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Date Submitted: 2021-02-22

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Natural caffeine from decaffeination processes is widely used by pharmaceutical, cosmetic and soft-drink industries. Supercritical CO₂ extraction (SFE²CO₂) is extensively exploited industrially, and one of its most representative applications is the decaffeination process, which is a greener alternative to the use of organic solvents. Despite its advantages, extraction kinetics are rather slow near the CO₂ critical point, meaning that improvements are highly sought after. The effect exerted by a combination of SFE²CO₂ and ultrasound (US²SFE²CO₂) has been investigated in this preliminary study, with the aim of improving mass transfer and selectivity in the extraction of caffeine from green coffee beans. This hybrid technology can considerably enhance the extraction efficiency and cut down process time. Further studies are in progress to demonstrate the complete decaffeination of green coffee beans of different types and origins.

Record Type: Published Article

Submitted To: LAPSE (Living Archive for Process Systems Engineering)

Citation (overall record, always the latest version):

LAPSE:2021.0052

Citation (this specific file, latest version):

LAPSE:2021.0052-1

Citation (this specific file, this version):

LAPSE:2021.0052-1v1

DOI of Published Version: <https://doi.org/10.3390/pr8091062>

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Communication

Highly-Efficient Caffeine Recovery from Green Coffee Beans under Ultrasound-Assisted SC-CO₂ Extraction

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Received: 2 August 2020; Accepted: 19 August 2020; Published: 1 September 2020



Abstract: Natural caffeine from decaffeination processes is widely used by pharmaceutical, cosmetic and soft-drink industries. Supercritical CO₂ extraction (SFE-CO₂) is extensively exploited industrially, and one of its most representative applications is the decaffeination process, which is a greener alternative to the use of organic solvents. Despite its advantages, extraction kinetics are rather slow near the CO₂ critical point, meaning that improvements are highly sought after. The effect exerted by a combination of SFE-CO₂ and ultrasound (US-SFE-CO₂) has been investigated in this preliminary study, with the aim of improving mass transfer and selectivity in the extraction of caffeine from green coffee beans. This hybrid technology can considerably enhance the extraction efficiency and cut down process time. Further studies are in progress to demonstrate the complete decaffeination of green coffee beans of different types and origins.

Keywords: caffeine; green coffee beans; supercritical CO₂ extraction; ultrasound; hybrid technology

1. Introduction

Caffeine is a xanthine alkaloid widely used in beverages (soft or energy drinks), as well as in pharmaceutical and cosmetic preparations [1]. The global caffeine market was valued at US\$ 231.1 million in 2018 and is expected to reach US\$ 349.2 million by 2027 expanding at a CAGR (Compound Annual Growth Rate) of 4.7% during the forecast from 2019 to 2027 [2]. This rising demand boosts the global caffeine market. Besides production via chemical synthesis, there is an urgent need to increase caffeine production via isolation from natural sources, the principle of which is coffee beans [3,4]. The decaffeination of green coffee beans commonly involves several steps, such as steaming, extraction, drying and caffeine recovery [4–6]. Growing concerns as to the use of organic solvents has stimulated the development of greener techniques for more sustainable and efficient caffeine extraction. Of the alternative green processes available, supercritical CO₂ extraction (SFE-CO₂) can be considered the technique of choice for decaffeination and the recovery of high-value lipophilic compounds from natural matrices [7,8]. A molecular dynamics simulation study demonstrated that, unlike extraction in water, SFE-CO₂ does not favour the aggregation of the caffeine obtained, thus facilitating subsequent purification steps [9]. The aim of extracting 97% caffeine from both Arabica and Robusta green coffee beans has been achieved by this technology in 11.5 h and 22 h, respectively, at 90 °C and 247 bar [10]. The efficiency of SFE-CO₂ can be further improved by the addition of a co-solvent, such as ethanol, in order to enhance the polarity of the system [11]. SFE is generally characterised by slow kinetics, meaning that mass-transfer intensification would be a welcome means to improve diffusion. Ultrasound-assisted extraction (UAE) is extremely beneficial, in this sense, thanks to the enhanced mass transfer that occurs under acoustic cavitation [12,13]. Farouk & Hasan [14] have carried out a study using a high-order numerical scheme, and the data seem to confirm that the kinetics of the SFE process are significantly accelerated by cavitation effects. Higher extraction

yields and shorter extraction times can therefore be achieved when SFE-CO₂ processes are assisted by ultrasound (US) [15]. Currently, US-SFE-CO₂ extractors are mainly available only on lab and pilot scales, and there is a distinct lack of industrial-scale data [16]. Extensive analysis on the synergistic effect of US with SFE-CO₂ have been summarized by Dassoff & Li, [17], namely micro- and macro-mixing, mechanical effects on the cell wall that enhance both convective mass transfer as well as internal diffusivity. Under CO₂ pressure the oxidative degradations that may occur under sonication are negligible. A pilot-scale process using an innovative US-SFE-CO₂ system has been proposed for oil extraction from different vegetal matrices [18].

The aim of this work is to evaluate the effectiveness of ultrasound assistance in the extraction of caffeine from green coffee beans using SFE-CO₂. This preliminary investigation should provide useful data to facilitate a drastic reduction in extraction time. The scalability of this hybrid technology for decaffeination will require further engineering studies. In this work, an SFE unit, equipped with a tightly fixed sonotrode with an immersion horn, has been used under sonication and silent conditions. Extract analysis was carried out using ultra-performance liquid chromatography–tandem mass spectrometry (UPLC-MS-MS).

2. Materials and Methods

2.1. Coffee Sample and Chemicals

Green coffee beans (Arabica, Brazil), that had been previously hydrated to reach 31% moisture, were kindly provided by Lavazza S.p.A (Settimo Torinese, Turin, Italy) and stored in vacuum bags. The densities of the dry coffee (710 kg/m³) and wet coffee (550 kg/m³) were calculated in order to select the most appropriate volume for the experiments. The more suitable amount used for the experiments was 185 g of wet coffee (water 31%) corresponding at 144.5 g of dry coffee (water 11%). A remarkable swelling of green coffee beans in water was observed during the humidification process. A caffeine standard (99.7%) was purchased from Alfa Aesar (Karlsruhe, Germany). Acetonitrile, trifluoroacetic acid (TFA) and magnesium oxide (MgO) were obtained from Merck KGaA (Darmstadt, Germany).

2.2. Supercritical CO₂ Extraction (SFE-CO₂) and Ultrasound-Assisted Supercritical CO₂ Extraction (US-SFE-CO₂)

The SFE-CO₂ and US-SFE-CO₂ of caffeine from green coffee beans were performed in a prototype designed and assembled by Weber Ultrasonics GA (Karlsbad, Germany) and FeyeCon B.V. (Weesp, The Netherlands). The prototype was equipped with a system that circulated fluid through the extraction chamber (11–13 kg h⁻¹ of CO₂), an insulating jacket and an immersion titanium horn for US-assisted procedures.

For SFE-CO₂, green coffee beans were weighed (185 g) and placed into the 1 L-capacity extraction vessel. Different pressure and temperature conditions were tested. Moreover, SFE-CO₂ efficiency was compared to that of the extraction with liquid CO₂ (LE-CO₂), with pressure and temperature being set under the critical point. Similar conditions used in SFE-CO₂ were applied for US-SFE-CO₂. US assistance was obtained thanks to a probe system equipped with a titanium horn (40 kHz; P = 90% W) that was placed in the extraction vessel. To avoid localized sample overheating, the horn was set to operate 5 min on and 2 min off for the whole extraction time (see Table 1 for tested conditions).

Each procedure was repeated three times to verify extraction method reproducibility, and all of the processes provided an aqueous extract that was subsequently freeze dried (Freeze drier LyoQuest-85, Telstar, Legnano, Italy). A 0.5 mg/mL aqueous solution of each obtained sample was prepared and transferred into a vial for UPLC-MS/MS analysis. Results are expressed as mean data ± standard deviation (SD).

Table 1. Experimental conditions for caffeine extraction from Arabica green coffee beans and caffeine determination using UPLC-MS/MS analyses. Reported data are the mean of two experiments.

Entry	Sample (g)	Temperature (°C)	Pressure (bar)	Extraction Method	Total Caffeine (mg)	Extract Caffeine %	Caffeine mg/g Coffee Beans	Decaffein. %	Time (h)
1	185	75	250	1 ^a	155.1 ± 10.6	83.2 ± 5.9	0.838 ± 0.06	8.86 ± 0.61	1
2	185	40	250	1 ^a	59.2 ± 4.5	76.2 ± 5.8	0.320 ± 0.02	3.38 ± 0.26	1
3	185	20	70	2 ^b	26.3 ± 3.8	80.2 ± 11.6	0.142 ± 0.02	1.50 ± 0.21	1
4	185	75	250	3 ^c	318.3 ± 19.7	90.1 ± 5.6	1.72 ± 0.1	18.19 ± 1.1	1
5	185	40	250	3 ^c	126.5 ± 10.4	83.9 ± 6.9	0.684 ± 0.06	7.23 ± 0.6	1
6	185	75	125	3 ^c	279.8 ± 15.8	74.1 ± 4.2	1.51 ± 0.08	15.98 ± 0.9	1
7	50	75	250	3 ^c	148.5 ± 9.3	69.0 ± 4.3	2.97 ± 0.18	31.4 ± 1.9	1
8	185	75	250	3 ^c	673.8 ± 25.8	87.3 ± 3.3	3.64 ± 0.12	38.5 ± 1.4	2
9	185	75	250	3 ^c	906.5 ± 30.6	91.6 ± 3.1	6.04 ± 0.2	51.8 ± 1.8	3
10	185	75	250	3 ^c	1104.3 ± 40.1	93.4 ± 3.3	5.97 ± 0.2	63.1 ± 2.3	4

^a Supercritical CO₂ extraction (SFE-CO₂); ^b extraction with liquid CO₂ (LE-CO₂); ^c ultrasound supercritical CO₂ extraction (US-SFE-CO₂).

2.3. Conventional Caffeine Extraction

In order to evaluate the total caffeine content in the green coffee beans used for the experiments, a conventional extraction was performed. Briefly, 100 mL of water and 4 g of MgO were added to 1 g of ground green coffee beans, and the obtained mixture was stirred for 1 hour at 90 °C, then filtered. The filtrate was brought to 250 mL with water and placed into a 250 mL graduated flask, and this solution was used for caffeine quantification via UPLC-MS/MS. The procedure was repeated three times to evaluate extraction-yield reproducibility. The efficiency of this conventional extraction method was confirmed by re-extracting, under the same conditions, the residual coffee sample derived from the filtration procedure.

2.4. Qualitative and Quantitative Analyses

Analyses were performed using a UPLC-MS/MS system (Acquity TQD LC/MS/MS System, Waters Corporation, Milford, MA, USA), equipped with a C-18 column (BEH C-18, 2.1 × 50 mm, 1.7 µm). Isocratic elution was carried out at 50 °C with 90:10 *v/v* of water (0.1% TFA)/acetonitrile (0.1% TFA). The flow rate was set at 0.4 mL min⁻¹.

For determination, we operated in atmospheric-pressure chemical ionization (APCI+) mode, following the transitions *m/z* = 195 → 138 (quantification) and *m/z* = 195 → 110 (qualitative confirmation of the peak), using 26 eV as the collision energy. The calibration curve of the UPLC-MS/MS method was determined using aqueous caffeine standard solutions (from 0.01 to 1 mg/mL); a linear regression with $R^2 = 0.9994$ was obtained using Waters QuanLynx software (LOD 0.005 mg/mL, LOQ 0.01 mg/mL).

3. Results and Discussion

3.1. SFE-CO₂, LE-CO₂ and US-SFE-CO₂ of Green Coffee Beans

Computational simulation studies on caffeine extraction from a fixed bed of coffee beans indicate that acoustic waves could significantly accelerate the kinetics of SFE thanks to their physical/mechanical effects on the treated vegetal matrix, therefore leading to an improvement of extraction rate and yield [9]. To the best of our knowledge, effective experimental works involving the hybrid technology US-SFE-CO₂ in coffee decaffeination have not been reported so far.

This study aims to evaluate the possibility of using the effect of cavitation to improve the SFE-CO₂ of caffeine from Arabica green coffee beans, in terms of reducing the process time and temperature and also enriching extracts.

Several experiments were carried out under US assistance, and silent conditions, using samples with 31% moisture. It was decided that all tests would be performed in a relatively short process time (1 h), although that does not lead to exhaustive caffeine extraction, which is an operation that usually

requires several hours [10]. Nevertheless, under these conditions, a preliminary assessment of the beneficial effects of US-SFE-CO₂ was performed. The highest extraction temperature was set at 75 °C.

Different conditions were applied in the first runs using SFE-CO₂ alone. The extraction vessel was filled to about 80% maximum volume with 185 g of matrix (Table 1, entry one and two). For the sake of comparison, LE-CO₂ (Table 1, entry three) was also performed. US-SFE-CO₂ was then initially carried out under the same experimental conditions as in SFE-CO₂ (Table 1, entries four and five). Subsequently, the influence of both lower pressure and sample amount were tested at the highest temperature (Table 1, entries six and seven, respectively).

Qualitative and quantitative analyses were performed using UPLC-MS/MS on the freeze-dried extracts in order to evaluate caffeine extraction yields and sample enrichment. Data (Table 1) were compared to the mean caffeine content in coffee (9.46 mg/g) obtained from exhaustive conventional water extraction in order to calculate the decaffeination percentage achieved.

Results clearly show that temperature plays a crucial role in extractions carried out under silent conditions (entries one, two and three). Although a poor extraction yield was observed when CO₂ was used in liquid conditions, extract purity was relatively high. Under supercritical conditions, yields were found to be directly correlated to increasing temperature and also gave better extract purity, which reached 83.2% at 75 °C. Despite reports by Machmudah et al. [8] on the solubility of caffeine in SC-CO₂ at pressures above 19 MPa/190 bar, caffeine solubility increases with increasing temperature, which however is in agreement with Saldana et al. [19].

3.2. US-SFE-CO₂ Efficiency

By comparing entries one and four, both carried out at 75 °C and 250 bar, it is possible to see that caffeine amount and decaffeination percentages were doubled thanks to the cavitation phenomenon. A better result if compared with data reported by Farouk & Hasan [14], that showed an enhancement of caffeine extraction yield by around 15%–25%. Moreover, our results evidenced the effect of sonication on extract purity (90.1%). A similar trend can be observed when comparing entries two and five, which were performed at low temperature (40 °C). These preliminary results demonstrate how US is a potential, efficient way of enhancing mass transfer processes in SFE. The use of US enabled higher yields in a shorter time, in agreement with Rodríguez et al. [20] who observed 109%–150% improvement at 30 min comparing SFE-CO₂ and US-SFE-CO₂ in cocoa butter extraction.

Lower pressure (125 vs. 250 bar) and lower filling volume (50 g vs. 185) (entry six and seven, respectively) confirmed the pivotal role of CO₂ pressure [21] as well as a better sound wave diffusion in the sonication cone of the horn tip. Entry four gave up to 90.1% of caffeine in the extract and 18.19% of sample decaffeination. The obtained results showed that the caffeine extraction yield was lower, by about 12%, at 125 bar (entry six). US intensity must be strong enough to induce vibrational effects [22] when a probe system equipped with a titanium horn (40 kHz; P = 90% W) was employed. In the case of a lower sample amount in the extraction vessel (entry seven) higher mass extraction was achieved; a caffeine amount of 2.97 mg per gram of coffee bean was raised, whereas 1.72 mg/g was obtained in entry four. These values reveal that there is an increase in the sonication effect when less vessel volume was occupied by the matrix, thus allowing for better propagation of acoustic waves at lower pressure. Anyway, under these conditions, extracts showed 20% less of caffeine content. This, as observed by field emission scanning electron microscopy by Balachandran et al. [23] that reported 200 µm surface damage in ginger particles, is more likely due to stronger cell-wall rupture and then to higher metabolite release, which results in our case in a lower selectivity for caffeine.

In order to evaluate decaffeination kinetics, the best extraction conditions (entry four) were used for longer times, 2, 3, 4 h (entries eight, nine, ten). It was found that longer extraction times gave a higher decaffeination percentage, up to 63.1% after 4 h, with no significant influence on extract purity.

4. Conclusions

In this preliminary study on caffeine extraction from Arabica green coffee beans, SFE-CO₂ and US-SFE-CO₂ have been compared under different experimental conditions. Results show that, in 1 h of extraction time, the effect of acoustic waves can lead to a doubling of caffeine extraction yield and around 10% higher extract purity. The best experimental parameters (US-SFE-CO₂, 75 °C, 250 bar, 185 g of sample amount) were also tested at longer process times, and thus 63.1% decaffeination was achieved in 4 h. These experimental data lay the foundation for further studies into caffeine US-SFE-CO₂ from coffee beans, both as an improvement of the decaffeination process in the coffee industry, and as an effective technique to produce purer extracts in shorter times for industrial use.

Author Contributions: Conceptualization, A.B. (Arianna Binello) and G.C.; methodology, J.M. and G.C.; validation, A.B. (Alessandro Barge); formal analysis A.B. (Alessandro Barge); investigation, J.M.; data curation, J.M.; writing—original draft preparation, J.M. and A.B. (Arianna Binello); writing—review and editing G.C.; supervision, G.C. All authors have read and agreed to the published version of the manuscript.

Funding: The Manunet Transnational Call 2019 Project “Ultraclean” is warmly acknowledged.

Acknowledgments: Inga Grigaliunaite (FeyeCon, Weesp-Holand) is warmly acknowledged for the valuable technical assistance.

Conflicts of Interest: The authors declare no conflict of interest.

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