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Extraction of chilli pepper (var. Byedige) with supercritical CO_2: Effect of pressure and temperature on capsaicinoid and colour extraction efficiency

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Abstract

The influence of operating parameters (pressure from 100 to 400 bar and temperature of 40, 60 and 80 °C) on the extraction efficiency of capsaicinoids and colour components from chilli pepper (variety Byedige) was studied. Capsaicinoid content and colour value were determined in raw material and residue material after extraction. The colour intensities of residue material and obtained extracts were given by ASTA (American Spice Trade Association) and CU (Colour Unit) value, respectively. Total extraction yield and extraction efficiency of capsaicinoids increased with increasing pressure at constant temperature as well as with increasing temperature at constant pressure. The highest extraction yield for total solids of 12.8% was obtained at 400 bar and 40 °C, where almost 96% of capsaicinoids and 80% of colour components were removed from the raw material. The highest CU value of chilli pepper extract, obtained by a single step extraction at 40 °C and 400 bar, was approximately 15,000 CU. Calculated mass transfer coefficients of chilli pepper extract from solid material varied from 2×10^{-7} to 11×10^{-7} m s^{-1}in the pressure range of 100–400 bar and temperature range 40–80 °C. It was observed that the mass transfer coefficient is a linear function of the density of carbon dioxide in the range of applied operating conditions.

Keywords: Chilli pepper; Supercritical fluid extraction; Capsaicinoids; Colour intensity; Mass transfer coefficient

1. Introduction

Fruits of Capsicum plants are among the most heavily consumed spices throughout the world, due to their unique flavour and pungency. The pungency is caused by capsaicinoids, among which the most abundant components are capsaicin (C), dihydrocapsaicin (DC) and nordihydrocapsaicin (NDC), with a content in chilli peppers from 0.05% in the mildly pungent types to as high as 1.30% in the hottest chillies. Capsaicin, as the most important among pungent principles, is a powerful irritant of the receptors participating in circulatory and respiratory reflexes, and is used in stimulating medicines and in food preparations (Surh & Lee, 1995).

Quality of obtained product is strongly dependent upon the quality of fruit and the production method (Biacs, Czinkotai, & Hoschke, 1992; Mínguez-Mosquera & Pérez-Gálvez, 1998; Okos, Csorba, & Szabad, 1990). The quality and quantity of colour pigments (carotenoid compounds), which are originally found in pericarp fruit tissue, exert a considerable impact on the commercial value of many foodstuffs, such as fruits, juices, wines, teas and many other products. In the traditional process, the dried and ground Capsicum fruit is extracted by organic solvents, whose residue content in the product is governed by strict food regulations due to various effects on human health. The lipophilic nature of carotenoids makes supercritical carbon dioxide (CO_2) the most widely used supercritical fluid (SCF) for extraction, due to its greatly favourable properties (Knez, Posel, Hunek, & Golob, 1991). Škerget, Knez, and Novak (1998) have shown a separation of paprika

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Nomenclature

AARD	average absolute relative deviation (%)
ASTA	American Spice Trade Association
CU	colour unit
C	capsaicin
DC	dihydrocapsaicin
NDC	nordihydrocapsaicin
HPLC	high performance liquid chromatography
PSVA	pelargonacid vanillymide
A	absorbance
A_s	specific surface area (m^{-1})
Δc	concentration difference (g m^{-3})
d	particle diameter (m)
m	mass (g)
P	pressure (bar)
Q_v	flow rate of solvent (kg h^{-1})
T	temperature (°C)
V_t	total bed volume (l)
w_{CAPS}	concentration of capsaicinoids, (μg g^{-1})

Greek letters

β_a	mass transfer coefficient, (m s^{-1})
ψ	bed void fraction,
ρ	density of solvent, (kg m^{-3})
ρ_α	apparent density of material, (kg m^{-3})
ρ_s	solid density of material, (kg m^{-3})
η	extraction efficiency, (%)
τ	extraction time, (h)

components (aromatic and colouring) by employing a two-stage extraction procedure with SC-CO_2. They determined that the optimal operating pressure for the extraction of aromatic components at temperature 40 °C is 150 bar and, for the separation of colouring components, the pressure 400 bar, where the extract had a high CU value of 180,000 CU. The authors also correlated their findings with solubility data of β-carotene in CO_2 (Škerget & Knez, 1997), which were in the range from 0.6 to 5.5 g m^{-3} (100–300 bar, 25 and 40 °C). Knez and Steiner (1992) found that the solubility of capsaicin, the most abundant capsaicinoid, in CO_2 was in the range from 0.6×10^{-2} to 17.1×10^{-2} g m^{-3} (70–350 bar, 25, 40 and 60 °C). Preparation of paprika extracts, using SC-CO_2, has been studied by Jarén-Galán, Nienaber, and Schwatrz (1999), where the extracts were evaluated for pigments such as capsorubin, capsanthin, zeaxanthin, β-cryptoxanthin and β-carotene. The authors investigated continuous and discontinuous extraction of paprika with SC-CO_2 and made a comparison with paprika extracts obtained by traditional extractions with acetone or hexane. At a constant pressure, increasing the extraction volume (50–200 l), as well as at constant extraction volume and increasing the pressure (≈140–480 bar), caused an increase in concentration of the major pigment capsanthin. The best conditions for the discontinuous extraction were initial low pressure at 137 bar, followed by a second extraction step at 413 or 482 bar, where the oil was almost completely extracted in the first stage, while the second stage produced the highest obtainable amount of pigments, almost twice the pigment concentration obtained by traditional organic solvent extraction methods. Peusch, Müller-Seitz, Petz, Müller, and Anklam (1997) determined the capsaicinoid content in different paprika and chilli pepper extracts obtained with SC-CO_2. They showed that co-extractives in the capsicum powders act as an "internal" modifier by influencing the polarity of the solvent. The capsaicinoid yields obtained by supercritical fluid extraction were comparable to those obtained by organic solvent extraction, using various solvents of different polarities under reflux. Daood et al. (2002) determined contents of carotenoids, tocopherols and capsaicinoids in pungent spice paprika extracts obtained with supercritical CO_2 (35–55 °C, 100–400 bar) and subcritical propane (25 °C, 50–80 bar). Highest carotenoid recovery in extract (17.5% of the initial content in starting material) and most of the capsaicinoid extraction efficiency (5% in residue) was achieved at 400 bar and 35 and 55 °C, respectively. Subcritical propane was inefficient for extracting capsaicinoids and 78% remained in the residues. In general, the colour content of propane-extracts was 4–5 times higher that that of SC-CO_2 extracts.

The extractable colour in the food industry is usually expressed in ASTA (American Spice Trade Association) unit value for paprika or chilli pepper plant material and in Colour Units (CU) for their extracts. One ASTA unit is approximately equivalent to 40 CU. Data on colour intensity values of chilli pepper extracts related to extractable colour, expressed in commercial units used by food manufacturers and, further on, the influence of operating conditions for high pressure extraction of chilli pepper (variety Byedige) with CO_2, were not available. The purpose of the present study was to demonstrate a semi-continuous extraction of ground chilli pepper (variety Byedige) with CO_2 under different operating conditions of pressure (100–400 bar) and temperature (40–80 °C). Hence, chilli pepper material was analysed for capsaicinoids (capsaicin, nordihydrocapsaicin, dihydrocapsaicin) and colour intensity given by ASTA value; the obtained chilli pepper extracts were analysed for colour intensity given by CU value. The total yield of extraction was also studied as a function of employed extraction conditions. The influence of

temperature and pressure on the extraction of capsaicinoids and colour components was determined. Additionally, a mass transfer study was established for the region of constant extraction rate.

2. Materials and methods

2.1. Materials

Ground chilli pepper (variety Byedige, grown in north of Andra Pradesh, India) and the external standard of n-nonanacid vanillylamide (pelargonacid vanillymide, PSVA), purity 97%, required for analytical purposes, was donated by RAPS GmbH & CO., KG, Kulmbach in Germany. All solvents used for analytical purposes were purchased from Merck, Germany. Carbon dioxide (purity 99.5%) was purchased from Messer-Ruše, Slovenia.

2.2. Methods

2.2.1. General

Sieve analysis of ground material was performed in order to determine the particle size distribution, and its moisture content was measured with a Metller Toledo DL31 Karl Fischer Titrator. The solid density of material was measured by helium pycnometer (multi volume pycnometer 1305, Micrometrics, USA), whereas bulk density was measured by weighing a known volume of solid material.

2.2.2. Determination of colour intensity values

The ASTA value of chilli pepper samples was evaluated according to the ASTA 20 method (ASTA, 1968). Between 0.07 and 0.11 g of chilli pepper was weighed into a tared 100 ml flask; acetone was added to the mark, the mixture stirred and, after 16 h of extraction at room temperature in the dark, an aliquot of the transparent decanted extract was taken. The absorbance (A) of the solution was measured at 460 nm in comparison to a standard glass reference. The absorbance was measured by UV–Vis spectrophotometer (Varian Cary 1E, Varian, Walnut Creek, California, USA). The ASTA colour value was calculated from the equation

$$\mathrm{ASTA} = \frac{A \cdot 16.4 \cdot I_\mathrm{f}}{m_\mathrm{s}}, \tag{1}$$

where I_f is a correction factor for the apparatus, calculated from the absorbance of potassium dichromate, ammonium sulphate and cobalt sulphate, and m_s is the mass of raw material in g. The absorbance of each sample solution was measured three times in two parallel trials. The standard deviation value was in the range of 2%.

Colour Unit (CU) value of extracts was determined using method MSD 10 (AOAC, 1984). 1 g of extract was weighed in a tared 100 ml flask and acetone added to the mark. 1 ml of the solution was transferred into a tared 100 ml flask and diluted to the mark with acetone. Absorbance (A) of this solution was measured with the above-mentioned UV–Vis spectrophotometer at 462 nm and CU value was calculated as follows:

$$\mathrm{CU} = \frac{A \cdot 66000 \cdot I_\mathrm{f}}{m_\mathrm{o}}, \tag{2}$$

where m_o is the mass of extract in g. The absorbance of each sample solution was measured three times in two parallel trials. The standard deviation value was in the range of 5%.

2.2.3. Capsaicinoid content

The analytical method for determining capsaicinoid in chilli pepper samples was supplied by RAPS GmbH & CO., KG (Weinreich, 2001). The analytical method involved high performance liquid chromatography (HPLC), where the quantifications of capsaicin (C), dihydrocapsaicin (DC) and nordihydrocapsaicin (NDC) were performed via a calibration curve of external standard of PSVA. The HPLC system consisted of a pump and a diode array detector (Varian 9012 HPLC pump, Varian 9065 detector, Walnut Creek, California).

2.2.4. Extraction procedure

The extraction experiments were performed in a semi-continuous high-pressure flow-up apparatus, whose detailed description can be found in the paper by Hadolin, Škerget, Knez, and Bauman (2001). Approximately 25 g of ground chilli pepper was charged into the extractor and the temperature was regulated and maintained at constant value. Liquefied CO_2 was pumped, with a high-pressure pump, through a preheating coil, over the bed of sample in the extractor. The extract was collected in a separator at 1 bar and 25 °C, and the flow rate of released CO_2 was measured by a flow meter. A semi-continuous extraction was carried out by extracting the solid material in cycles. During each cycle, up to 200 g of CO_2 were passed over the material. This was followed by interrupting the continuous extraction mode, while maintaining constant conditions (pressure, temperature) and weighing the extract (±0.1 mg), in order to obtain extraction curves for the kinetics. The interruptions were as short as 1 min maximum.

A semi-continuous extraction mode enabled us to obtain extraction curves for extraction kinetics. Extraction experiments were conducted by extracting chilli pepper with supercritical CO_2 over a pressure range of 100–400 bar at temperatures of 40, 60 and 80 °C. Extraction experiments were run until a total extraction yield was reached. Total yield of extraction η (1 g of extract per 100 g of material) was calculated by the equation

$$\eta(\%) = \frac{m_{\text{extract}}}{m_{\text{raw material}}} \times 100\%, \quad (3)$$

where m_{extract} is mass of extract and $m_{\text{raw material}}$ is mass input of ground chilli pepper. The efficiency of capsaicinoid extraction from chilli pepper was calculated by the formula

$$\eta_{\text{CAPS}}(\%) = \frac{w_{\text{caps1}} - w_{\text{caps2}}}{w_{\text{caps1}}} \times 100\%, \quad (4)$$

where η_{CAPS} is the extraction efficiency of capsaicinoids, w_{caps1} is the content of capsaicinoids in raw material, and w_{caps2} is the content of capsaicinoids in residue material after extraction. Content of capsaicinoids is given as μg capsaicinoids per g of material on a dry basis. The efficiency of colour extraction was calculated from the equation

$$\eta_{\text{colour}} = \frac{\text{ASTA}_1 - \text{ASTA}_2}{\text{ASTA}_1} \times 100\%, \quad (5)$$

where η_{colour} is the extraction efficiency of colour components, and ASTA_1 and ASTA_2 are the colour intensity values of raw material and residue material after extraction, respectively.

2.2.5. Mathematical model

The mass transfer coefficients were calculated for the region of constant extraction rate. During the constant rate period, the steady state mass transfer prevails. Mass transfer coefficients were calculated for each extraction curve using a model of constant mass transfer rate and taking into account the porosity of material. The model assumes that mainly the convection across the phase boundary between solid and fluid influences the rate of the extraction process.

A similar approach was taken by Brunner (1984), who analysed extraction of an oil from solid material as a steady state mass transfer process. The quantity of extract (m) was evaluated as the product of mass transfer coefficient β_a, specific area (A_s), total bed volume (V_t) and a mean concentration difference of extract between solid and fluid (Δc_m):

$$m = \beta_a \cdot A_s \cdot V_t \cdot \Delta c_m, \quad (6)$$

$$\Delta c_m = \frac{\Delta c_{\text{in}} - \Delta c_{\text{out}}}{\ln \frac{\Delta c_{\text{in}}}{\Delta c_{\text{out}}}}, \quad (7)$$

$$A_s = \frac{6(1-\psi)}{d}, \quad (8)$$

$$\psi = 1 - \frac{\rho_b}{\rho_s}, \quad (9)$$

where Δc_{in} and Δc_{out} are concentration differences of chilli pepper extract at the mass transfer interface and the bulk of the gas at inlet and outlet of the bed, respectively; d is the particle diameter, ψ is the void bed fraction and ρ_b and ρ_s are bulk and solid densities of material, respectively.

3. Results and discussion

Chilli pepper (variety Byedige), with capsaicinoid content of 0.21%, ASTA value of 60.7, was extracted with supercritical CO_2 in a semi-continuous mode. The results of the present work indicate that chilli pepper extract, with a medium pungency and colour level, was obtained. Physical properties, content of each capsaicinoid and colour intensity value of raw material chilli pepper (variety Byedige) are given in Table 1. Values of operating temperature, pressure, and flow rate of CO_2, as well as for extraction time and total yields for the semi-continuous high-pressure extraction of chilli pepper, are shown in Table 2. The extraction times varied due to the different operating pressures and temperatures required to reach a total yield of extraction, which is influenced by the solvent density. Generally, the solvent power increases with increasing density. The density of CO_2 was calculated using an empirical equation proposed by E. Bender (Sievers, 1984). Flow rate of CO_2, in all experiments, was maintained at a relatively low value of approx. 0.23 kg CO_2/h, and it was considered that the initial extraction process was in equilibrium and that the constant extraction rate was controlled by solubility limitations. An exception was observed at 40 °C, 300 and 400 bar, where the flow rate was higher (0.43–0.49 kg CO_2/h), probably due to the high density of CO_2.

Extraction curves at constant pressure and temperature, represented as extraction yield vs. kg of CO_2 per kg of raw material are shown in Figs. 1(a)–(c). The observed steps on extraction curves are explained by longer interruptions for sampling between two extraction cycles. Constant extraction rate generally increased with increasing pressure from 100 to 300 bar at all temperatures. Further increase of pressure to 400 bar had no influence on the constant extraction rate. The amount of CO_2 per kg of raw material required to reach a total

Table 1
Characteristics of raw material chilli pepper variety Byedige

Property	Value
Median particle size	540×10^{-6} m
Average particle diameter	360×10^{-6} m
Moisture content	4.0% (w/w)
Solid density	1220 kg m^{-3}
Apparent density	504 kg m^{-3}
ASTA	60.7
Capsaicinoids: NDC	153.0 μg g^{-1}
C	1004 μg g^{-1}
DC	955 μg g^{-1}
Total capsaicinoids	2111 μg g^{-1}

Table 2
Extraction conditions and calculated mass transfer coefficients

T (°C)	P (bar)	ρ (kg m^{-3})	Q_v (kg CO$_2$ h^{-1})	τ (h)	η (%)	$\beta_a \times 10^7$ (ms^{-1})
40	100	627	0.22	19.7	8.05	10.8
40	200	841	0.23	8.5	10.8	3.81
40	300	911	0.43	9.3	10.3	2.17
40	400	957	0.49	6.0	10.6	–
60	100	290	0.23	5.5	0.10	–
60	200	724	0.23	7.1	11.3	4.50
60	300	830	0.24	7.0	11.7	3.14
60	400	891	0.25	5.4	11.8	1.60
80	200	595	0.22	10.7	9.78	7.77
80	300	746	0.24	7.0	12.6	4.38
80	400	824	0.24	5.6	12.8	4.34

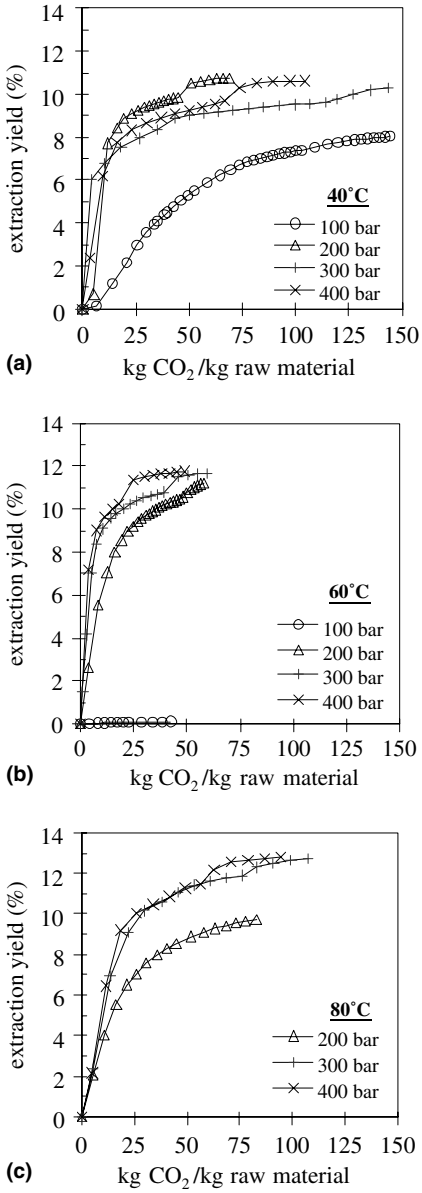

Fig. 1. Kinetics of semi-continuous extraction of chilli pepper Byedige with CO_2: (a) 40 °C, (b) 60 °C, and (c) 80 °C.

extraction yield, where a horizontal line represents the extraction curve, depends on the operating pressure and temperature. Since the flow rate of solvent was kept at constant low value during all extraction experiments (approx. 0.23 kg CO_2/h), it is clear that the operating pressure and temperature directly influence the extraction time, which varied from 5.4 to 19.7 hours. The shortest extraction times, of 5.4 and 5.6 h, were reached at 400 bar, 60 and 80 °C, respectively, while longest extraction time was 19.7 h at 100 bar and 40 °C. The total yield of extraction was determined to be highest at 400 bar and 80 °C at 12.8%, and lowest at 100 bar and 60 °C at 0.10% (Fig. 2). This is due to the low solvent power of CO_2 caused by its low density.

It was assumed that the linear sections of extraction curves (tangent of the straight line) represented the equilibrium solubility of chilli pepper extract in CO_2 expressed as g of extract per kg of CO_2. Fig. 3 shows the relationship between the extraction pressure and equilibrium solubility of chilli pepper extract in CO_2, where it can be observed that equilibrium solubility increased exponentially up to 20 g extract/kg CO_2 with increasing pressure and decreased with increasing temperature. These results are well in accordance with equilibrium

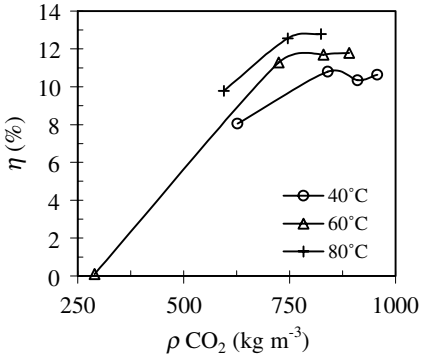

Fig. 2. Total yield of semi-continuous extraction of chilli pepper Byedige with CO_2 vs. solvent density.

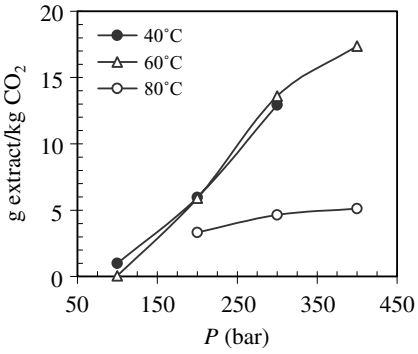

Fig. 3. Equilibrium solubility of chilli pepper extract in CO_2 vs. pressure.

solubility data of the system pungent spice paprika extracts-CO_2 obtained by Daood et al. (2002).

The effect of solvent density on the extraction efficiency of capsaicinoids and colour components is represented in Figs. 4(a) and (b). The capsaicinoid contents and ASTA values of the residues are shown in Table 3. With increasing solvent density, the extraction efficiency of capsaicinoids increased and reached a constant value of approximately 95%. The least amount of capsaicinoids was extracted at 100 bar and 60 °C (extraction efficiency of 9.5%) when the yield of extraction was also the lowest, all due to the low density of CO_2 and the low solubility of compounds of interest. Almost 96% of the

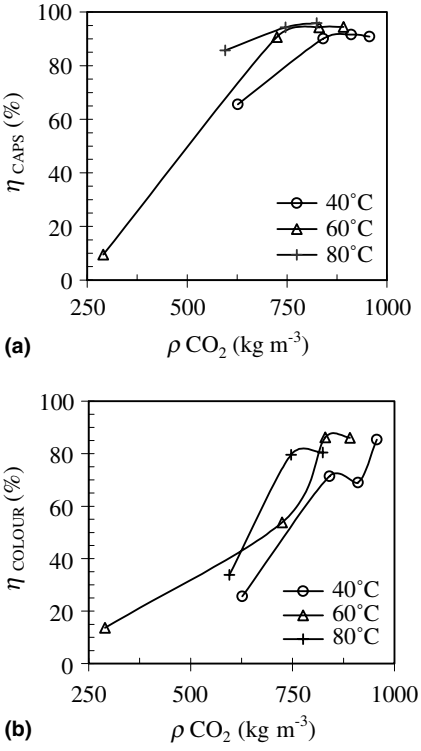

Fig. 4. Extraction efficiency vs. solvent density: (a) capsaicinoids and (b) colour components.

Table 3
Capsaicinoid content and ASTA value in chilli pepper residue materials

T (°C)	P (bar)	Capsaicinoids in residue (μg g^{-1})				ASTA of residue
		NDC	C	DC	Total	
40	100	65.3	348	313	726	45.1
40	200	18.8	109	81.2	209	17.4
40	300	14.2	92.3	70.7	177	18.8
40	400	18.9	93.0	80.9	193	8.9
60	100	144.1	924	844	1911	52.4
60	200	16.2	101	78.6	196	28.1
60	300	14.0	60.9	45.5	120	8.4
60	400	14.7	60.5	42.1	117	8.5
80	200	30.2	152	121	303	40.2
80	300	12.1	63.1	46.2	121	12.4
80	400	9.3	43.8	33.2	86.3	11.9

capsaicinoids were extracted at 400 bar and 80 °C, which was the highest extraction efficiency achieved in our study with a single step extraction. An increasing density of CO_2 caused enhanced capsaicinoid yield, whereas values above 720 kg m^{-3} did not lead to major changes. This confirms results described by Peusch et al. (1997). A similar trend was observed regarding the enhanced colour extraction yield; the amount of colour components in the extract increased with increasing CO_2 density. The colour fraction in the residue steeply decreased until a solvent density of 750 kg m^{-3} was reached, after which the colour extraction efficiency remained in the range 80–85%. The maximum colour extraction efficiency achieved was 86.2% at 60 °C and 300 bar. The CU values of obtained extracts, as a function of operating conditions, are shown in Fig. 5. CU value of chilli pepper extract increased exponentially with increasing solvent density. The highest CU value of chilli pepper extract obtained was 15,000 CU at 40 and 60°C and 400 bar.

Mass transfer coefficients calculated for the region of constant extraction rate (Eq. (6)), are given in Table 2 and are presented in Fig. 6. The void bed fraction was

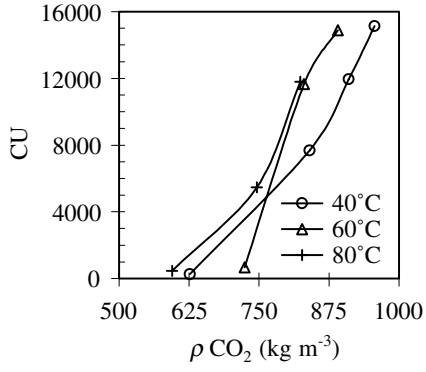

Fig. 5. CU value of chilli pepper extracts vs. solvent density.

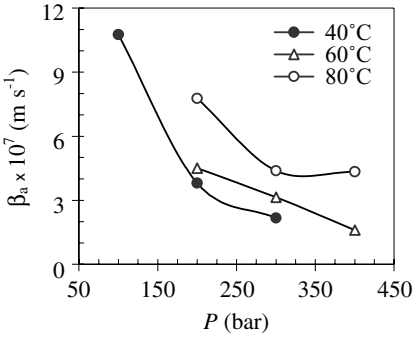

Fig. 6. Mass transfer coefficient vs. pressure.

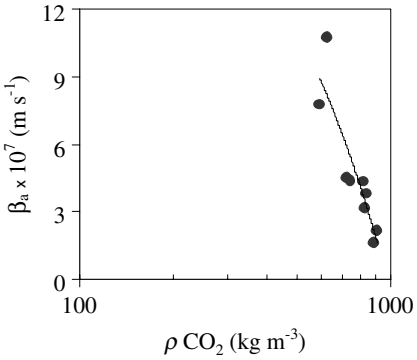

Fig. 7. Mass transfer coefficient vs. solvent density.

calculated from solid and bulk density (Eq. (9)) and equals 0.587. Mass transfer coefficient showed a decreasing trend with increasing pressure at constant temperature. It, however, increased with increasing temperature at constant pressure. The values of mass transfer coefficients are in the range 2×10^{-7} to 11×10^{-7} m s^{-1}. However, a linear trend was observed for the dependency of mass transfer coefficient on solvent density, as shown in Fig. 7. The average absolute relative deviation (AARD) between experimental and calculated mass transfer coefficients, using the equation for a straight line, is on average 21.2%. Therefore, a rough estimation of mass transfer coefficient can be made on the basis of solvent density, using Eq. (10), in the ranges 40–80 °C and 100–400 bar. The following linear equation is very helpful in performing preliminary scale-up calculations, necessary for designing a CO_2 extraction process for the investigated chilli pepper variety:

$$\beta_a \cdot 10^{-7}(\text{m s}^{-1}) = -0.0231 \cdot \rho_{CO_2}(\text{kg m}^{-3}) + 22.657. \quad (10)$$

A separation between colour components and capsaicinoids can be achieved successfully at a CO_2 density of approximately 625 kg m^{-3} (100 bar, 40 °C). Under these operating conditions, the extraction efficiency of capsaicinoids was 66% at 40 °C and 86% at 80 °C, and extraction efficiencies of colour components were 26% at 40 °C and 34% at 80 °C.

The highest CU value of obtained chilli pepper extract was 15 000 CU. Chilli pepper extract producers tend to decrease the ASTA value of residue to almost zero and hence extract all the colour components present in chilli material by obtaining high CU values of extracts. The quality of raw material is of primary choice in obtaining satisfactory results for the extraction of colour and pungency components. In our study, the raw material was of low to medium quality chilli pepper in terms of colour intensity.

The obtained extracts in this work, which varied in colour from orange, light red to intensive dark red, have several advantages over chilli pepper extracts conventionally obtained with organic solvents (hexane or acetone). Chilli pepper extracts obtained with supercritical CO_2 had no residues of toxic solvents. Additionally, an extract with tailor-made properties, regarding the content of capsaicinoids and colour intensity value, was obtained by varying the extraction parameters.

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