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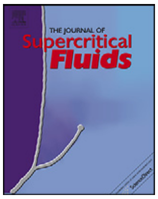

Supercritical fluid extraction of vetiver roots: A study of SFE kinetics

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ABSTRACT

The volatile oils from the *Vetiveria zizanioides* oil are particularly appreciated in perfume and cosmetic products but may also be used in the food industry as aroma and flavor agent. The objective of this work was to study the improvement over the conventional process on the quantity and quality of vetiver extracts recovered by supercritical technology (SFE). The pressure effect (100–300 bar) at 40 °C, and the influence of amount of ethanol used as cosolvent (0, 5 and 10%, v/v) were studied. Supercritical extraction process was compared to the hydrodistillation, based on vetiver extract quantity and quality; SFE extracts and presented khusimol contents of 14–29% over hydrodistillation and for SFE, the global yields and kinetic parameters obtained using 10% (v/v) of ethanol were statistically different from extraction using 0 and 5% of ethanol. The TLC and GC showed similar chemical profiles for SFE and HD, but were aware some compounds that were observed by TLC just during the t_{CER} region. Mathematical modeling was performed for vetiver kinetics obtained by SFE + cosolvent and Sovová model showed the best adjusts for all curves.

1. Introduction

Volatile oil recovered from natural products has a great interest to the cosmetic, pharmaceutical and food industries, being used by its sensorial properties mainly to the development of new flavors, aromas and perfumes. One important volatile oil used in cosmetic area is obtained from vetiver roots (*Vetiveria zizanioides* (L.) Nash ex Small), which is a species widely spread in tropical regions of Asia, Africa, Oceania, and Central and South America [1,2]. This oil is highly appreciated by the perfume industry, where it is used as a fixative in several fragrances with an odor contributor in bases, such as rose and chypre. The color of vetiver extracts goes from amber to dark brown, and its odor has sweet, earthy, and woody notes. Additionally, vetiver can be applied in food products as an aromatizing agent of canned asparagus and peas, and as flavor agent in some beverages [3–7].Composition profile of *Vetiveria zizanioides* (L.) oils obtained from roots cultivated in Italy [8] and USA [9] were studied, and the main identified compounds were khusimol, (*E*)-isovalencenol, α- and β-vetivone in both cases. While in the Italian extracts the presence of zizanoic acid and junenol was noticed, the American ones presented vetiselinenol; these differences in composition may be attributed to the edaphoclimatic conditions. Some regional producers use the khusimol content as a quality mark of the volatile oil, and then researchers studied the valorization of vetiver production in order to improve the extract quality in terms of composition. In the essential oils rich in zizanoic acid, the quality of the product can be improved by separation of the acid and subsequent conversion to khusimol [6]. Some vetiver varieties are appreciated like Haiti and Bourbon (Chomchalow, 2000, as cited by Martinez, 2004 [6]). Although, in Brazil the production is still small, the extraction process can be optimized in order to fractionate the extract and to obtain a fraction with high quality, monitored by the khusimol content [6], and in this way, increasing the valorization of Brazilian vetiver oil.

Some biological activities are also attributed to the vetiver roots extracts such as antifungal [9], antioxidant [10], and anti-inflammatory [11]. The vetiver oil can also be used for nursing care residents with dementia-related behaviors, in order to increase mental alertness and cognitive function [12]. These properties may open new possibilities to the utilization of vetiver extracts in the pharmaceutical industry.

Supercritical fluid extraction can be used by Martinez et al. [6] to extract volatile oil from vetiver roots. These fluids present an alter-

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native to the conventional methods of steam distillation and solvent extraction. The supercritical carbon dioxide is a hydrophobic solvent and its polarity can be changed by using some polar cosolvents to improve the extraction of more hydrophilic compounds such as the oxygenated terpenes and sesquiterpenes. Several authors used ethanol as cosolvent for supercritical carbon dioxide. Among them, Chang et al. [13] used water and ethanol as cosolvents for the extraction of green tea volatile oil; Wang et al. [14] studied SFE of ginseng roots and proved that the use of cosolvent (6% molar, of ethanol) increased the yield; Badalyan [15] studied the extraction of ginger oleoresin using ethanol as cosolvent; under subcritical conditions, an addition of 2% of ethanol increased the yield to approximately 10%. Zancan et al. [16] have determined that the addition of ethanol or isopropyl alcohol significantly affected the content of gingerols and shogaols in ginger SFE extracts. Braga et al. [17] have shown that the best cosolvent for SFE of turmeric (*Curcuma longa* L.) was a mixture of ethanol and isopropyl alcohol. According to these authors, the cosolvent increases the extract yield of some interesting species used in food and pharmaceutical industries and, in some cases, SFE may be competitive with conventional extractions.

During the extraction, three regions with different mass transfer mechanism can be observed: the constant extraction rate (CER) period, when the external particles surfaces of particles are completely covered with oil; the falling extraction rate (FER) period, when patches without oil appear on particle surfaces; and the diffusional period (DP), when there is no free oil at the surface of the particles. In general, during the first two periods more than 70% of the extractable substances are obtained, with the CER period accounting for approximately 50% of it [18–20]. Therefore, the process can be modeled by considering the convective process. The mass transfer coefficient can be represented by mass transfer in the SCF phase [21]. The kinetic parameters observed in the CER period are: extraction rate (M_{CER}), extraction time (t_{CER}), extraction yield (R_{CER}) and the concentration of the extract in the supercritical phase at the bed outlet (Y_{CER}), calculated as the ratio between M_{CER} and the mass solvent flow rate (Q_{CO_2}).

The overall extraction curves (OEC) prediction capacity, due to the process parameters has a fundamental importance not only for the conception point of view but also for the industrial unit optimization. Moreover, mathematical modeling is probably the main tool to predict parameters involved in the process. The determination of t_{CER} is also fundamentally important in the estimation of the manufacturing process cost. For instance, Rosa and Meireles [22] have demonstrated that the manufacturing cost increases according to the extraction time, larger than t_{CER}. Mathematical models allow generalize experimental results and are useful in the development of scaling-up procedures from laboratory to pilot and industrial scale units. However, because of particularities of each vegetal matrix, different mechanisms of mass transfer and thermodynamic balance are considered in different models. In general, two different approaches have been proposed for the mathematical modeling of the SFE of volatile oils: (i) empirical model such as the Langmuir-like isotherm [23] and (ii) models based on differential mass balances. Among these models, the most studied are the Crank [24], Tan and Liou [25], Goto et al. [26] and Sovová [27] models.

Therefore, the objective of this work was to improve the vetiver roots extraction process using supercritical technology for its use in food and cosmetic industries. The influence of the extraction pressure and the percentage of cosolvent on the extraction kinetic, extract composition and yield were studied, and compared with the hydrodistillation process. Furthermore, modeling was performed using common models to predict kinetic extraction using low cosolvent contents.

2. Materials and methods

2.1. Raw material

Vetiver (*Vetiveria zizanioides* L.) roots were obtained from a local producer in São Paulo state, Southeastern of Brazil. Vetiver dried roots were air-conditioned for 48 h and milled in a knife mill (Tecnal TE-631, Piracicaba, Brazil). The particles were classified according to their particle size in a vibratory sieve system (Series Tyler, W.S. Tyler, Salisbury, NC) and stored in a domestic freezer (Metalfrio, Double-action, São Paulo, Brazil) at approximately −10 °C. Particles with mean diameter smaller than 3.0×10^{-4} m were selected for the extraction procedures.

The raw material moisture content was determined using a microwave method (CEM, Model Smart 5, Matthews, NC) at 100% of potency, using 0.025 mg/s at maximum temperature and time of 70 °C and 10 min, respectively, in the Laboratório de Aplicação de Microondas ao Processamento de Alimentos, DEA/FEA-UNICAMP. This procedure was ninefold to obtain a method precision.

The fixed-bed apparent density (d_a) was calculated using the mass of solid used to fill the extraction cell, and its volume. The real or true density of the vetiver particles (d_r) was determined by helium picnometry (Micromeritics, model Multivolume Picnometer 1305, Norcross, Georgia) at the Central Analítica de Análises Químicas, IQ-UNICAMP. The total porosity was determined using the particle true density and the bed apparent density, and the mean particle diameter was calculated according to A.S.A.E. S319.2 method [28].

2.2. Extractions methods

The hydrodistillation (HD) was accomplished in a Schilcher-like apparatus [29]. The total extraction time was 3 h. The volatile oil was collected and storage in a fridge (Brastemp, model 7501, São Paulo, Brazil) at −5 °C for further analysis.

The extract global yield obtained by SFE was determined in a Speed SFE system (Applied Separations, model 7071, Allentown, PA) with a 5-mL extraction column (Thar Designs, CL 1165, Pittsburgh, PA). The raw material packed bed was prepared by manual packing of the grounded particles inside of the extraction column and a glass wool plug was placed at both sides of it in order to avoid the drag of small particles by the solvent. A static period of 5 min was used to allow the contact between the particles and the supercritical solvent and after that, a CO_2 (Gama Gases Especiais, 99.0%, Campinas, Brazil) mass flow rate of $(9–12) \times 10^{-5}$ kg/s was allowed during 5 h. The exit tubing line was washed with ethyl acetate to recover the extract deposited on it. The solvent was separated from the extract using a rotovap system (Laborota model 4001, Viertrieb, Germany) with vacuum control (Heidolph Instruments GMBH, Viertried, Germany). The effect of extraction pressure (100–300 bar) on global yield was studied at 40 °C, which was selected based on the results of Martinez et al. [6].

The kinetic assays with and without cosolvent were carried out in another extraction system. The unit has an extractor cell of approximately 2.35×10^{-6} m^3 (length of 37.5×10^{-2} m, internal diameter of 2.83×10^{-2} m) and maximum allowable pressure of 400 bar, described by Braga et al. [17]. The CO_2 (99.5%, Gama Gases Especiais, Campinas, Brazil) was introduced into the system using a programmable HPLC-type pump (Thermo Separation Products, series 3200, Waltham, MA) and the cosolvent (ethanol 99.5% at 0, 5 or 10%, v/v at environmental conditions, Ecibra, Brazil) was introduced using a slave HPLC pump (Thermo Separation Products, series 3500, Waltham, MA). The bed was formed with 20×10^{-3} kg of vetiver particles packed inside a nylon basket (mesh 80). Thus, the bed apparent density was kept constant at 353.5 kg/m^3. To fill