

# ADSORPTION OF BURITI OIL (*Mauritia flexuosa*, Mart.) IN $\gamma$ -ALUMINA USING SUPERCRITICAL CO<sub>2</sub>

<sup>1</sup>Cunha, M.A.E.; <sup>2</sup>Machado, N. T\*.; <sup>2</sup>Araújo, M. E, <sup>3</sup>França, L.F.

<sup>1</sup> University of the State of Pará, Center for Natural Science and Technology.

Travessa Enéas Pinheiro 2626, Campus V, Belém-Pará-Brazil.

Phone: 55-091-32769511, Fax: 55-091-237617, CEP: 66095-100

<sup>2</sup> Laboratory of Separation Processes and Applied Process Thermodynamics, Faculty of Chemical Engineering-UFPA

<sup>3</sup> Laboratory of Separation Processes, Faculty of Food Engineering-UFPA, Belém-Pará-Brazil

[machado@ufpa.br](mailto:machado@ufpa.br), Fax: 0051-91-32017291

**Abstract:** In this work, in order to study systematically the enriching of fat-soluble substances by supercritical adsorption/desorption processes, adsorption of buriti oil (*Mauritia flexuosa*, Mart.) in columns packed with  $\gamma$ -alumina has been determined experimentally. The experiments were carried out in a laboratory scale high pressure extraction unit, adapted to be used as an adsorption cell, at 15, 20, and 25 MPa, 333 K, and solvent flow rate of  $Q_{CO_2} = 10.6$  L/min, using an assemble of packed columns of 22 cm<sup>3</sup> filled with 50 g of  $\gamma$ -alumina adsorbent, as well as by traditional methods reported in the literature to measure the adsorption of diluted liquid solutions within porous solids. The adsorbent was characterized by x-ray powder diffraction, particle and pore size distribution, particle porosity and specific area. A Freundlich type isotherm has been used to model the experimental data. The results show that adsorbent capacity increases with higher pressures, showing a maximum of 82.42 mg buriti oil/g at 25 MPa. In addition, experimental results show that equilibrium capacity of buriti oil in  $\gamma$ -alumina measured by both methods give similar results.

**Keywords:** Adsorption, supercritical carbon dioxide, vegetable oils, buriti.

## 1. Introduction

The oil of buriti (*Mauritia flexuosa*, Mart.), a native occurring palm in the Amazon region, obtained by mechanical pressing of pulp, contains between 20-30 % (wt.) of a yellow-orange oil with the highest content of carotenes (~ 3600 ppm) in vegetable oils reported in the literature (França *et al.*, 1999), a natural substance of special interest in the food and pharmaceutical industries.

Despite the development of several processes to recover and enrich carotenes from the palm oil reported in the literature including esterification, and transesterification of palm oil, followed by selective adsorption of the carotenes in packed columns and desorption by using organic solvents (Choo *et al.*, 1991), sterification of palm oil, followed by distillation under high vacuum (Ooi *et al.*, 1991), and adsorption of palm oil within alumina based adsorbents in stirred tanks, followed by supercritical desorption in packed columns using carbon dioxide as solvent (Raiol *et al.*, 2000), no data has been reported concerning the development of methods and or processes to recover and enrich carotenes from buriti oil (*Mauritia flexuosa*, Mart.).

Studies reported in the literature concerning the selective separations of substances adsorbed within porous adsorbents by supercritical adsorption/desorption processes, particularly fat-soluble substances presented in vegetable oils, are scarce. Among those, the

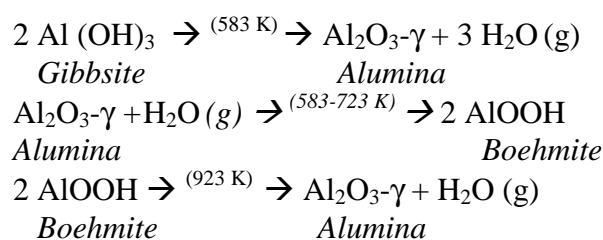
separation of  $\alpha$ -tocopherol acetate from a synthetic mixture of tocopherols using silica gel as adsorbent (Fleck, 2000), desorption of andiroba oil (*Carapa Guianensis*, Aubl.) compounds in packed beds of  $\gamma$ -alumina loaded with andiroba oil at different state conditions (Machado *et al.*, 2005), adsorption isotherms of oleic acid (Machado *et al.*, 2007) and  $\alpha$ -tocopherol acetate (Machado *et al.*, 2007) in packed columns using  $\gamma$ -alumina as adsorbents at different state conditions, fractionation of copaíba oil resin (*Copaifera officinalis*) by supercritical desorption in packed columns with  $\gamma$ -Alumina as adsorbent (Machado *et al.*, 2009). In addition, adsorption of chemical species or solutes of diluted liquid solutions in solids adsorbents at normal pressures may also be carried out in stirred tanks and or orbital shakers as described elsewhere (C. J. Radke, J. M. Prausnitz, 1972).

In this work, in order to develop a data basis to study systematically the performance of  $\gamma$ -alumina to selectively fractionate and enrich fat-soluble substances present in buriti oil, particularly carotenes and tocopherols, adsorption of buriti oil in  $\gamma$ -alumina using supercritical CO<sub>2</sub> has been investigated in a laboratory scale high pressure extraction unit, adapted to be used as an adsorption cell, at 15, 20, and 25 MPa, 333 K, and solvent flow rate of Q<sub>CO<sub>2</sub></sub> = 10.6 L/min, and the results compared with adsorption measurements of buriti oil diluted in n-hexane within porous  $\gamma$ -alumina carried out in orbital shakers at 0.1013 MPa and 333 K.

## 2. Materials and Methods

**2.1 Materials** - Aluminum hydroxide used as raw material for the adsorbent preparation was delivered by Alunorte S/A (Barcarena-Pará-Brazil). Carbon dioxide 99.90 % [vol/vol] pure was supplied by Linde Gases Ltda (Belém-Pará-Brasil). Buriti oil (*Mauritia flexuosa*, Mart.) was obtained by exhaustive supercritical carbon dioxide extraction of buriti pulp at 25 MPa and 333 K using a SFE unit described elsewhere (França *et al.*, 1999).

**2.2 Absorbent Preparation and Characterization** - Aluminum hydroxide Al<sub>2</sub>O<sub>3</sub> (*Gibbsite*), the precursor of  $\gamma$ -alumina, was washed with water at 373 K to remove the residual sodium hydroxide, dried in an oven with air circulation at 333 K for 24 hours (Fabbe, São Paulo, Brazil, Model 179), and stored in a desiccator. Thermal transformation of aluminum hydroxide have been carried out at 673 K, 773 K, 873 K and 923 K during 03 (three) hour in an electrical furnace (Químis, São Paulo, Brazil, Model: 5B) with automatic temperature control, to produce predominately alumina of  $\gamma$  type as shown in Figure 1, showing a mass loss of 35 % [wt.] at 673 K, 15 % [wt.] at 773 K, resulting a total mass loss of 50% [wt.], caused by the loss a hydroxyl (OH) group. No mass loss has been observed at 873 and 923 K. The X-ray diffraction depicted in Figure 1 has identified the following: formation of crystalline aluminum mono-hydroxide (*Boehmite*) and formation of transition  $\gamma$ -alumina. The chemical equations representing the thermal decomposition of Al<sub>2</sub>O<sub>3</sub> and formation of  $\gamma$ -alumina are shown bellow.



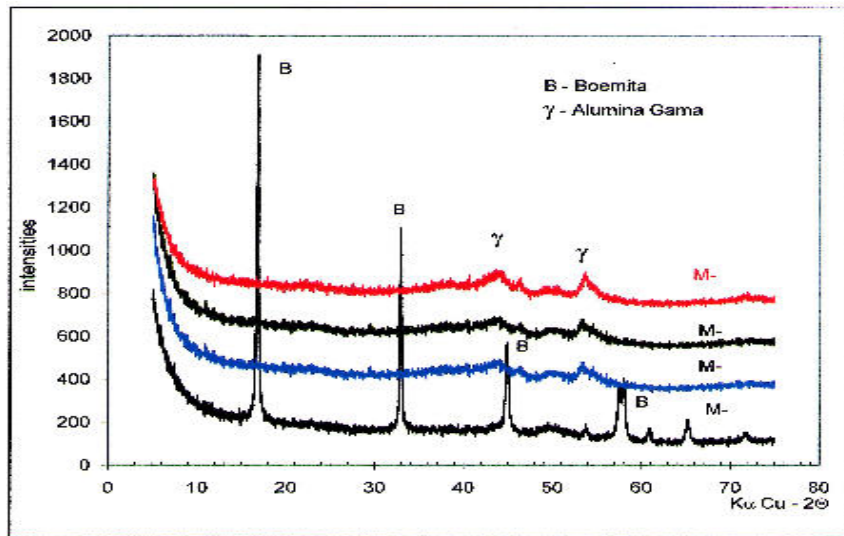


Figure 1: X-ray diffraction of boehmite and  $\gamma$ -alumina.

The adsorbent ( $\gamma$ -Alumina) was characterized by X-Ray Powder Diffraction, Scanning Electron Microscopy, Particle Size Distribution, Pore Size Distribution, Particle Porosity and Specific Area. The mineralogical identification of the adsorbents has been performed by X-ray powder diffraction using the powder method (Philips, Holland, Model PW 3710). The particle size distribution was carried out in and particle diameter analyzer (Malvern Instruments, USA, Model Mastersize S), and the results are shown in Figure 2. The specific area and pore size distributions of adsorbents were measured using the BET method (Monosorb Quantacrome, USA) as shown in Figure 3.

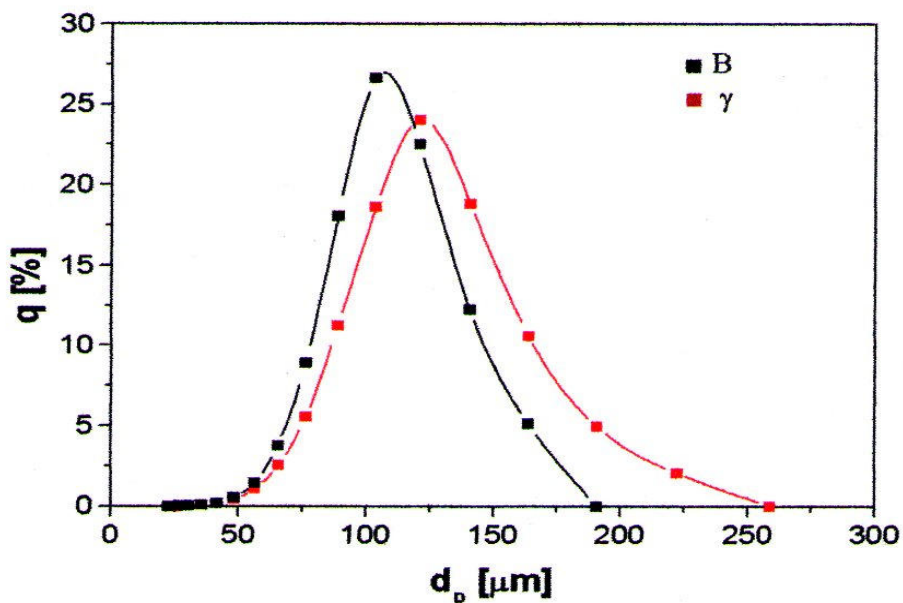


Figure 2: Particle size distributions of boehmite (B) and  $\gamma$ -alumina.

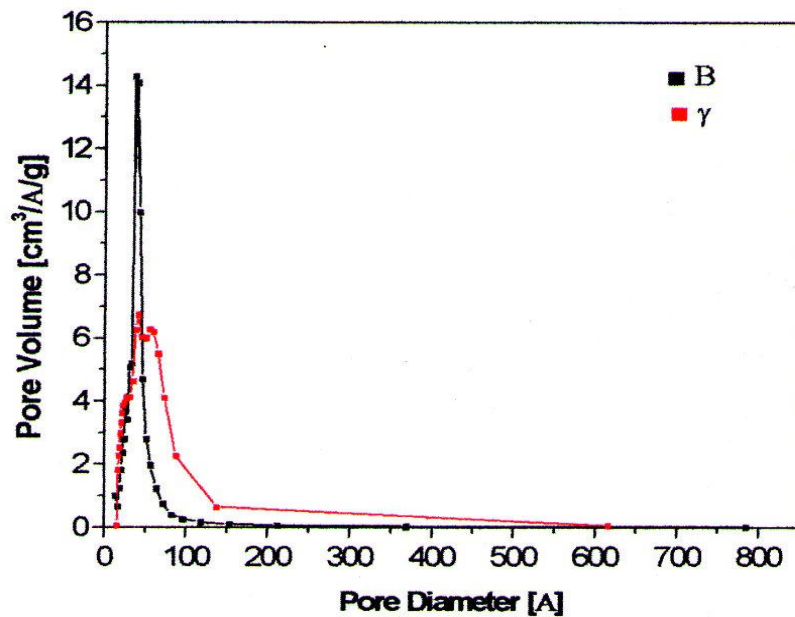


Figure 3: Pore size distributions of boehmite (B) and  $\gamma$ -alumina.

The experimental values for particle average pore diameter, particle porosity, particle mean sauter diameter, and particle specific area of  $\gamma$ -alumina are depicted in Table 1.

Table 1: Particle average pore diameter, particle porosity, particle mean sauter diameter, and particle specific area of Boehmite and  $\gamma$ -alumina.

Alumina	Average Pore Diameter [nm]	Particle Porosity $\varepsilon_p$ [-]	Sauter Diameter $d_p$ [ $\mu\text{m}$ ]	Specific area $a_p$ [ $\text{m}^2/\text{g}$ ]
Boehmite	5.535	0.210	118.77	151.92
$\gamma$ -Alumina	7.883	0.305	141.52	153.79

**2.3 Experimental Apparatus** – A schematic diagram of the high pressure apparatus used in this work is depicted in Figure 4. The unit consists of high pressure vessel of 1000  $\text{cm}^3$ , adapted to be used as an adsorption cell, two cylinders of 22  $\text{cm}^3$ , a membrane compressor, which raises the pressure from 3 to 40 MPa, a carbon dioxide reservoir, a sampling system, a gas meter, and a control unit that displays the system temperature and pressure. A complete description of the high pressure unit is found elsewhere (França *et al.*, 1999).

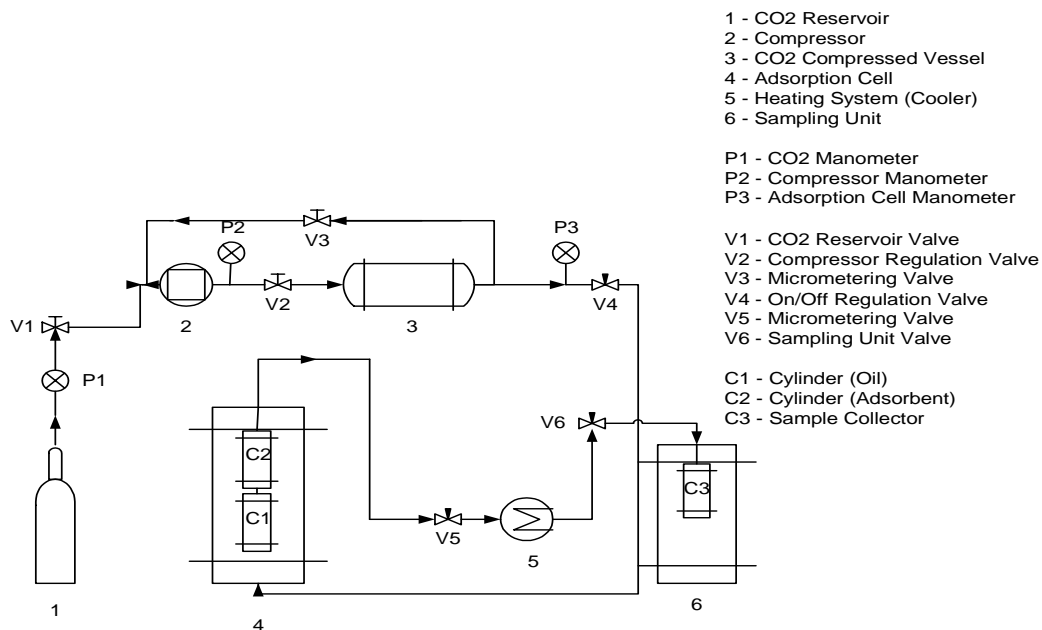


Figure 4: Experimental set-up of the high pressure adsorption unit.

**2.4 Experimental Procedure (Supercritical Adsorption)** – All the adsorption experiments were carried out using 20 g of buriti oil and 50 g of  $\gamma$ -alumina. The oil was placed inside the lower cylinder of 22 cm<sup>3</sup> (C1) depicted in Photography 1, while  $\gamma$ -alumina is placed inside the upper cylinder of 22 cm<sup>3</sup> (C2) depicted in Photography 2.



Photography 1: Stainless steel cylinder of 22 cm<sup>2</sup>.

Both cylinders have 02 (two) flanges, whereas 03 (three) slices of filter paper between 02 (two) external stainless steel screens of mesh 200# were placed in order to avoid the oil to spread outside the lower cylinder and the adsorbent particles to spread out the upper cylinder. Afterwards the cylinders were assembled within the high pressure vessel as depicted in Photography 2.



**Photography 2: Assemble used to measure the solubility by the dynamic method.**

The carbon dioxide was recycled in a closed loop for at least for 05 (five) hours, by closing valves  $V_5$  and  $V_6$ , and opening valves  $V_1$ ,  $V_2$ ,  $V_3$  (micrometer/recycle valve), and  $V_4$ , in order to maintain the system pressure constant as well as to saturate carbon dioxide until equilibrium was reached. Afterwards, valves  $V_5$  and  $V_6$  were open and the flow rate was set low ( $9.6-10 \text{ g}_{\text{CO}_2}/\text{min}$ ). The low flow rate makes it possible the fresh carbon dioxide that enters the high pressure vessel to achieve equilibrium within the sampling intervals of time. Carbon dioxide saturated with buriti oil passed through the fixed bed of  $\gamma$ -alumina where the oil adsorbed within the adsorbent. Samples from the gaseous phase were taken every 05 (five) minutes by opening valves  $V_5$  and  $V_6$ . The condensed phase was weighted by gravimetric method. The  $\text{CO}_2$  released into the atmosphere was measured using a gas flow meter. Since, ambient pressure and temperature are measured at gas meter inlet, the density of carbon dioxide can be computed using the Bender equation of state. The equilibrium capacity of  $\gamma$ -alumina adsorbent is achieved when the weight of condensates was kept constant within the sampling intervals of time when the exit gaseous concentration equal the solubility of buriti oil under the investigated state conditions. The equilibrium capacity of  $\gamma$ -alumina adsorbent is computed as the mass of oil adsorbed, determined by gravimetric methods, divided by the initial mass of  $\gamma$ -alumina. The total time interval for the adsorption experiments carried out at 333 K, and pressures of 15, 20, and 25 MPa was 05 (five), 05 (five), and 03 (three) hours respectively.

#### 2.4.1 Experimental Procedure (Adsorption of Diluted Liquid Solutions in Solids) -

All the adsorption experiments were carried out using approximately 1.0 gram of buriti oil diluted in 19.0 grams of n-hexane and 5.0 grams of  $\gamma$ -alumina at 0.1013 MPa and 333 K using an orbital shaker with agitation and temperature control. Buriti oil and n-hexane weighted by gravimetric methods were placed inside an *Elermeyer* of 250. Afterwards, the mixture was shaken until homogenization and the mass of  $\gamma$ -alumina added to the solution. The *Elermeyer* has been closed hermetically and placed inside the orbital shaker (Marconi, São Paulo, Model: JKL10) and let the solids and solution in contact for 03 (three) hours until equilibrium between the condensed phase and solids were achieved. Afterwards, the filtrate was separated by filtration and dried in an oven with air circulation at 338 K for 24 hours (Fabbe, São Paulo, Brazil, Model 179) in order to remove the organic solvent. The mass of buriti oil adsorbed within porous  $\gamma$ -alumina was determined by gravimetric methods and the capacity, expressed in grams of oil per gram of  $\gamma$ -alumina, was computed.

2.5 Adsorption Isotherms – The adsorption isotherms for oil buriti were determined experimentally using a new methodology described as follows. Since, the solubility of buriti oil has been measured for the same state conditions ( T = 333 K, and 15, 20, 25 and 30 MPa), showing a linear behavior for the cumulative mass of oil versus time, using the same apparatus configuration, experimental procedures, and process parameters of the adsorption experiments, except the absence of  $\gamma$ -alumina adsorbents within cylinder (C2), application of a mass balance makes it possible to obtain the adsorption kinetics by the difference of cumulative mass of buriti oil versus time between equilibrium and adsorption experiments for the same state conditions and process parameters as shown in equation (1).

$$m_{\text{Adsorption}} = \sum m_{\text{Condensates}}(t) * \Delta t \Big|_{\text{Solubility}} - \sum m_{\text{Condensates}}(t) * \Delta t \Big|_{\text{Adsorption}} \quad (1)$$

Where  $\sum m_{\text{Condensates}}(t) * \Delta t \Big|_{\text{Solubility}}$  and  $\sum m_{\text{Condensates}}(t) * \Delta t \Big|_{\text{Adsorption}}$  are the cumulative mass of condensates weighted within the sampling intervals of time for the solubility and adsorption experiments respectively,  $\Delta t$  is the total time intervals of both solubility and adsorption experiments, equal in both experiments. Equation (2) shows a mass balance of buriti oil for the adsorption in supercritical media.

$$M_{\text{Buriti Oil (C2)}} \Big|_{(0)} = M_{\text{Buriti Oil (C2)}} \Big|_{(t)} + m_{\text{Adsorption}} \Big|_{(t)} + \sum m_{\text{Condensates}}(t) * \Delta t \Big|_{\text{Adsorption}} \quad (2)$$

Equation (2) shows that initial mass of buriti oil in cylinder (2) is the sum of remaining mass of buriti oil in cylinder (2), mass of buriti oil adsorbed inside the fixed bed of  $\gamma$ -alumina adsorbent, and the cumulative mass of buriti oil inside cylinder (C3) for  $t > 0$ . In all cases, the mass balance closure delivered quite exact results. A Freundlich type isotherm has been used to model the experimental data. Since, the concentration of buriti oil in the gaseous phase was for a fixed pair (T, P), the adsorbent capacity was described as a function of pressure as follows.

$$q = K * P^N \quad (3)$$

Where  $K$  and  $N$  are the capacity coefficient and the exponent respectively, determined by fitting the experimental data.

### 3. Results and Discussion

The adsorption experiments of buriti oil in  $\gamma$ -alumina using supercritical  $\text{CO}_2$  as carrier gas were carried out at 15, 20, and 25 MPa, 323 K, and solvent flow rate of  $Q_{\text{CO}_2} = 10$ . L/min. The adsorption break-through curves were used to correlate the Freundlich type isotherm constants, given by equation (3). Figure 5 shows the adsorption break-through kinetic at 333 K and 25 MPa expressed in form of cumulative mass of buriti oil adsorbed in  $\gamma$ -alumina versus time. It may be observed that buriti oil soluble in supercritical  $\text{CO}_2$  has been continuously adsorbed in the fixed bed of  $\gamma$ -alumina until saturation, confirmed by a flat line in Figure 5.

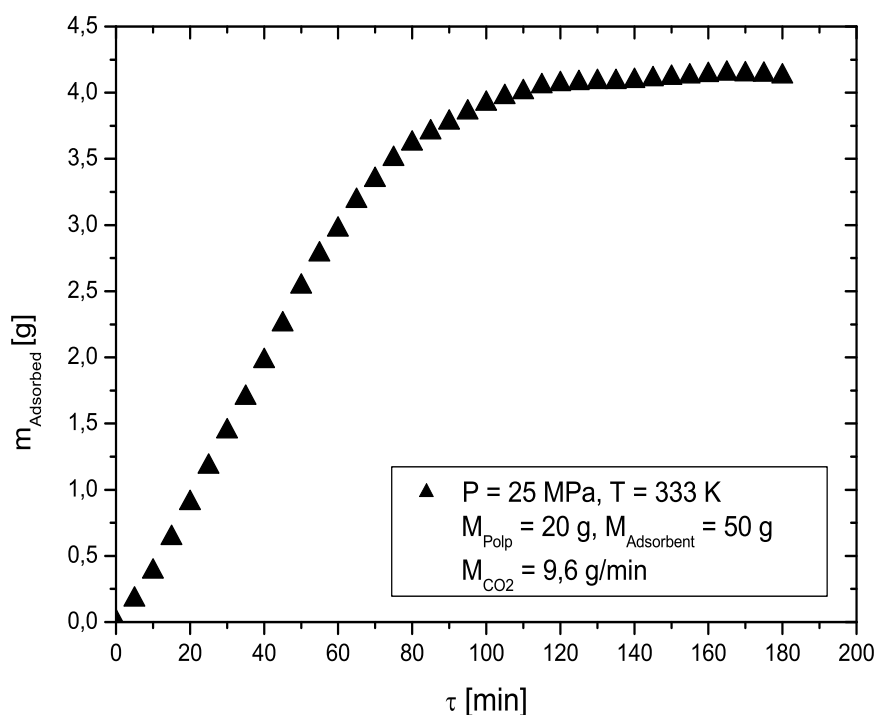


Figure 5: Adsorption kinetic of oil buriti in  $\gamma$ -alumina using SC-  $\text{CO}_2$  at 333 K and 25 MPa.

Table 2 shows the capacity of  $\gamma$ -alumina to absorb buriti oil using supercritical  $\text{CO}_2$  as carrier gas at 25 MPa and 333 K, and  $\gamma$ -alumina at 0.1013 MPa and 333 K using traditional methods. The results shows that capacity of  $\gamma$ -alumina obtained in both methods are very close, which corroborates to assert this methodology to measure the adsorption of vegetable oils in supercritical carbon dioxide.



Table 2: Capacity of  $\gamma$ -alumina adsorbent using supercritical CO<sub>2</sub> and traditional methods.

P [MPa]	T [K]	Mass $\gamma$ -alumina [g]	Mass oil [g]	Mass n-hexane [g]	Mass oil adsorbed [g]	Adsorbent Capacity [mg <sub>Oil</sub> /g <sub><math>\gamma</math>-alumina</sub> ]
0.10	333	5.0095	1.014	19.0030	0.4257	84.98
0.10	333	5.0063	1.012	19.0118	0.4298	85.85
25	333	50.001	20.001	-	4.1212	82.42

The capacity of  $\gamma$ -alumina to adsorb buriti oil as has been investigated by means of a Freundlich type isotherm as shown in Figure 6. The experimental results show that capacity of  $\gamma$ -alumina increases as pressure increases, showing a maximum of approximately 82.424 mg<sub>Buriti Oil</sub>/g <sub>$\gamma$ -Alumina</sub> by 25 MPa. This is due to the fact that the solubility of vegetable oils in supercritical CO<sub>2</sub> increases at higher pressures.

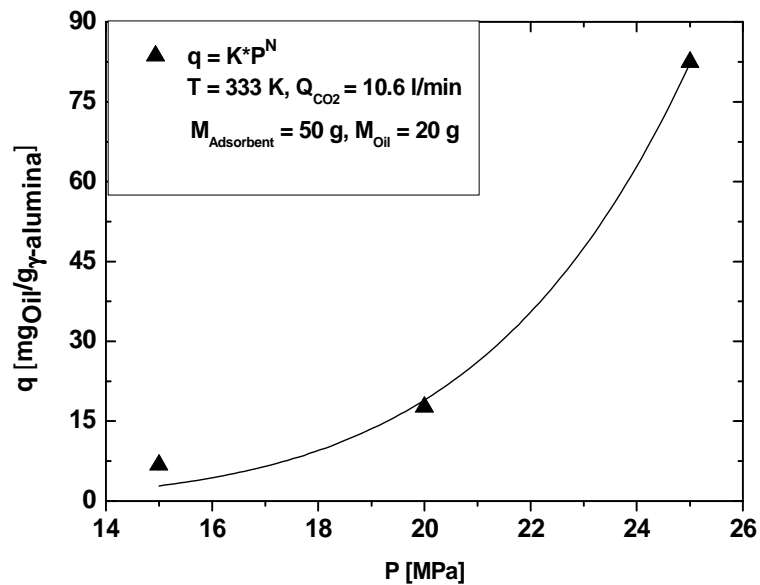


Figure 6: Capacity of oil buriti in  $\gamma$ -alumina using supercritical CO<sub>2</sub>.

Table 2 shows the capacity of  $\gamma$ -alumina adsorbent and the values K and N.

Table 2: Capacity of  $\gamma$ -alumina adsorbent and the values K and N.

P [MPa]	q [mg <sub>Oil</sub> /g <sub>Adsorbent</sub> ]	K [g <sub>Oil</sub> /g <sub>Adsorbent</sub> *MPa <sup>N</sup> ]	N [-]	R <sup>2</sup>
15	6.762	10 <sup>-5</sup>	4.821	0.957
20	17.652			
25	82.424			

#### 4. Conclusions

The experimental results show that buriti oil can be adsorbed under supercritical conditions on  $\gamma$ -alumina type adsorbent. Loading rates up to 82.424 mg of buriti oil/g adsorbent have been achieved at 25 MPa and 333 K and may be recovered by supercritical desorption, in order to enrich fat-soluble substances. In addition, the capacity of  $\gamma$ -alumina obtained in both methods are very close, which corroborates to assert this methodology to measure the adsorption of vegetable oils in supercritical carbon dioxide.

#### References

- [1] L.F. França; G. Reber; M.A.M. Meireles; N.T. Machado and G. Brunner, Supercritical extraction of carotenoids and lipids from buriti (*Mauritia flexuosa*), a fruit from the Amazon region, *The Journal of Supercritical Fluids* 18 (1999), 35–47.
- [2] Choo, Y. M.; Goh, S. H., Ong, A. S. H. and Kam, T. S. Recovery of carotenoids, tocopherols, tocotrienols and sterols from esterified palm oil, U. K. patent n. GB 2218989 B, (1991).
- [3] Ooi, C. K.; Choo, Y. M. and Ong, A. S. H. Recovery of carotenoids, U. S. Patent n. 5019668, (1991).
- [4] Raiol, I. A. S, Araújo, M. E, França, L.F; Neves, R. F, Machado, N. T. Recovery of Carotenoids from Activated Alumina by Supercritical CO<sub>2</sub>. Proceedings of the 5th International Symposium on Supercritical Fluids, Atlanta, USA, 2000.
- [5] Fleck, U.: Reinigung schwer flüchtiger Substanzen mittels Extraktion mit überkritischen Gasen, Doctor thesis at the Technical University Hamburg-Harburg, 2000.
- [6] Rodrigues, J. E.; França, L.F.; Araújo, M.E.; Machado, N. T. Kinetics of Supercritical Carbon Dioxide Desorption of Andiroba (*Carapa guianensis*, Aubl.) Oil Compounds. In: Proceedings of the 7th ISSF, Orlando-USA, 2005. v. 1. p. 1-2.
- [7] França, L. F.; Machado, N. T.; Corrêa, N. C. F. ; Zetzi, C.; Brunner, G. Measurement of adsorption isotherms of oleic acid in supercritical CO<sub>2</sub> using  $\gamma$ -alumina as adsorbent. In: Anais VII SLACA, 2007, Campinas-São Paulo, Brazil.
- [8] França, L. F.; Machado, N. T.; Corrêa, N. C. F.; Zetzi, C.; Brunner, G. Measurement of Adsorption Isotherms of  $\alpha$ -Tocopherol Acetate in Supercritical CO<sub>2</sub> using  $\gamma$ -Alumina as Adsorbent. In: Anais VII SLACA, 2007, Campinas-São Paulo, Brazil.
- [9] Möbius. C; N. C. F. Corrêa; L. F. França; N. T. Machado; Zetzi, C; Brunner. G. Fractionation of Copaiba Oil resin (*Copaifera officinalis*) by Supercritical Desorption in Packed Columns with  $\gamma$ -Alumina as Adsorbent. Proceedings of 9th ISSF, Arcachon, France, 2009.
- [10] C. J. Radke, J. M. Prausnitz. Ind. Eng. Chem. Fundamen., 1972, 11 (4), 445-451.