J. of Supercritical Fluids 82 (2013) 116–121

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Decaffeinated black tea: Process optimization and phenolic profiles

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ARTICLE INFO

Article history:
Received 16 April 2013
Received in revised form 4 July 2013
Accepted 6 July 2013

Keywords:
Decaffeination
Black tea
Supercritical fluid extraction
Phenolics
Caffeine

ABSTRACT

The low-quality black tea was extracted at 27 different conditions using a lab-scale supercritical fluid extraction system according to four factor, three level Box–Behnken design [pressure (150–450 bar), temperature (40–80 °C), modifier flow rate (0.5–1.0 ml/min), and ethanol concentration in aqueous solution (75–100%)] at constant CO_2 flow rate (2 l/min). Response surface methodology was used in order to optimize the extraction conditions for obtaining minimum caffeine and maximum phenolic profiles of the decaffeinated black tea. The R^2 values for caffeine and phenolics were 99.5 and 96.6%, respectively. The lowest caffeine and the highest phenolics were obtained at following conditions [pressure (300 bar), temperature (53 °C), modifier flow rate (0.70 ml/min), and ethanol concentration (87.5%)] for 1 h. Using these conditions, the average loss of caffeine and phenolics in the decaffeinated tea were 99.8 and 3.3%, respectively. The present work suggests that optimum extraction conditions found can be applied for a pilot or large-scale production of decaffeinated black tea.

1. Introduction

Tea is one of the most popular beverages consumed worldwide. Black, green, and oolong teas are produced and consumed abundantly in different regions of the world. Black tea represents 78% of the total global production, followed by green tea at 20% and oolong tea at 2% [1]. Caffeine, the most consumed alkaloid, is one of the few plant products with which the general public is readily familiar, because of its occurrence in beverages such as tea and coffee, as well as various soft drinks. It has several adverse effects on human health such as palpitations, gastrointestinal disturbances, anxiety, tremor, increased blood pressure, and insomnia, among others [2–6]. There is, therefore, an increased demand for decaffeinated beverages throughout the world.

Different extraction techniques have been attempted to remove caffeine from black and green tea leaves, either partially or completely such as microwave-assisted extraction [6], supercritical carbon dioxide [5,7–16], subcritical water extraction [17], hot water extraction [18–20], microwave-enhanced vacuum ice water extraction [21], solvent extraction [22], and high pressure extraction [23].

Decaffeination technique applying supercritical carbon dioxide (SC-CO_2) [24], which has been widely used for decaffeinated coffee for a long time, has obtained increased interest in food processing. This technique has great advantages (such as convenience, non-explosiveness, non-toxicity, and selective extraction) as compared to conventional techniques that use organic solvents [4,25]. SC-CO_2, which is nearly non-polar solvent, easily extracts non-polar substances from the plant matrices. Since caffeine has a relatively high polarity, it is, therefore, necessary to add a high polarity solvent such as water or ethanol when extracting caffeine using SC-CO_2. Ethanol has been reported to be a suitable co-solvent for the extraction of caffeine from green tea [4,9].

Black tea is processed in either of two ways: Orthodox or CTC [26,27]. It is usually graded on one of four scales of quality (such as whole leaf, broken leaf, fanning, and dust). In Turkey, more than 50% of black tea is processed by ÇAYKUR Tea Processing Plant, which processes black tea according to its own seven different grades [high-quality tea (grades 1–3) and low-quality tea (grades 4–7)]. The low quality groups of teas are marketed after being blended with high quality group categories according to the demands [28].

Meanwhile, to the best of our knowledge, there have been no reports of caffeine extraction from black tea sample except the studies about tea stalk and fiber wastes of black tea [10,11]. Most of the studies were about the decaffeination of green tea, green tea powder using only ethanol/CO_2, water/CO_2, chloroform/CO_2 or the mixture of ethanol/water/CO_2 [4,5,7–9,12,13,15]. Apart from the performed studies, we worked with different ethanol concentrations in aqueous solution (75–100%) throughout the extraction period. The objective of this study was to optimize the extraction conditions for producing a decaffeinated tea from the low-quality black tea, while keeping the maximum content of health promoting phenolic compounds. The effects of different extraction conditions, such as temperature, pressure, modifier flow rate, and ethanol concentration in aqueous solution, on caffeine and phenolic profiles of

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http://dx.doi.org/10.1016/j.supflu.2013.07.002

Table 1
Coded and uncoded levels of independent variables for Box–Behnken design and responses.

	Coded level				Uncoded level				Responses	
	X1	X2	X3	X4	P (bar)	T (°C)	Modifier flow rate (ml/min)	Ethanol concentration (%)	Caffeine (mg/100 g)	Phenolics (mg/100 g)
1	+1	+1	0	0	450	80	0.75	87.5	14.37	508
2	+1	−1	0	0	450	40	0.75	87.5	31.31	1726
3	−1	+1	0	0	150	80	0.75	87.5	7.62	358
4	−1	−1	0	0	150	40	0.75	87.5	20.48	1399
5	0	0	+1	−1	300	60	1.00	75.0	0	77
6	0	0	+1	+1	300	60	1.00	100	1330	3131
7	0	0	−1	−1	300	60	0.50	75.0	0	169
8	0	0	−1	+1	300	60	0.50	100	1385	3206
9	0	0	0	0	300	60	0.75	87.5	3.06	1430
10	+1	0	0	−1	450	60	0.75	75.0	0	140
11	+1	0	0	+1	450	60	0.75	100	1485	3425
12	−1	0	0	−1	150	60	0.75	75.0	0	136
13	−1	0	0	+1	150	60	0.75	100	1462	3359
14	0	+1	+1	0	300	80	1.00	87.5	3.63	321
15	0	+1	−1	0	300	80	0.50	87.5	0	894
16	0	−1	+1	0	300	40	1.00	87.5	24.13	1786
17	0	−1	−1	0	300	40	0.50	87.5	30.54	1532
18	0	0	0	0	300	60	0.75	87.5	3.08	1478
19	+1	0	+1	0	450	60	1.00	87.5	2.4	1333
20	+1	0	−1	0	450	60	0.50	87.5	19.38	1419
21	−1	0	+1	0	150	60	1.00	87.5	15.27	1529
22	−1	0	−1	0	150	60	0.50	87.5	24.51	1400
23	0	+1	0	−1	300	80	0.75	75.0	0	81
24	0	+1	0	+1	300	80	0.75	100	1345	3325
25	0	−1	0	−1	300	40	0.75	75.0	0	411
26	0	−1	0	+1	300	40	0.75	100	1160	2970
27	0	0	0	0	300	60	0.75	87.5	2.11	1437

decaffeinated black tea were studied according to Box–Behnken design.

2. Materials and methods

2.1. Samples

Low-quality black teas (grades 4–7) were procured from the ÇAYKUR Tea Processing Plant in Rize at the beginning of the first harvest season of June 2011. Graded teas (10 kg from each grade) were obtained from the same processing line and mixed up equal amounts in order to represent the low-quality black teas. They were kept in their pack in a temperature-controlled cabinet (at ~5 °C with relative humidity of 65–70%) at the Food Institute (TÜBİTAK Marmara Research Center, Gebze, Turkey) until they were processed.

2.2. Reagents

All chemical reagents were obtained from Sigma–Aldrich-Fluka Co. Ltd. (Prolab, Istanbul, Turkey), unless otherwise stated. The high purity carbon dioxide (99.95%) was purchased from the local supplier (HABAŞ Ltd., Kocaeli, Turkey).

2.3. Methods

2.3.1. Supercritical fluid extraction (SFE)

The experiments were conducted in a lab-scale extractor system (*Spe-ed* SFE-2, Applied Separations Inc., Allentown, PA). The system consisted of an extractor with an internal volume of 10 ml. One and half gram of dried black tea (with original sample size) was packed inside a stainless steel extraction vessel. A certain quantity of glass wool was packed into the two ends of the vessel in order to prevent the escape of the tea particles from the extractor. Liquid CO_2 from a siphon-tube passed through a chiller at 273 K and then was compressed to the desired working pressure using a pump. It was then heated to supercritical conditions using an oven where extraction vessel is found. The modifier mixture (ethanol/water) was added to SC-CO_2 at different ratio using a pump (Model 1500, LabAlliance, Scientific Systems, Inc., State College, PA). All extractions were conducted under dynamic conditions for 1 h periods. The sample size was not considered in the extractions and SC-CO_2 was pumped at a constant flow rate (2 l/min) and directed to the bottom of the vessel for up-flow configuration. The tea meal obtained after extraction was dried in the oven at 50 °C for 45 min for removing the possible modifier residues.

2.3.2. Experimental design

Response surface methodology (RSM) was applied to optimize the extraction conditions for the removal of caffeine from the low-quality black tea using SFE with ethanol–water mixture as modifier. Four factor, three level Box–Behnken design was used. The independent variables were pressure, temperature, co-solvent flow rate, and ethanol concentration (volume percentage of ethanol in ethanol–water mixture). Uncoded and coded values of the independent variables together with the experimental points used according to the Box–Behnken design are shown in Table 1.

2.3.3. Determination of phenolic compounds

Phenolic compounds were extracted from the dried tea meal and analyzed according to the method described by Serpen et al. [29], with some modifications. One gram of low-quality decaffeinated tea was extracted with 10 ml of hot water (80 °C) for 10 min. The supernatant was collected into a flask after centrifugation at 7500 × *g* for 5 min. The residue was further extracted with 10 ml of hot water (80 °C) for 10 min and then 5 ml hot water for 10 min. The combined extract was diluted with water at a ratio of 1:5 (v/v), and 1 ml of extract was passed from 0.45 μm nylon filter and transferred into High Performance Liquid Chromatography (HPLC) vial. Chromatographic analyses were performed on an HPLC system consisting of a LC-20AD pump, SPD-M20A DAD detector, SIL-20A HT autosampler, CTO-2OAC column oven, DGU-20A5 degasser, and CMB-20A communications bus module (Shimadzu Corporation, Kyoto, Japan). An Atlantis dC18 column (4.6 mm × 250 mm,