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Kinetic and Isotherms Adsorption of the Palm and Andiroba Vegetable Oils on γ-Alumina

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ABSTRACT

Vegetable oils refining process purpose is the removal of free fatty acids, phospholipids, trace of metals, peroxides, aldehydes, carotenes, sterols and others compounds, that affect the flavor or oxidative stability of the refined oil. Among these compounds, Free Fat Acids (FFA) may be used in the food, cosmetic and pharmaceutical industries in its original composition or as derivatives. Nevertheless, during the refining process of crude vegetable oils, chemical and thermal decomposition or separation of the most valuable substances occur, including the Free Fat Acids (FFA). In this work, the isotherms of Langmuir and BET has been used to modeling the adsorption capacity of FFA of the crude palm and andiroba oils adsorbed on thermally activated γ-alumina AG.450 and on γ-alumina AG.650, obtained from consecutive bath adsorptions experiments. Additionally, experiments varying the adsorption time, from 1-30 min, permitted the adsorption kinetic study by one second-order model. The results has been analyzed by the correlation coefficients and errors of the predict versus experimental data of FFA capacity on γ-alumina, demonstrating the high accuracy of the model applied.

Key words: Free fat acids, palm oil and iroba oil, γ-alumina, adsorption

INTRODUCTION

Vegetable oils contain triglycerides, carboxylic acids (FFA) and substances in minor concentrations, as phosphatides, carotenoids, tocopherols, squalene, sterols, alcohols, etc. The concentration of carboxylic acids (free fat acids) is one quality parameter measured by the acid index. The FFA cause deletery effect over the palates characteristics, odoriferous and of color of the vegetable oils, which needs being removed by the chemical refine (neutralization) or physical refine (distillation/water stripping) process, besides may cause process looses associated with the bleaching stage.

Although, the FFA have deletery effect over the palm oil (*Elaeis guineenses,* Jacq.) and andiroba oil (*Carapa guianensis*, Aubl.), they are widely used in the pharmaceutic, food and cosmetic industries as its original composition (ex: palmitic, oleic, linoleic, omega-3 or 6, α-linoléico, etc.) or as its derivate composition (ex. isopropyl palmitate, isopropyl myristic, etc.) (Kalustian, 1985).

The FFA adsorption improvement in the bleaching stage may represent an alternative adsorbent and gains in the vegetable oils industries. Adsorbent use as silica gel (Chang and

Pelura, 1989), resin adsorption (Nishimoto and Nagagawa, 1996) or with diatomaceous earth, γ-alumina, activated carbon (Cunha *et al*., 2010) has been proposed to remove the odoriferous and fat-soluble vegetable oil substances.

Modeling of the kinetic and of the adsorption isotherms of FFA from vegetables oils, with adsorption second-order kinetic model and with the isotherms of Irving Langmuir and BET, provides initial data to the project of adsorption columns and knowledge regarding of the selectivity behavior of the adsorbent versus vegetable oils substances.

In this study, the bath adsorption of the palm and andiroba oils on thermally alumina activated (γ-alumina) has been studied, where a sequence of consecutive adsorptions were applied (use of the same adsorbent in the fixed bed and vegetable oil is recycled) becoming possible the Langmuir and BET models use to predict the behavior of FFA concentration of the vegetables oils equilibrium condition. Additionally, a second-order kinetic equation has been used to predict the experimental vegetable oil FFA behavior, of the palm on γ-alumina AG.450 and andiroba oil on γ-alumina AG.650, evaluating the yields, correlation coefficients and errors of the experimental data versus predicted by the models.

MATERIALS AND METHODS

Crude palm oil (*Elaies guineensis,* Jacq.) was supplied by Agropalma S/A (Belém-Pará-Brazil) and crude andiroba oil (*Carapa guianensis,* Aubl.) by Brasmazon Ltd A (Ananindeua-Pará-Brazil). The Aluminum hydroxide $Al(OH)_3$ used as adsorbent was supplied by Alunorte S/A (Barcarena-Pará-Brazil) and the carbon dioxide 99.99% [vol/vol] pure, was provided by Gáspará S/A (Belém-Pará-Brazil).

Physical-chemical characterization of the vegetable oils: Crude palm oil was physical-chemically characterized at Laboratory of Quality Control (CRA S/A, Belém-Pará-Brazil), according to AOCS official methods in terms of peroxide value by AOCS Cd 8b-90, Moisture by AOCS Ca 2c-25, melting point by AOCS Cc 1-25, phosphorous by AOCS Ca 12-55, Insoluble Impurities by AOCS Ca 3a-46, UV Extinction by AOCS Ch 5-91 and carotenes by spectrophotometry.

Crude andiroba oil was physical-chemically characterized at BRAZMAZON LTDA according the Adolf Lutz methods in terms of free fatty acids, iodine value, refraction index, unsaponifiables, solidification point, insoluble impurities and density.

Thermal activation of the adsorbent (γ-alumina): Aluminum hydroxide $Al(OH)_3$ sample was previously washed with water at 373.15 K to remove the residual sodium hydroxide. In the next, it was dried in an oven with air circulation at 333.15 K for 24 h (Fabbe, São Paulo, Brazil, Model 179) and stored in a desiccator. The thermal transition of the sample was applied at 723.15 and 923.15 K.

Thermal transformation (calcination) of the aluminum hydroxide, has been carried out using an electrical furnace (Químis, São Paulo, Brazil, Model: Q.318.24) with automatic temperature control. During the calcination process, it is possible to obtain the alumina adsorbent through alternative routes (Wefers and Misra, 1972) as showed in the Fig. 1.

Adsorbents specific area were measured using BET method, in a surface area analyzer (Quantacrome, USA, Model: Monosorb) and the particle size distribution were carried out in a particle diameter analyzer (Malvern Instruments, USA, Model Mastersize S).

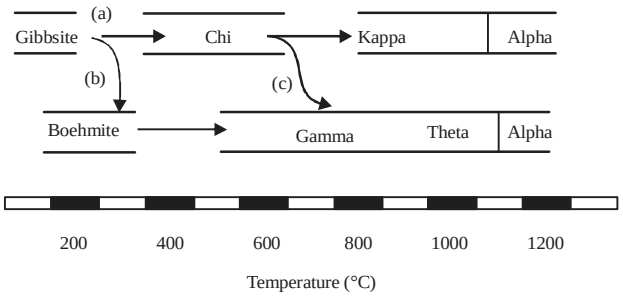

Fig. 1: Alternative routes to obtain the adsorbent γ-alumina through the thermal activation of the aluminum hydroxide (Whittington and Ilievski, 2004)

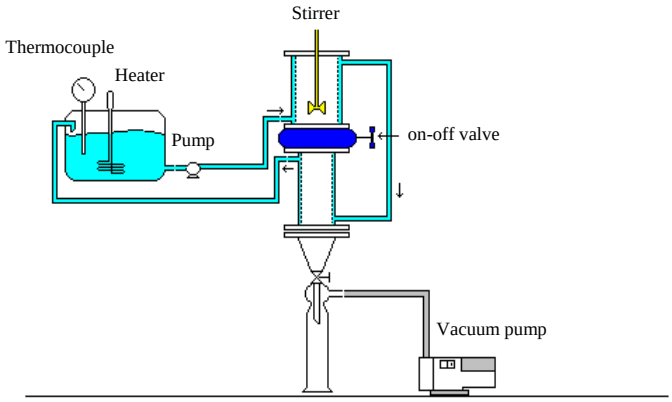

Fig. 2: Schematic diagram of the experimental batch adsorption apparatus

The aluminum oxide, as the γ-alumina, are adsorbents classified as been of the type II, once have the positive charges on the surface (Al^{3+} sites) and consequently acid characteristics, associated with hydroxyl (OH) groups on the surface (Oscik, 1982).

Adsorption experimental apparatus: The experimental apparatus described in Fig. 2, consists of a stainless steel jacket cylindrical reactor (Refrinox Representation and Commerce Ltd., Belém-PA) of 250 mm height and 55 mm diameter (Adsorption Unit), a stainless steel jacket cylindrical reactor (Refrinox Representation and Commerce Ltd., Belém-PA) of 195 mm height and 45 mm diameter (Filtration Unit), a on-off valve (Niagara S.A, Model: 539-150), which connects both adsorption and filtration units, a mechanical stirrer (Veb-Labortechnik, Model: UR2), a digital thermometer, a sealing flange (Refrinox Representation and Commerce Ltd., Belém-PA) with a sphere valve, a heating system containing a stainless steel water reservoir with 180×255×150 mm, a recirculation pump (AL-KO Geräte Gmbh, Model: SPI 500), an electrical resistance (Model: Cherubino-127 volts), a digital temperature control (Weg, Model: CW37.11E) and a vacuum system containing a stainless steel collector (Refrinox Representation and Commerce Ltd., Belém-PA) of 275 mm height and 50 mm internal diameter and a vacuum pump (Edwards, Model: RV3).

Adsorption experimental procedure: Crude palm oil was heated up to 313 K during 1 h in order to homogenize the mixture. The heating system was turned on, as well as the recirculation pump in order to allow that the hot water within the jacket of the adsorption and filtration units continually recycle up to the temperature target. Afterwards, the crude oil was introduced inside the adsorption unit with the on-off valve closed and the mechanical stirrer was turned on. When the temperature target was achieved, the adsorbent was introduced inside the adsorption unit and the mixture agitated for a determined time. After the adsorption process was finished, the on-off valve was opened and the mixture falls to the filtration unit by gravity and the on-off valve was immediately closed. The vacuum pump was activated and the sphere valve coupled to the sealing flange, which connects the filtration unit to the stainless steel collector, was opened. The filtrate/percolate vegetable oil was collected, weighted and the free fatty acids content measured. The adsorbent alumina loaded with vegetable oil was weighted, covered with aluminum paper. The consecutive adsorptions experiments consist of recycling the vegetable oil, after each adsorption experiment without pre-heating the vegetables oils, during three or four times and keeping all remaining variables constants. In the kinetic, study just the adsorption time is varied. In both studies, all the remaining parameters keep constants and the procedure is accomplished as explained.

Adsorption experiments: Table 1 shows the parameters and raw materials used in each adsorption experiment regarding the study of consecutives adsorptions. The adsorption isotherms has been used to modeling the curves of FFA capacity obtained. The use of consecutives adsorptions, to obtain the isotherms of adsorption, have as approximation the use of the same adsorbent consecutively (it may represent lower consumption).

Table 2 shows the parameters and raw materials used in each adsorption experiment, regarding the kinetic adsorption study. The kinetic equation of second-order has been used to modeling the curves of FFA capacity.

The capacity of adsorption is expressed as the ratio of the adsorbed substance mass in the adsorbent surface (defined as adsorbate) per adsorbent mass used.

Chemical analysis of free fatty acids: The acids index (IA) is defined as the mass in mg of hydroxide of potassium necessary to neutralize the free fat acids present in 1 g of vegetable oil, calculated according the Eq. 1:

$$IA = \frac{V_{NaOH} \times f \times 5.16}{M} \quad (1)$$

Table 1: Parameters and raw materials used in consecutive adsorption experiments

Vegetable oil	γ-alumina	Time (min)	M_{oil} initial (g)	$M_{\gamma\text{-alumina}}$ (g)	Temperature (K)
Palm	AG. 450	2	150.17	10.0	328.15
Andiroba	AG. 650	3	150.04	10.0	323.15

Table 2: Parameters and raw materials used in the adsorption kinetic study

Vegetable oil	γ-alumina	Time (min)	M_{oil} initial (g)	$M_{\gamma\text{-alumina}}$ (g)	Temperature (K)
Palm	AG. 450	2.5; 5; 10; 20; 30	100.0	5.0	328.15
Palm	AG. 650	1; 5; 30	100.0	5.0	328.15
Andiroba	AG. 650	1.0; 2.5; 5; 10; 20	100.0	5.0	323.15

Where:

V_{NaOH} = Volume of Hidroxide of Sodium (NaOH) in [ml] at 0.1 N used to the titulation
f = Factor of the hydroxide solution
M_{oil} = Mass of the vegetable oil sample (Moretto and Fett, 1998)

The concentration of FFA ($C_{FFA,f}$) in the fluid phase (vegetable oil) is calculated as present by the next Eq. 2, expressed as (mg_{FFA} cm^{-3}).

$$C_{FFA,f} = I.A_f \times \rho_{oil} \tag{2}$$

where, the mass of adsorbate ($M_{adsorbate}$) is expressed in (mg), the mass of adsorbent ($M_{\gamma\text{-alumina}}$) in (g), the $I.A_f$ is the final acids index in the vegetable oil after the adsorption and the densities of the palm and andiroba oils are 0.910 g cm^{-3} at 328.15 K and 0.934 g cm^{-3} at 323.15 K, respectively. The FFA concentration equilibrium results ($C^*_{FFA,\ f}$) expressed as (mg_{FFA} cm^{-3}), used in the adsorptions isotherms study were obtained considering the adsorbent saturation capacity as ($X^*_{FFA,\gamma\text{-alumin}} = 0.45$), feed average acid index of the vegetables oils from the consecutives adsorptions (Table 5 and 6), according the Eq. 3, based on Henry's Law:

$$C^*_{FFA,f} = \left(\frac{X^*_{FFA,\ \gamma\text{-alumina}}}{X_{FFA,\ \gamma\text{-alumina}}} \right) \times IA \times \rho_{oil} \tag{3}$$

Adsorbent capacity in terms of FFA, obtained after each consecutive adsorption experiment, is obtained by Eq. 4 associated with the mass balance component (FFA) in the vegetable oil, expressed as ($mg_{FFA}/g_{\gamma\text{-alumina}}$):

$$X_{FFA,\gamma\text{-alumina}} = \left(\frac{M_{adsorbate}}{M_{\gamma\text{-alumina}}} \right) \times \frac{(IA_i - IA_f)}{\rho_{oil}} \tag{4}$$

where, the acid index before the adsorption process (IA_i) and after the process, final acid index (IA_f), are expressed as (mg_{NaOH}/g_{oil}) obtained by the methodology described by Moretto and Fett (1998).

Isotherms of adsorption

Isotherm of Langmuir (1918): Langmuir (1918) presented a model which describes the volume of gas adsorbed in a solid surface. The model is classified as been applied to localized adsorption with only a monolayer cover formation. The model assumptions are that all adsorption has the same mechanism, finite number of sites with the same capacity end energy, which consider interaction absence among the molecules (Langmuir, 1918).

Considering the equilibrium condition in one long time ($t \to \infty$) and writing the Langmuir linear equation form in terms of FFA concentration, according to Eq. 5, the parameters K_{Lang} and X_m^{Lang} may be obtained, expressed as:

$$(mg_{FFA}/g_{\gamma\text{-glumina}})^{-1}$$

and

$$X_m^{LANG}$$

where, $(mg_{FFA}/g_{\gamma\text{-glumina}})^{-1}$ and X_m^{Lang} are the capacity in one instant τ and in the equilibrium condition (equivalent a complete monolayer formation), respectively.

$$\frac{1}{X_{FFA,\gamma\text{-alumina}}} = \frac{1}{X_m^{Lang.}} + \frac{1}{X_m^{Lang.} K_{LANG.} C_{FFA,f}} \quad (5)$$

Isotherm of Brunauer *et al.* (1938): A state of dynamic equilibrium is proposed by the Brunauer, Emmet e Teller model, denominated as BET model or Isotherms of BET, which the rate of molecules adsorption from the gas phase and the condensation in empty sites is equal the evaporation of molecules from the occupied sites. The first layer have heat of adsorption different from the all subsequent layers. Starting from the second layer, the model assumes that the heat of adsorption is equal the latent heat of condensation of the adsorbed liquid (Brunauer *et al*., 1938).

The BET model assumptions are based on kinetics equations and equilibrium conditions, analogous the Langmuir model. The adsorption sites have the same capacity, energy; and mechanism, which consider only horizontal interactions of adsorbed molecules. The adsorption occurs in multilayers on the adsorbent (Brunauer *et al*., 1938).

The BET equation may be writing in terms of concentration, where $C_{FFA,f}$ is the concentration of the adsorbate on the adsorbent surface and $C^*_{FFA,f}$ the equilibrium concentration of the adsorbate (free fat acids) in the equilibrium condition, expressed as (mg_{FFA}/g_{oil}). The linear form of the Eq. 6 permit to obtain the constant of the BET model K_{BET} and the capacity related with the complete monolayer formation X_m^{LANG} (Oscik, 1982), expressed as $(mg_{FFA}/g_{\gamma\text{-alumina}})$ and $(mg_{FFA}/g_{\gamma\text{-alumina}})^{-1}$, respectively.

$$\frac{\left(C_{FFA,f} / C^*_{FFA,f}\right)}{X_{FFA,\gamma-alumina}\left(1-\left(C_{FFA,f} / C^*_{FFA,f}\right)\right)} = \frac{1}{X_m^{BET} K_{BET}} + \frac{K_{BET}-1}{X_m^{BET} K_{BET}} \times \frac{C_{FFA,f}}{C^*_{FFA,f}} \quad (6)$$

Kinetic model of adsorption

Second-order model: Second-order rate equation in solution systems is presented according the Eq. 7 (Xu *et al*., 2006).

$$\frac{dX_{FFA,\gamma\text{-alumina}}}{d\tau} = K_2 X^2_{FFA,\gamma\text{-alumina}} \quad (7)$$

The Eq. 8 was integrated with the boundary conditions of $X_{FFA,\gamma\text{-alumina}} = 0$ at $\tau = 0$ and $X_{FFA,\gamma\text{-alumina}}$ at $\tau = 0$, providing the equation in the linear form as follows:

$$\frac{1}{X_{FFA,\gamma\text{-alumina}}} = \frac{1}{X^*_{FFA,\gamma\text{-alumina}}} + K_2 \tau \quad (8)$$

The constant of the adsorption kinetic model of second-order is K_2, expressed as ($g_{\gamma\text{-glumina}}/mg_{FFA}$ min). The equation has been used to describe fluoride adsorption onto acid-treated spent bleaching earth (Mahramanlioglu *et al*., 2002) and phosphamidon adsorption on an antimony (V) phosphate cation ex-changer (Varshney *et al*., 1996).

RESULTS AND DISCUSSION

Vegetable oil

Crude palm oil characterization: Table 3 shows the physical-chemical characterization of CPO (crude palm oil).

Crude andiroba oil characterization: Table 4 shows the physical-chemical characterization of the andiroba crude vegetable oil.

Adsorbent characterization (γ-alumina): The specific area of the adsorbents presented values of 168.3 and 145.6 $m^2\ g^{-1}$ for the adsorbents alumina AG.650 and AG.450, respectively. The particles sizes distributions presented particle diameter (D_{50}) of the γ-alumina AG.450 and AG.650 were 130 and 135 mm, respectively.

Modeling of the adsorption isotherms: Table 5 shows the FFA capacity results of consecutives adsorptions of the palm vegetable oil on γ-alumina AG.450. The total reduction of FFA

Table 3: Physical and chemical analysis of the crude palm oil

Physical and chemical analysis	Results
Acids index (mg_{NaOH}/g_{oil})	7.75
Peroxide value (mEq kg^{-1})	0.028
Melting point (K)	308.8
Phosphorous (ppm)	16.52
UV-Extintion (233-269 nm)	$E^{1\%}$ 233 nm = 0,66- $E^{1\%}$ 269 nm = 0,24
Total carotenes (ppm)	774
Moisture (%)	0.37
Impurities (%)	0.028

Table 4: Physical and chemical analysis of the crude andiroba oil

Physical-chemical analysis	Results
Fat acids (%)	
Meristic (C14:0)-(tetradecanóico)	18.1
Oleic (C18:1ω-9)-(cis-9-octadecanóico)	58.9
Linoleic (C18:2ω-6)-(cis-cis-9,12-octadecanóico)	9.2
Palmitic (C16:0)-(hexadecanóico)	9.3
Density at 288.15 (K)	0.923 g cm^{-3}
Refraction index Zeiss at 313.15 (K)	1.4601-1.4613
Iodine index (Hanus)	68.2-62.8
Unsaponifiable	1.9-2.6
Solidification point (K)	287.15-191.15
Acids idex (mg_{NaOH}/g_{oil})	31.81

Table 5: Vegetable palm oil on γ-alumina ag.450-results of the consecutives adsorptions

M_{Oil} (g)	$M_{Adsorbate}$ (g)	Reduction of IA (%)	$X_{oil,\gamma\text{-alumina}}$ (g_{oil} / $g_{\gamma\text{-alumina}}$)	I.A (mg_{FFA}/ g_{oil})	$C_{FFA,f}$ (mg_{FFA}/cm^3)
Crude oil	-	-	-	7.75	-
150.17	3.37	6.93	0.3370	7.19	0,511
131.00	2.80	7.23	0.2800	6.67	0,473
105.38	2.18	6.59	0.2180	6.23	0,400
Total	8.35	21.07	-	-	-
Average			0.2783	-	-

concentration of the crude palm vegetable oil after three consecutives adsorptions reached 21.07% (proving the adsorbent ability to adsorb FFA). Figure 3 shows the modeling of these data using the isotherm of Langmuir and in the Fig. 4 the adjustment of the same FFA capacity experimental data using the BET isotherm. The comparison results (Fig. 3 and 4) indicates the best correlation coefficient, mediums errors and residual of the Langmuir model to predict the FFA capacity experimental data of the crude palm oil on γ-alumina AG.450. The number of consecutives adsorptions resulted in a complete monolayer formation.

Regarding the results of consecutives adsorptions of the crude andiroba vegetable oil on γ-alumina AG.650, the results are present in Table 6. The total reduction of FFA concentration after four consecutives adsorptions reached 40.29%. Figure 5 shows the modeling of the FFA capacity experimental data using the BET model, where the results of coefficient correlation

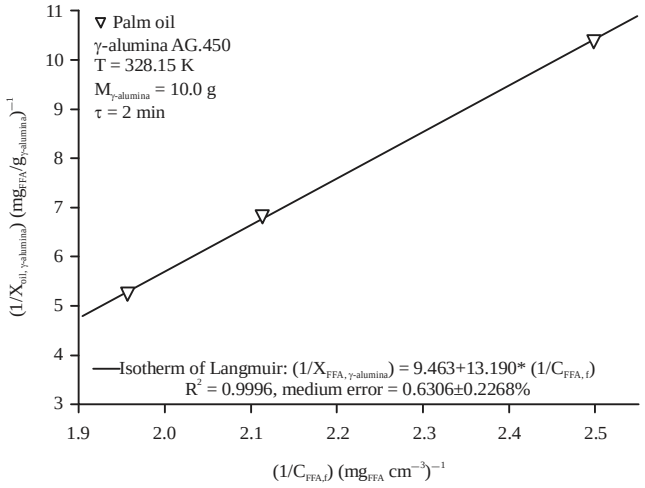

Fig. 3: Modeling of the FFA palm oil adsorption capacity on γ-alumina AG. 450 using isotherms of Langmuir

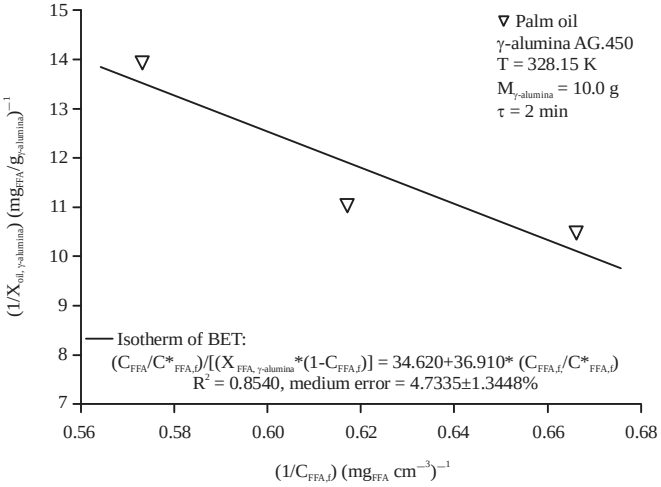

Fig. 4: Modeling of the FFA palm oil adsorption capacity on γ-alumina AG.450 using isotherms of BET

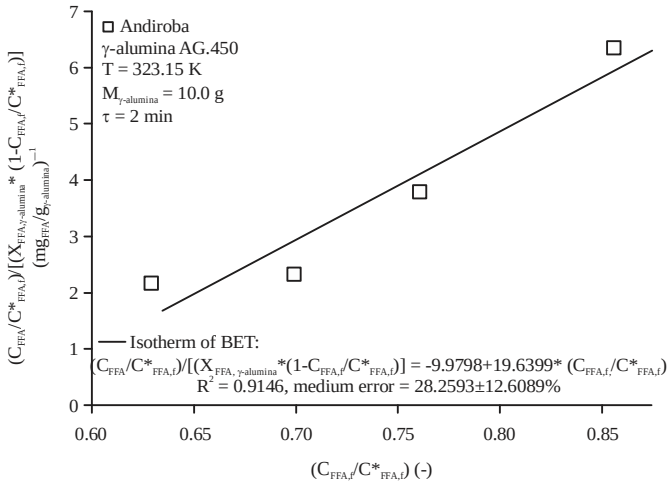

Fig. 5: Modeling of the FFA palm oil adsorption capacity on γ-alumina AG.650 using isotherms of BET

Table 6: Andiroba oil on γ-alumina ag.650- results of the consecutives adsorptions

M_{Oil} (g)	$M_{Adsorbate}$ (g)	Reduction of I.A (%)	$X_{oil,\gamma\text{-alumina}}$ ($g_{oil}/g_{\gamma\text{-alumina}}$)	I.A (mg_{FFA}/g_{Oil})	$C_{FFA,f}$ (mg_{FFA}/cm^3)
Crude oil	-	-	-	31.81	
150.04	2.66	10.30	0.266	28.27	3,319
123.61	3.69	8.06	0.368	25.99	2,141
117.89	3.87	10.04	0.386	23.38	2,453
94.26	3.06	11.06	0.305	20.79	2,429
Total	10.62	40.29		-	-
Average	-	-	0.331	-	-

evidenced the high ability of the model predict the experimental data. The formation of multilayers on the adsorbent surface, after four consecutive experiments, is one of the reasons why the BET model presented adjustment for the andiroba vegetable oil adsorption results.

This results, modeling study of palm oil adsorption on γ-alumina 450 and of the andiroba on γ-alumina 650, are in agreement with the literature, such as reported by (Cunha *et al*., 2012), which performed a material balance on the adsorption column to compute the cumulative mass of adsorbing species in γ-alumina, on supercritical adsorption process. It was applied a pseudo-first order kinetic model as well as an integral kinetic model. A Langmuir type isotherm has been used to model the experimental adsorption data.

Table 7 presents the parameters obtained from the Langmuir model, applied to the palm vegetable oil adsorption on γ-alumina AG.450 and the parameters to the BET model, applied to the andiroba oil on γ-alumina AG.650.

Adsorption experimental results of capacity varying with time are present in Table 8, to the vegetable palm oil on γ-alumina AG. 450 and on γ-alumina AG.650 and to the andiroba vegetable oil on γ-alumina AG. 650. It demonstrates that above 20 min, the adsorption capacity results presented values below of 0.25 while the adsorption capacity results presented higher values in reduced times. The literature present values of capacities to industrial adsorbents of 0.5 (saturation values). The palm oil constituents adsorbent capacity present in Table 8, are in agreement that obtained by (Araujo *et al*., 2006), where a study of palm oil solubility and modeling the constituents desorbed from γ-alumina on carbon dioxide has been accomplished. Similar results were obtained by (Azevedo *et al*., 2011), where a study of FFA and carotenoids adsorption on γ-alumina has been accomplished, associated with supercritical carbon dioxide desorption.

Table 7: Adsorption isotherms parameters

Isotherm of Langmuir (Palm oil on γ-aluminaAG.450)		Isotherm of BET (Andiroba oil on γ-alumina AG.650)	
X_m^{LANG}	$1/K_{LANG}$	$X_m^{BAT.}$	$1/K_{BET}$
$mg_{FFA}/g_{\gamma\text{-glumina}}$	$(mg_{FFA}/g_{\gamma\text{-glumina}})^{-1}$	$mg_{FFA}/g_{\gamma\text{-glumina}}$	$(mg_{FFA}/g_{\gamma\text{-glumina}})^{-1}$
- 0.07581	-0.7174	0.1154	2.199

Table 8: Results of adsorption capacity of vegetables oils on -alumina

Time (min)	Palm oil on AG.450 $X_{oil,\gamma\text{-alumina}}$ ($g_{oil}/g_{\gamma\text{-alumina}}$)	Palm oil on AG.650 $X_{oil,\gamma\text{-alumina}}$ ($g_{oil}/g_{\gamma\text{-alumina}}$)	Andiroba oil on AG.450 $X_{oil,\gamma\text{-alumina}}$ ($g_{oil}/g_{\gamma\text{-alumina}}$)
Crude vegetable oil)	(7.75)*	(7.75)*	(66.63)*
1.0	-	0.510	0.394
		(5.61)	(59.65)
2.5	0.434	-	0.329
	(5.55)		(60.93)
5.0	0.368	0.294	0.345
	(5.75)	(4.52)	(59.86)
10.0	0.255	-	0.362
	(5.75)		(60.20)
20.0	0.280	-	0.313
	(6.88)		(61.69)
30.0	0.245	0.242	-
	(6.88)	(5.14)	

Parentheses: Results of acids index of the vegetables oils expressed as [mg_{FFA}/g_{Oil}] and *correspond the I.A of the crude vegetable oil

Table 9: Constant of velocity of the second order adsorption kinetic model

Constant of velocity ($mg_{FFA}g\gamma\text{-}_{glumina}$)	Palm oil on γ-alumina AG.450	Palm oil on γ-alumina AG.650	Andiroba oil on γ-alumina AG.650
K_2	0.1520	2.20×10^{-2}	1.1922×10^{-2}

Kinetic study: Table 9 results were used in terms of FFA concentration (Eq. 3 use) to the adsorption kinetic study. Results of FFA concentration are present in Fig. 6-8. The FFA capacities of the palm vegetable oil on γ-alumina AG.450 and on AG.650 are present on Fig. 6 and 7, respectively. The results are in agreement of a kinetic of second-order to the palm oil adsorption on γ-alumina AG.450 and on AG.650, with correlation coefficient results of 0.9622 and 0.9723, respectively. Errors also evidenced the excellent adjustment of the FFA capacity experimental data with the second-order model kinetic proposed. Regarding the capacity of the andiroba vegetable oil on γ-alumina AG.650, according to Fig. 8, the same behavior has been obtained with correlation coefficient of 0.9636. These results confirm the high agreement of the predicted versus experimental data for the second-order kinetic used.

The comparison of the FFA adsorption capacity in Fig. 6, 7 and 8 evidenced the highest FFA adsorption capacity, in each condition of time, of the adiroba oil on γ-alumina AG. 650>palm oil on AG.650>palm oil on AG.450, confirmed by the velocities constants results of the second-order kinetic model obtained from the angles of each curve presented in these figures, according Table 10. These results are consequence of the higher initial concentration of FFA of the crude andiroba vegetable oil than crude palm vegetable oil, once the "Driving force" for the adsorption phenomenon is the vegetable oil solute concentration (FFA). Recent studies, as reported by Correa *et al*. (2014), investigated the effect of the process variable free fat acids of organic liquid product (product of the palm oil cracking) in the adsorption of γ-alumina (5%). The same behavior results has been obtained with the current research, where an increase of the FFA concentration resulted in an increase of the initial FFA adsorption rate.

Regarding the FFA adsorption capacity of the palm oil on γ-alumina AG.650 versus on AG.450, the results are consequence of the higher superficial area (SSA) of the γ-alumina AG.650 versus on AG.450 (it resulted of the higher temperature calcination condition of the γ-alumina AG.650 versus

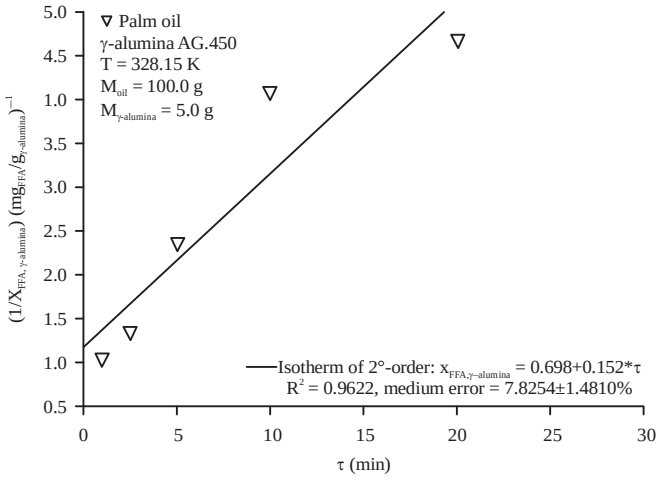

Fig. 6: Adsorption kinetic of the palm oil on γ-alumina AG.450

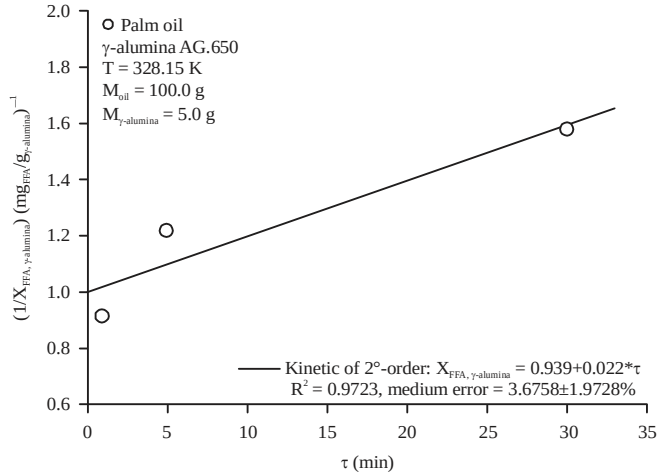

Fig. 7: Adsorption kinetic of the palm oil on γ-alumina AG.650

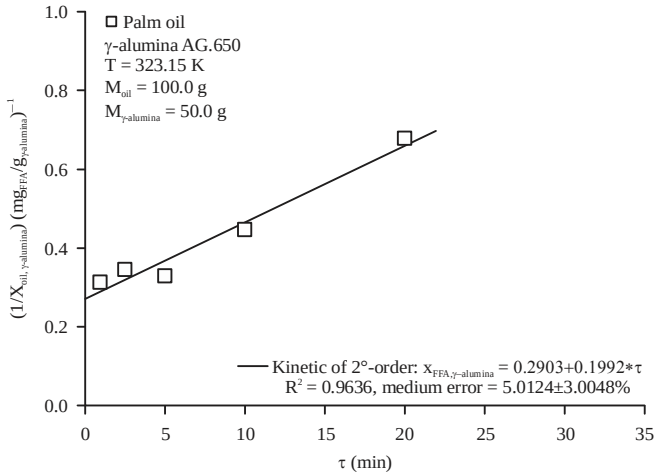

Fig. 8: Adsorption kinetic of the andiroba oil on γ-alumina AG.650

AG.450). The electropositive characteristic of the γ-alumina (Al^+) is responsible for attracting the group hydroxyl (OH) present in the FFA and the carboxylic group from the triglycerides (R-C-C = O-R').

CONCLUSIONS

Consecutive adsorption experiments of the crude palm and andiroba vegetables oils on γ-alumina showed the ability of this adsorbent reduce the free fat acids of the vegetables oils in 21.07 and 40.29%, respectively. These results (with blands adsorbents or adsorptions equilibrium studies) could be able to represent a reduction of consumptions (ex: caustic soda, specific energy consumption or adsorbent) in vegetables oils refining process, once in the bleaching stage part of the FFA could be adsorbed with the other substances currently removed. The modeling, using the isotherms of Langmuir presented the best agreement to predict FFA adsorption capacity to the palm oil on AG.450 while the BET model has been demonstrated the good ability of experimental data prediction of the andiroba oil on γ-alumina AG.650, with correlations coefficients of 0.9996 and 0.9146, respectively.

The kinetic study of the crude vegetable palm oil adsorption on γ-alumina AG.450 and on γ-alumina AG.650 and of the crude vegetable andiroba oil on γ-alumina AG.650, demonstrated excellent agreement of the second-order kinetic model for predicting the free fat acids mass adsorbed on γ-alumina, with results of correlation coefficient of 0.9622, 0.9723, 0.9636, respectively.

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