superior capacity for caffeine extraction. The highest yields of caffeine were obtained with ethyl lactate both in SFE-static mode (the cosolvent soaking the vegetal material before CO₂ pumping) and SFE-dynamic mode (the mixture of CO₂ + cosolvent was continuously pumped into the extraction cell). The general trend of cosolvent effect was ethyl lactate > ethanol > ethyl acetate,

which corresponds with the behaviour observed in the pressurized liquid extraction of caffeine from green coffee beans [32].

The analysis of the overall extraction curves obtained in the SFE-static approach indicate that extraction velocity in the early extraction stages is around 7 times higher using CO₂+EL than with pure supercritical CO₂. Consequently, the convective mass transfer coefficients resulted for the model of Sovová, indicate the highest value for the CO₂+EL supercritical solvent ($k_{YA} = 6.5 \cdot 10^{-2} \text{ s}^{-1}$) around 2.6 times higher than for supercritical CO₂.

Thus, ethyl lactate is a suitable green alternative to be employed as cosolvent in SFE to remove caffeine from natural matrices, reducing the extraction time and/or the amount of CO₂ employed.

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411

412

Appendix

The mass extracted (m) as a function of extraction time (t) is calculated according to the following equations:

$$\text{Constant extraction rate period: } m = Q Y^* [1 - \exp(-Z)] t \quad (1)$$

$$\text{Falling extraction rate period: } m = Q Y^* [t - t_{CER} \exp(Z_w - Z)] \quad (2)$$

Diffusion controlled extraction rate period:

$$m = m_{SI} \left\{ X_o - \frac{Y^*}{W} \ln \left[1 + \left[\exp \left(\frac{W X_o}{Y^*} \right) - 1 \right] \exp \left[\frac{W Q (t_{CER} - t)}{m_{SI}} \right] \left(\frac{X_k}{X_o} \right) \right] \right\} \quad (3)$$

Where:

$$Z = \frac{m_{SI} k_{YA} \rho}{Q (1 - \varepsilon) \rho_s} \quad (4)$$

$$W = \frac{m_{SI} k_{XA}}{Q (1 - \varepsilon)} \quad (5)$$

$$Z_w = \frac{Z Y^*}{W X_o} \ln \left\{ \frac{X_o \exp [W Q (t - t_{CER}) / m_{SI}] - X_k}{X_o - X_k} \right\} \quad (6)$$

$$t_{CER} = \frac{m_{SI} (X_o - X_k)}{Y^* Z Q} \quad (7)$$

$$m_{SI} = X_o F \quad (8)$$

Being ε the bed porosity, F the mass of solid loaded in the extraction cell, ρ_s the solid density, Q the CO₂ mass flow rate, ρ the CO₂ density, Y^* the solubility of the solute CO₂ and X_o the global yield.

Model parameters which are adjusted according to the experimental OEC are the intra-particle solute ratio (X_k) and the fluid phase and solid phase mass transfer coefficients (k_{YA} and k_{XA}).

433 Eq. (7) defines the time at which the constant extraction rate ends (t_{CER}). The time at
434 which the falling extraction rate period begins (t_{FER}) is given by:

435
$$t_{FER} = t_{CER} + \frac{m_{SI}}{WQ} \ln \left[\frac{X_k + X_p \exp(WX_o / Y^*)}{X_o} \right] \quad (9)$$

436

Table 1. Single Reaction Monitoring (SRM) transitions and the corresponding collision energies selected for the analysis of the main catechins and caffeine of green tea.

Compound	Precursor ion	Daughter ion	Collision energy (V)
(+)-catechin	290.971	138.987	20
Epicatechin	290.971	138.987	20
Epigallocatechin	306.932	138.989	15
Epicatechin gallate	443.029	123.034	32
Epigallocatechin gallate	459.035	138.999	23
Caffeine	195.066	138.055	19

Table 2. Extraction yield (g of extract / g of tea), caffeine concentration (g of caffeine / g of extract), caffeine yield (mg of caffeine / g of tea) and caffeine recovery (g of caffeine extracted / g of caffeine in tea) in the static and dynamic SFE of green tea leaves using pure CO₂, CO₂+EL, CO₂+ETOH and CO₂+EAC. Extraction conditions: 30 MPa and 343 K.

Extraction mode	Solvent	Extraction yield (%)	Caffeine concentration (%)	Caffeine yield (mg/g)	Caffeine recovery (%)
Static	Pure CO ₂	3.7	15.9	5.9	21.9
	CO ₂ +EL	9.1*	14.3	13.0	48.3
	CO ₂ +ETOH	10.9	9.9	10.8	40.2
	CO ₂ +EAC	8.1	8.1	6.6	24.6
Dynamic	CO ₂ +EL	7.8*	18.2	14.2	52.6
	CO ₂ +ETOH	8.7	10.1	8.8	32.6
	CO ₂ +EAC	7.5	5.5	4.1	15.2

* Mean value between duplicate experiments

Table 3. Caffeine recovered (mg of caffeine in the extract / mg of caffeine in green tea leaves x 100) at different extraction times corresponding to the static-SFE of green tea leaves using different cosolvents. Extraction conditions: 30 MPa, 343 K, 210 min.

t (min)	CO ₂	t (min)	CO ₂ +EL	t (min)	CO ₂ +ETOH	t (min)	CO ₂ +EAC
14	3.1	14	24.3	14	14.4	14	4.9
60	15.6	37	29.6	47	28.5	37	10.5
120	19.6	86	41.0	71	32.4	96	17.8
180	21.3	210	48.3	94	34.3	210	24.6
210	21.9			148	38.1		
				210	40.2		

Table 4. Parameters of the model of Sovová corresponding to the green tea leaves static-SFE at 30 MPa, 343 K and using different cosolvents.

	Y^* (kg/kg)	X_o (kg/kg)	k_{YA} (s ⁻¹)	k_{XA} (s ⁻¹)	AARD*
CO ₂	0.00029	0.0060	0.025	0.00026	6.67
CO ₂ +EAC	0.00043	0.0067	0.025	0.00013	3.72
CO ₂ +ETOH	0.00134	0.0109	0.045	0.00019	2.48
CO ₂ +EL	0.00220	0.0132	0.065	0.00017	8.92

* Absolute Average Relative Deviation = $\frac{100}{N} \sum \frac{|Y_{exp} - Y_{cal}|}{Y_{exp}}$

461 **Figure captions**

462

463 **Figure 1.** Sovová's model fitting of the overall extraction curves obtained in the static-
464 SFE of caffeine from green tea leaves at 30 MPa and 343 K. (a) CO₂; (b) CO₂+EAC; (c)
465 CO₂+ETOH; (d) CO₂+EL. Dashed lines: falling rate period.

466

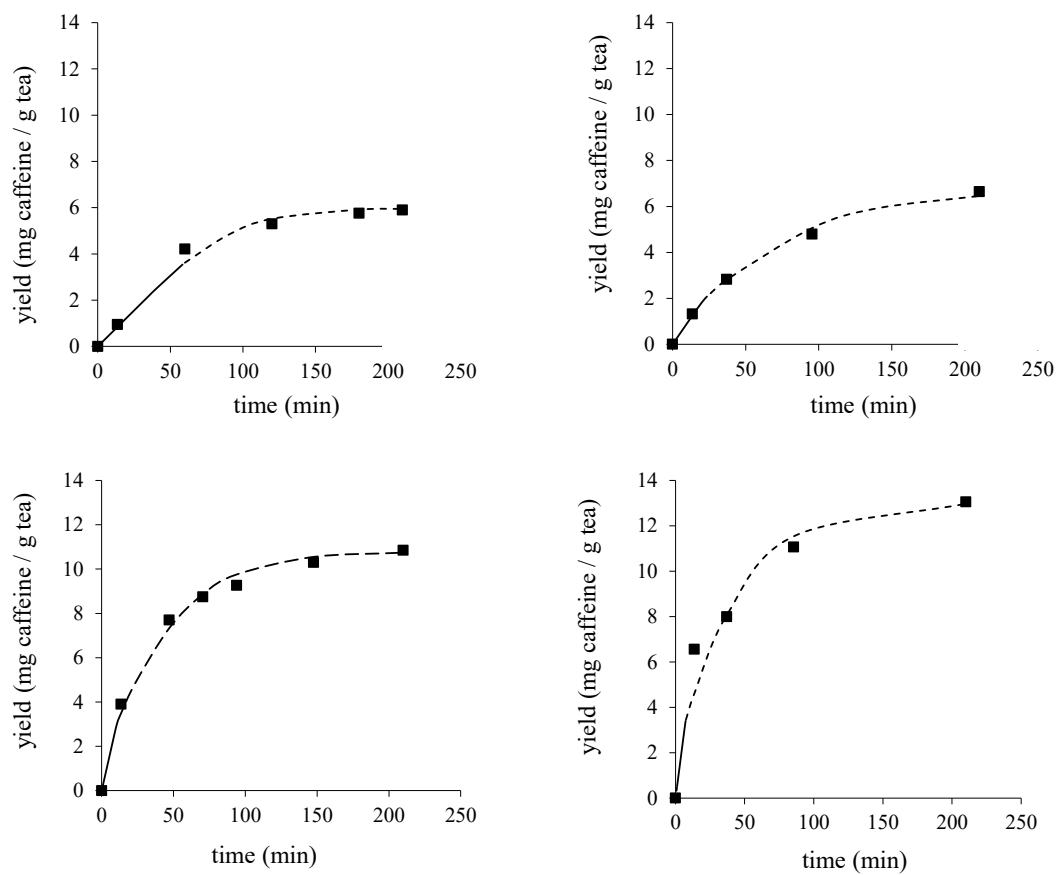


Figure 1. Sovová's model fitting of the overall extraction curves obtained in the static-SFE of caffeine from green tea leaves at 30 MPa and 343 K. (a) CO_2 ; (b) $\text{CO}_2 + \text{EAC}$; (c) $\text{CO}_2 + \text{ETOH}$; (d) $\text{CO}_2 + \text{EL}$. Dashed lines: falling rate period.