

Cross-current liquid-liquid extraction of yerba mate (*Ilex Paraguariensis*) using near-critical CO₂ + hydrated ethanol

Luis I. Granone^a, Francisco A. Sánchez^{b,c}, Pablo E. Hegel^{b,c,*}, Selva Pereda^{b,c,d}

^aDepartamento de Química y Bioquímica, Facultad de Ciencias Exactas y Naturales, Instituto de Investigaciones Físicas de Mar del Plata, IFIMAR (CONICET-UNMdP), Deán Funes 3350, 7600 Mar del Plata, Argentina.

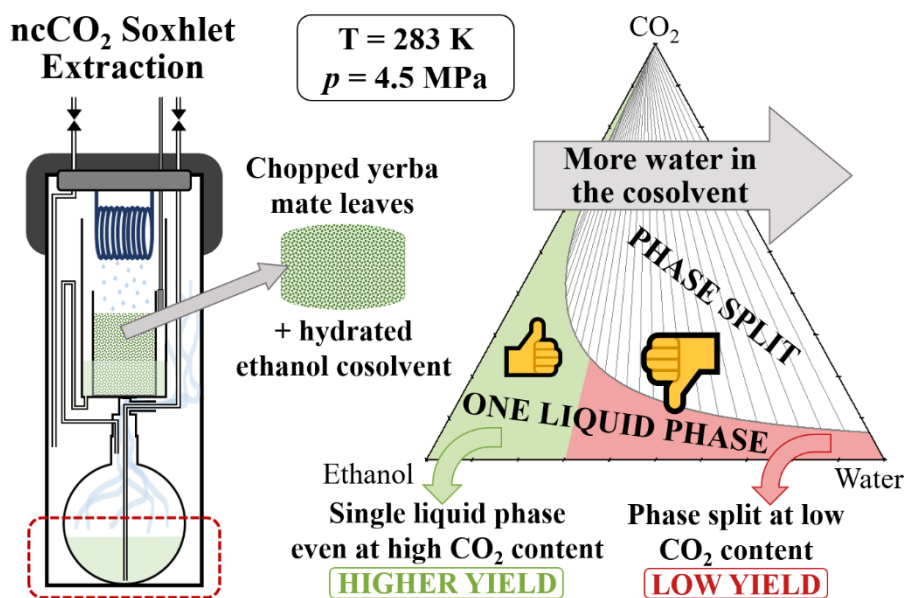
^bPlanta Piloto de Ingeniería Química, PLAPIQUI (CONICET-UNS), Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina.

^cDepartamento de Ingeniería Química, Universidad Nacional del Sur (UNS), Avenida Alem 1253, 8000 Bahía Blanca, Argentina.

^dThermodynamics Research Unit, School of Engineering, University of KwaZulu Natal, Howard College Campus, King George V Avenue, 4041 Durban, South Africa.

*corresponding author email address: phegel@plapiqui.edu.ar

GRAPHICAL ABSTRACT



ABSTRACT

Yerba mate (*Ilex paraguariensis*) leaves, recognized for their numerous health benefits, are extensively used in Argentina, Brazil, Paraguay, and Uruguay for the preparation of traditional infusions. Nevertheless, in line with coffee or tea, there are increasing concerns regarding the elevated content of caffeine found in yerba mate beverages and its potential adverse effects on human health [1]. Various well-established industrial decaffeination methods are available, including organic solvent extraction, water extraction, and supercritical fluid extraction using carbon dioxide (scCO₂, $T > 304.1\text{ K}$, $p > 73.7\text{ MPa}$) [2]. Solvent extraction typically employs dichloromethane and ethyl acetate, which are solvents subjected to strict emission and health protection laws. Water extraction is more environmentally friendly, but it exhibits a limited



selectivity towards other components, resulting in the co-extraction of aroma precursor compounds alongside caffeine. In contrast, CO₂ is a readily available, non-toxic, and non-flammable solvent and has a superior selectivity towards caffeine [3,4]. Therefore, extraction using scCO₂ overcomes the limitations associated with both solvent and water extraction methods. However, it does require the installation and maintenance of costly high-pressure equipment [2].

A more affordable alternative to scCO₂ is liquid CO₂ under near-critical conditions (ncCO₂). This extraction method offers most of the benefits and advantages of scCO₂ extraction but requires lower operating temperatures (below 304.1 K) and, more importantly, lower operating pressures (below 73.7 MPa). As a result, the equipment, maintenance, and operational costs are significantly reduced [2].

In this work, we studied the decaffeination of yerba mate using a ncCO₂ Soxhlet extraction method at 283 K and 4.5 MPa. Chopped yerba mate leaves are processed in a dried form or impregnated with hydrated ethanol as a cosolvent. A maximum overall extraction yield of 2.68 wt. % is achieved when the water content in the cosolvent mixture is set at 15.0 wt. %. This resulted in a 32.8 wt. % reduction in the caffeine content of yerba mate leaves impregnated with a cosolvent-to-feed ratio of 1.0 g g⁻¹. Interestingly, regardless of the percentage of water in the cosolvent mixture, less than 1.6 wt. % of the total content of two of the main antioxidant compounds present in yerba mate leaves, caffeic acid and chlorogenic acid, are coextracted in the process. The overall extraction yield remains close to the maximum when cosolvents with a water percentage between 4.4 and 22.5 wt. % are used. In contrast, overall extraction yields below 1.0 wt. % are obtained when cosolvents with water percentages exceeding 30 wt. % are used. In order to explain this observation, the thermodynamic phase equilibrium at 283 K and 4.5 MPa for a ternary CO₂-ethanol-water mixture is modeled using the group contribution plus association equation of state (GCA-EoS). The predictions of the model reveal that when the water percentage in the cosolvent is near that of maximal extraction yield, the CO₂-ethanol-water mixture forms a single liquid phase even at high CO₂ contents, which is expected to favor the extraction process. Under low extraction yield conditions, where the water percentage exceeds 30 wt. %, the GCA-EoS predicts a phase split into a water-rich and a CO₂-rich liquid phase at low CO₂ contents. In this context, it is expected for the CO₂-rich liquid phase to exhibit a rather low solvent power, and for the water-rich phase to act as a diffusion barrier, thus hindering the extraction.

The use of the ncCO₂ Soxhlet extraction method presented in this work serves as proof of principle for the ncCO₂ decaffeination of cosolvent-impregnated yerba mate leaves with negligible coextraction of antioxidant compounds. Although the high-pressure Soxhlet extraction is not suitable as a large-scale process, the information it provides holds substantial potential for the conceptual design of scalable semi-continuous systems.

- [1] Ramalakshmi, K. and Raghavan B., *Crit. Rev. Food Sci. Nutr.* **1999**, 39, 441-456.
- [2] Pietsch, A., in *The craft and science of coffee* **2017**, Academic Press, 225-243.
- [3] Saldaña, M. D. A. et al., *J. Agric. Food Chem.* **2002**, 50, 4820-4826.
- [4] Hegel, P. E. et al., *J. Supercrit. Fluids* **2021**, 172, 105200.

Keywords: near-critical CO₂ extraction, high-pressure Soxhlet, yerba mate, decaffeination.