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Extraction of citronella grass solutes with supercritical CO_2, compressed propane and ethanol as cosolvent: Kinetics modeling and total phenolic assessment

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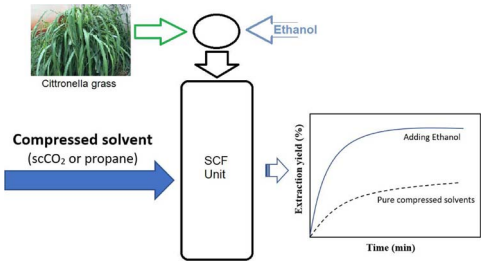
GRAPHICAL ABSTRACT



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ABSTRACT

This study reports the experimental and kinetic modeling of citronella grass extraction by $scCO_2$, compressed propane, $scCO_2$ + ethanol, compressed propane + ethanol. Extraction yields were improved by adding ethanol as cosolvent for both compressed solvents. Kinetics and the extraction yield at equilibrium (Y_e) were in general investigated at the pressure range from 2 to 20 MPa at 20 °C, 40 °C and 60 °C. At temperature of 40 °C and similar pressures, propane was advantageous over CO_2 in terms of the both kinetic paremeters k (increased from 4.1 ± 0.5 s^{-1} to 7.3 ± 0.7 s^{-1}) and Y_e (increased from 2.35 ± 0.08% to 3.76 ± 0.09%). Moreover, using compressed propane + ethanol both extraction parameters (k = 16 ± 4 s^{-1} and Y_e = 6.3 ± 0%) were further improved. The total phenolic content was similar for all extracts evaluated at different extraction conditions and methods, except for the extract obtained by hydrodistillation, where higher value was obtained (1.4 ± 0.4 mg GAE g^{-1}) when compared to compressed solvents.

1. Introduction

Citronella (*Cymbopogon winteranius* Jowitt ex Bor) is an aromatic plant native to the Southeast Asia whose popularity has increased after its repellency against to the *Aedes aegypti* mosquito was identified [1]. Although citronella is mainly known for this property, since the FDA, FEMA [2], and independent researchers [3] have concluded that the citronella oil and its major component geraniol are safe, the citronella oil has been suggested for different applications. For instance, in the composition of bioplastic films in the food industry due its hydrophobic, antioxidant and bioactive properties [4–8].

Among several variables that may have positive influences on the extraction yield of solutes and on the quality of the extracts obtained from citronella, and other plants in general (e.g., genetic and agronomic factors), the innovations in the techniques of solid-liquid extraction have been particularly explored in the literature [9–13]. In the

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Nomenclature

a_t	Total external area of the particles
a_m	Effective mass transfer area
α	Confidence level
β_c	Mass ratio between the cosolvent and the raw leaves of citronella
d	Diameter of citronella leaves
D	Diffusivity of solutes
D_e	Effective diffusion coefficient in the solid
ε	Void fraction of the bed
FDA	US food and drug administration
FEMA	Flavor and extract manufacturers' association of the US
φ	Internal fractional void space
γ	Ratio between the volume of solvent and mass of raw solid ($m^3\,kg^{-1}$)
γ_m	Mass ratio between the and the raw solid ($kg\,kg^{-1}$)
k	Rate constant of extraction (s^{-1})
k_m	Transport coefficient between the bulk stream and particle surface
μ	Viscosity of solvent (Pa s)
P	Pressure of extraction (bar)
ρ	Density of solvent ($kg\,m^{-3}$)
R^2	Coefficient of determination
t	Extraction time (s)
T	Temperature of extraction (°C)
$U_{k,95}$	Uncertainty in the rate constant of extraction for a confidence level of 95%
$U_{Y,95}$	Uncertainty in the yield of solutes at equilibrium for a confidence level of 95%
v	Interstitial solvent velocity in the packed bed
Y	Yield of extraction (%)
Y_e	Yield of extraction at equilibrium (%)

particular case of citronella oil extraction, the reason for testing novel methods of extraction is that the conventional ones, such as hydrodistillation and Soxhlet, have detrimental effects on the quality of the extract, usually attributed to the high temperatures and long extraction times required by these methods [14–16].

As an alternative to the traditional methods, the extraction with supercritical carbon dioxide has been emphasized [17,18], since the operation is commonly performed at low temperature, and one of the most important advantages of using this technique is to prevent loss of thermolabile compounds by evaporation or thermal degradation. However, the low toxicity, non-carcinogenic nature, selectivity, inertness, low critical pressure and temperature are additional important properties of supercritical CO_2 as solvent [19,20]. Similar advantages are obtained by using compressed propane, which is the main reason for many investigations that have considered its use as solvent with analogous purposes [16,21,22]. At the current circumstances, both the solvents are positively recommended because of their non-polar nature that make them especially suitable for the extraction of lipophilic compounds, such as the essential oil from citronella [20]. To increase the extraction yield, combinations of polar solvents, usually referred as modifiers or cosolvents, with supercritical CO_2 or compressed propane have been suggested [23–25].

To summarize, in view of the growing importance of citronella oil and its chemical compounds in general, extraction of solutes from citronella leaves was investigated mainly by using supercritical CO_2 and compressed propane with and without ethanol addition as a polar cosolvent. In particular, it was examined the influence of pressure and temperature on the kinetics of citronella solutes recovery and on the extraction yield at equilibrium. Total phenolic content in the extracts obtained at differnt conditions (i.e., supercritical CO_2 with and without ethanol at 40 °C and ≠ P; compressed propane with and without ethanol at ≠ T and P), and extracts obtained by Soxhlet extraction with a non-polar (hexane at 68 °C) and a polar solvent (ethanol at 78 °C), and by hydrodistillation was also examined.

2. Materials and methods

2.1. Materials

All samples of citronella leaves used in this study were obtained in a residential area in the southern area of the Brazilian city of Nova Londrina (State of Paraná, Brazil). They were washed with distilled water, dried with paper towels, and cut manually in small pieces of almost the same dimensions. Thus, they were placed in an air-circulating oven at 50 °C for drying up to constant weight (i.e., 24–48 h) (Nova Etica, Brazil). The treated leaves were further reduced in size with a knife-mill and mechanically separated (Bertel, Brazil) using a Tyler series sieves with 8, 12, 20, 24, 32 and 48 meshes. Except for the material retained on the top and on the bottom, the leaves were mixed and packed in low density polyethylene bags, sealed in a vacuum sealer (Ianuen Maschinen AG, model CH9100, Herisau, Switzerland) and stored in a freezer at −18 °C ± 2 °C to be used in the extraction experiments.

Citronella leaves used in the extraction experiments shaped like discs with an average diameter of 6.5×10^{-4} m obtained from the data of size analysis following the methodology suggested by Gomide [26], and 2.2×10^{-4} m thick measured using a digital pachymeter (Mitutoyo 500-144B, São Paulo, Brazil). The real density of the particles used in this study was 1240 ± 10 kg, measured using a helium pycnometer (Quantachrome Ultrapyc 1200e), at the Analytical Central-Institute of Chemistry/Unicamp, Campinas, Brazil, and the apparent the density 273 ± 5 kg, mesured in the extraction vessel, given a bed porosity of 0.78.

2.2. Experiments of extraction in the packed bed

The extraction experiments using supercritical CO_2 ($scCO_2$) (99.5% purity in the liquid phase, White Martins SA, Ponta Grossa, Brazil), compressed propane (CP) (99.5% purity in the liquid phase, White Martins SA, Ponta Grossa, Brazil), supercritical CO_2 + ethanol ($scCO_2$ + EtOH), and compressed propane + ethanol (CP + EtOH) were performed in a bench-scale extraction unit. Ethanol used was

Table 1
Operating conditions, and tuned parameters of Eq. (1) for the extraction with supercritical CO_2 ($scCO_2$). $\gamma = 15 \times 10^{-3} \pm 1 \times 10^{-3}\,m^3$ of used solvent per kg of raw solid.

Run	P (MPa)	T (°C)	ρ ($kg\,m^{-3}$)	μ × 10^5 (Pa s)	γ_m ($kg\,kg^{-1}$)	$k \pm U_{k,95} \times 10^4$ (s^{-1})	$Y_e \pm U_{Y,95}$ (%)
1	9	40	485.50	3.48	7.6	4.1 ± 0.5[a]	2.35 ± 0.08[a]
2	12	40	717.76	5.85	10.0	4.6 ± 0.7[a,b]	3.0 ± 0.1[b]
3	20	40	839.81	7.83	12.0	5.1 ± 0.8[b]	3.5 ± 0.1[c]

k or Y_e followed by the same letters do not differ statistically by the t-test for an α = 0.05.