Obtención de parámetros óptimos de un carbón activado cubano de cáscara de coco para almacenamiento de metano

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Recibido: 01 de junio de 2016. Aceptado: 19 de diciembre de 2016.

Palabras clave: carbón activado, isotermas de adsorción, metano, modelo deToth.
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RESUMEN. El material que se investiga es un carbón activado (CA) cubano obtenido de la cascara de coco. El objetivo del presente trabajo es investigar si el CA cubano pudiera ofrecer efectos beneficiosos para el almacenamiento de metano. Se desarrolló un plan factorial 3^2 en el que se relacionan dos parámetros fundamentales: temperatura °C (X_1) y tiempo min. (X_2), y su influencia sobre diferentes variables de salidas: rendimiento, resistencia mecánica, índice de iodo, cenizas y adsorción de melaza. A partir de la optimización por respuesta múltiple del sistema de ecuaciones polinomiales se obtuvieron los siguientes resultados: T = 800 °C y t = 85 min y para las variables de salida: rendimiento = 59,4 %, índice yodo = 1057 mg/g, resistencia mecánica = 96 %, cenizas = 5,6 %, melaza = 22,4 %. Bajo esas condiciones óptimas se obtuvo $CA_{óptimo}$ siendo caracterizado con N_2 (77 K), reportando V_{micro} (0,63 cm^3/g) y W_m (1,3 nm) determinados por DR respectivamente. Se determinó la adsorción de metano a T (298K) y 3.5 MPa. Los datos de adsorción respondieron a la isoterma de tipo I (materiales microporosos) y capacidad de adsorción de 144,7 cm^3/g. Para la evaluación de los datos se empleó el modelo de Toth con el que se obtuvo muy buen ajuste. Un F-test para D.E demostró la no existencia de diferencias significativas (95 %).Un análisis lineal entre $N_{calculado}$ (mmol/g) vs $N_{experimental}$ (mmol/g) alcanzó R^2 (99,4). Por todo lo anterior $CA_{óptimo}$ puede ser considerado un buen candidato para el almacenamiento de metano

ABSTRACT. The material studied is a Cuban AC (activated carbon) from coconut shell as starting material. The objective of present work is to investigate if the Cuban AC could produce any beneficial effects on methane storage. A factorial designs 3^2 plans was development, considering the variability of two parameters were related: temperature °C (X_1) and time min. (X_2) and its influence on output variables such as: yield, mechanical resistance, index of iodine, molasses and ashes. By means of the optimization of multiple response there were obtained for the system of equations the following optimized results: T= 800 °C and t = 85 min. and the output variables: yield = 59.4 %, iodine number = 1 057 mg/g, molasses = 22.4 %, mechanical stress = 96% and ashes = 5.6 % which represent very good experimental reproducibility. The $AC_{optimum}$ obtained under these conditions was evaluated with N_2 (77 K) reaching values of V_{micro} (0.63 cm^3/g) and W_m (1.3 nm) calculated by DR. The methane adsorption of $AC_{optimun}$ was carried out to ambient temperature (298 K) and 35 MPa. Experimental data showed characteristic of type1 isotherms. Toth model was employed to evaluate and describe the quantity of methane adsorbed in the $AC_{optimum}$. A good fit for Toth model was obtained, which are supported by (F-test) there is not a statistically significant difference (SD) at 95 % confidence level and lineal good fit R^2 (99.4) between $N_{calculated}$ (mmol/g) vs $N_{experimental}$ (mmol/g). Toth model indicates besides the heterogeneity of the methane- granular activated carbon system. The AC optimum can be considered a good candidate to storage of methane

INTRODUCCIÓN

Natural gas (methane 85 to 90 %) is a promising one due to its abundance and little pollution, especially as vehicle fuel allowing such less exhaustion than reformulated gasoline or diesel. However, it is hard to commercialize, since the low volumetric density at room. Commonly there are three methods to settle this problem, namely liquefied natural gas (LNG), compressed natural gas (CNG) and adsorbed natural gas (ANG). Among them, ANG is the most feasible approach, for its relatively low pressure (3.5 MPa) but high energy density. Previous studies have proven that porous carbon possessing large surface area and special porosity features might be the commercially potential adsorbent. The thickness of the methane compressed to 3.4 MPa can increase in a factor of 4 (for effect of packing)

with the use of adsorbents as the activated carbon obtaining a storage of methane of 180 V/V that is equivalent to a tablet of the same one of 16 MPa. Theoretical studies indicate that the size of good pore for the methane storage is of 0.8 nm (1.4 nm pore size from the center of the atom of carbon of both walls of the pore) that would correspond to a separation among the walls of the pore of some 2 times the diameter of the methane (molecular diameter of CH_4 of 0.4 nm). For this reason the investigations go guided toward the search of materials requires maximization of micropore volume avoiding the meso and macropores as much as possible since these, as well as the holes among particles, make diminish the density of packaging of the material adsorbents, what will produce a smaller relationship volume of stored methane and volume of deposit.[1-3]

In this paper experimental was carried out to determine the methane adsorption capacity of granular activated carbon from coconut shell under room temperature and pressure (35 bar). With that purpose a series of Cuban activated carbons were prepared by physical activation with steam. The objective of present work is to investigate if the AC Cuban from coconut shell could produce any beneficial effects on methane storage. This study was important to maintain the natural characteristics of this material, because it is necessary to settle the base line of their natural properties for later on to improve those that don't reach the appropriate level**.** An experimental design 3^2 has been drawn up to optimize the experimental conditions. Important parameters were considered in this study, such as: mechanical resistance, yield, molasses, iodine adsorption and ashes. Adsorption of iodine (micropores) and molasses (mesopores) adsorption were used for the initially analysis of the textural characteristics of these materials. The results obtained were exploited using response surface methodology. The response surface methodology is an appropriate tool to study optimization of the activation process to prepare activated carbons to be used in a given technological process in this case to storage methane.

These responses have been represented and studied in all experimental regions of activation time and activation temperature, the most influential factors in activated carbon preparation. These were optimized obtain an activated carbon ($AC_{optimum}$) with textural characteristics suitable to use in methane storage has been carried out. The optimal activated carbon ($AC_{optimum}$) was obtained under activation time (85 min) and temperature (800°C) respectively.

MATERIALS AND METHODS

During the accomplishment of the tests, constants stayed the following conditions, in agreement with the technological parameters of activation process of Baracoa Plant: partial pressure of $H_2O_{(v)}$ = 50 %, relation: kg $H_2O_{(v)}$/kg AC (3/1), fragments of 40 a 50 mm in length and 5 a 8 mm of diameters, load by test = 0.2 kg.

Experimental model development for the study was a factorial plan 3^2. Codified mathematical model employed for design was:

$$Y = B_O X_O + \sum_{i=1}^{K} B_i X_i + \sum_{j,i=1}^{K} B_{ij} X_i X_j + \sum_{i=1}^{K} B_{ii} X_i^2 \quad (1)$$

For the case that occupies to us the polynomial way is, $Y = B_O X + B_1 X_1 + B_2 X_2 + B_{12} X_1 X_2 + B_{11} X_1^2 + B_{22} X_2^2$ where: X_1 (temperature in °C), X_2 (time in min.), Y (response variable), X_1X_2 (parameters interaction), X_1^2, X_2^2 (quadratic effects), B_o (constant coefficients), B_1, B_2 (parameters coefficients), B_{12} (interactions coefficients), B_{11}, B_{22} (quadratic coefficients). The matrix was evaluated for the following variables of exit: yield, mechanical resistance, iodine number and ashes. The disturbances or entrance variables studied and the established levels were the following:

Table 1. Actual factors and their level.

Parameters	Code	Low (-1)	Center (0)	High (+1)
temperature (°C)	X_1	800	850	900
residence time (min.)	X_2	60	90	120

The regression analysis, to fit the equations, was realized with the aid of Statgraphics Plus version 5. The characteristics of the reliability of the analysis carried out was measured by the variability in the observed responses values expressed by coefficient of determination R^2, the probability P-value (95% confidence level) and Fisher's test.

Multiple Response Optimization

Response surface methodology is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. This procedure helps to determine the combination of experimental factors that simultaneously optimizes several responses. To find the combination of factors which achieves the overall optimum desirability a convenience function is created. The goals of the response are selected and set as it showed (Table 2). The general model used (general expression of the gradient method) is as follows:

$$\frac{dx_i}{ds} = \pm\left[\sum_{i=1}^{n}\left(\frac{\partial y}{\partial x_i}\right)^2\right]^{-1/2} * \left(\frac{\partial y}{\partial x_i}\right) \quad (2)$$

Where: $\frac{dx_i}{ds}$ variable change in the selected direction, $\frac{\partial y}{\partial x_i}$ changes in the value of the objective function according to X_i

Table 2. Optimization by multiple responses.

Answers	Convenience Low	High	Objective
yield	22.5	65.6	maximize
ashes	6	17	minimize
mechanical resist.	49	91	maximize
Iodine number	965	1258	maximize
molasses	11	75	minimize

Specific surface area by adsorption of N_2(77 K)

Adsorption isotherms of N_2 (77 K) was obtained on a Quantachrome Autosorb Surface Analyzer System. The BET isotherm, Eq. (3), is the most usual standard procedure used when characterizing an activated carbon. [3-,5]

$$\frac{\left(\frac{P}{P_o}\right)}{V_o\left(1-\frac{P}{P_o}\right)} = \frac{1}{(V_m C)} + \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right) \quad (3)$$

Where: P (mm Hg) is the applied pressure, P_o (mmHg) vapor pressure of N_2 at 77 K, V_o (cm^3/g) volume of adsorbed gas, V_m (cm^3) volume of gas adsorbed monolayer and C constant.

Application of the Dubinin-Radushkevich model to micropores

The isotherm was adjusted by the Dubinin-Radushkevich (DR) model, Eq. (4), of a single term developed on the basis of the theory of volumetric filling, which describes satisfactorily vapor adsorption microporous solid at temperatures below the critical temperature of the adsorbate: where W_a is the amount adsorbed in the micropores at the equilibrium pressure P_e; W_m is the maximum adsorption in the micropores (mmol/g); n = 2 is an empirical parameter that depends on the structure of the adsorbent and the adsorbate, the adsorption characteristic energy E_0(kJ/mol), β (0.33 to N_2) affinity coefficient; and the term A is the differential change of free energy, Eq. (5).[4,5]

$$W_a = W_m \exp\left(-\left(\frac{A}{\beta E_0}\right)^2\right) \quad (4)$$

$$A = -\Delta G = RT\ln\left(\frac{p_e}{p_0}\right) \quad (5)$$

For the determination of maximum adsorption and the characteristic energy of the system Eq. (6) is used:

$$\ln W_a = \ln W_m - \left(\frac{RT}{E_0}\right)^2\left(\ln\frac{P_0}{P_e}\right)^2 \quad (6)$$

A straight line is obtained on a graph $\ln W_a$ vs. $\ln P_0/P_e$ and whose intercept allows the calculation of maximum adsorption and slope characteristic energy E_0, which is related to the half aperture of the pores W_m (nm), Eq. (6), and the micropore volume (cm^3/g), where V_m is the molar volume(cm^3/mol) of the adsorbate at T(K) absolute. After calculating the maximum adsorption and the characteristic energy, the radius of gyration R_g(nm) is calculated using Dubinin-Steockli Eq. (7), where:[4]

$$W_m = 4.6699\exp^{-(0.0666 * E_0)} \quad (7)$$

$$R_g = 0.05 + 0.5W_m \quad (8)$$

Methane adsorption

The team which carried out adsorption processes at high pressure is brand Particulate System of HPVA-100 series, this equipment is designed for isotherms at high pressure using different gases as hydrogen, methane and carbon dioxide by volumetric analysis. The first stage of the process consisted of degassing of the sample to remove moisture and other components within it: the activated carbon is heated to 473 K reaching a vacuum for 12 h. The adsorption process was conducted at room temperature (298 K), submerging the sample chamber in a cooling bath throughout the process to ensure the temperature of 298 K; the final adsorption pressure reached in the process was 3.5 MPa. The isotherm obtained was adjusted by the Toth model isotherm (Eq.9) because of equation satisfies both the low and high end requirement and describes many systems with sub-monolayer coverage very well. The pattern of Toth is commonly used for heterogeneous activated carbon.[6]

$$N_{abs} = N_{max} \times \frac{bf}{[1+(bf)^t]^{\frac{1}{t}}} \quad (9)$$

Where: N_{abs}: moles adsorbed; N_{max}: maximum capacity; b, t: parameters of the model

RESULTS AND DISCUSSION

With the realized test resulted the equations and the influence that exert each one of the parameters studied on the selected dependent variables, as well as the possible interrelations between these last ones were determined (Table 3). Next, the analyses realized for each one of the equations of the obtained mathematical models from the experimental data are expressed.

The lack of fit test is designed to determine whether the selected model is adequate to describe the observed data, or whether a more complicated model should be used. The test is performed by comparing the variability of the current model residuals to the variability between observations at replicate settings of the factors. It can be concluded that the given models describe the investigated system very well throughout the experimental range. In all cases, the effects had p-values less than 0.05, indicating that they are significantly different from zero at the 95 % confidence level.

Table 3. Results polynomial adjustment system

Parameter	Final Equation (actual factors)	R^2	Lack of fit p-value (95%)	Durbin-Watson
Iodine number (mg/g)	$= 1150.4 + 84t + 85.96T$	95	0.73 > 0.05	0.14 > 0.05
Yield (%)	$= 46.6 - 12.34t - 10.52T + 2.7T^2 - 1.7tT - 2t^2$	97	0.053 > 0.05	0.49 > 0.05
Ashes (%)	$= 8.072 + 2.33T + 2.8t + 1.46t^2 + 1.67tT$	94	0.08 > 0.05	0.37 > 0.05
Mechanical stress (%)	$= 87.48 - 9t - 10. -6.5t^2 — 7.4tT - 4T^2$	96	0.055 > 0.05	0.32 > 0.05
Molasses (%)	$= 45.45 + 18.4.t + 21.2T$	98	0.056 > 0.05	0.14 > 0.05

Multiple Response Optimization

As one of the objectives of this work it is to determine the time and the temperature for the obtaining of AC_{opt}, the polynomials equations system were exploited using response surface methodology. (Fig. 1; Table 4). These responses have been represented and studied in all experimental regions of activation time and activation temperature, the most influential factors in activated carbon preparation. Optimization to obtain activated carbons with textural characteristics suitable to use in methane adsorption has been carried out. According to the calculation method used, the optimal point indicated an activation time of 94 min and 800 °C of activation temperature.

Table 4. Optimal value function of convenience = 0.68

Input variables	temperature	800 °C
	residence time	94 min
Output variables	yield	58 %
	iodine number	1080 mg/g
	mechanical resistance	93 %
	ashes	6 %
	molasses	26 %

The obtained material under those experimental conditions it was characterized with N_2 (77 K), (Fig. 2). The specific surface area was deduced by applying BET equation from isotherm and DR equation was used to calculate the micropores characteristics (Fig. 3; Table 5**)**. These results show an appropriate development of superficial area, V_m and size micropores to methane adsorption. The Table 6 reflects with very good reproducibility the characteristics predicted previously by means of MRO.

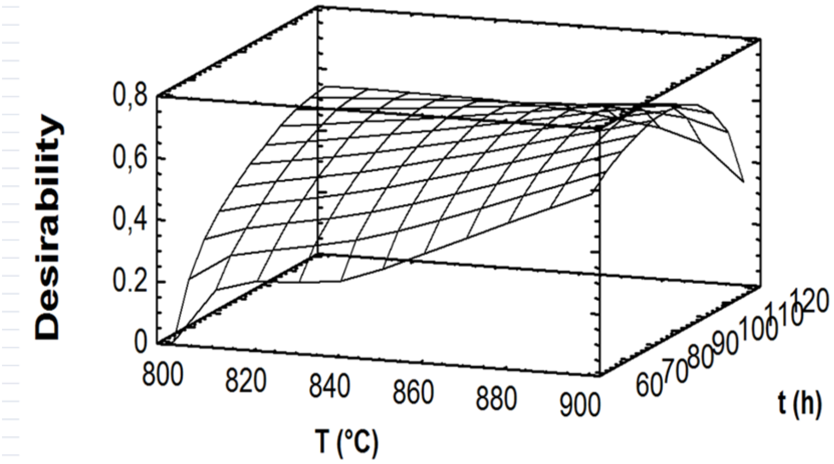

Fig. 1. *A three-dimensional system response surface plot for effect.*

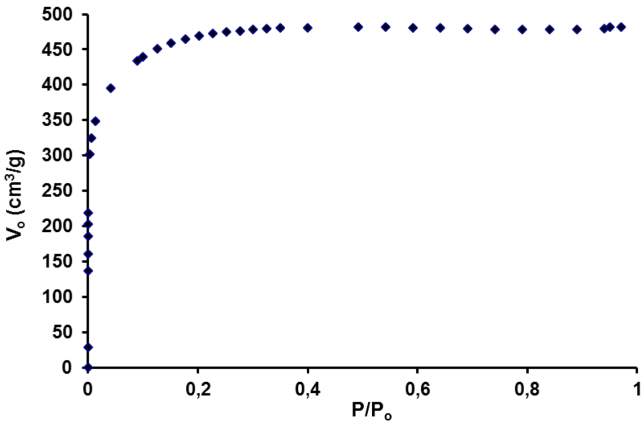

Fig. 2. *N_2 isotherms of $AC_{opt.}$ and DR*

Methane adsorption

The methane adsorption is carried out to near the ambient temperature (298 K). To this temperature is already the fluid under supercritical conditions since the critical temperature of the methane it is 190 K and it is in gassy state, for then, the process of adsorption is recommended to make it to discharges pressures to achieve the gas adsorption into the micropores of the material. Fig. 3 shows the isotherm of methane. It also exhibits a behavior type I in fluids to supercritical conditions, like it happens to the methane, in which one gives the adsorption for monolayer formation or for two layers near the surface of the solid to discharges pressures. In the Toth model, t is usually less than 1, the more t deviates from 1, the more heterogeneous the system is.[7]This equations characterize the heterogeneity of the methane-granular activated carbon system. The isotherm parameters were adjusted for the model of Toth, the same the following results were obtained: factor storage (98.4 V/V), N_{max} (7.5 mmol/g), t (0.85), b (0.15 MPa^{-1}) and efficiency dynamic (0.68 %). These results are in correspondence with those obtained by other authors with similar materials.[1-3,6,7] Other results using activated carbons synthesized from lignocellulosic residues such as waste olive oil have storage capacities of 59 V/V. Other authors have reported storage capacities between 64-94 V/V using coconut shells. Capacities up to 95 V/V with activated carbon from coconut shell activated with phospho- ric acid have also been reported. Other values for activated carbon derived from waste tires have reached storage capacity of methane between 45 - 50 V/V. [8-11]

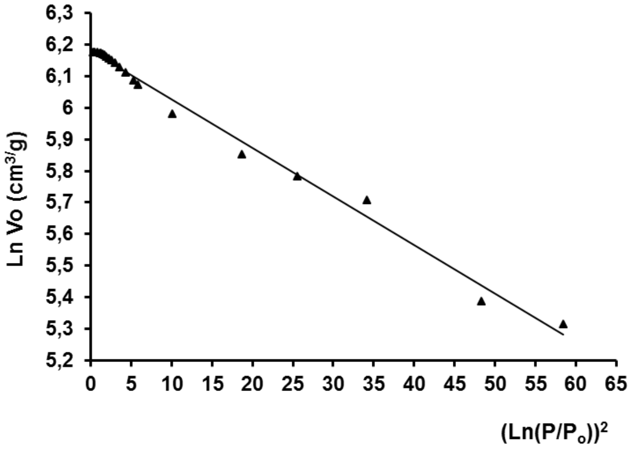

Fig. 3 *Adsorption isotherms from fitted by D-R (R^2=99)*

Earlier theoretical studies found that for methane adsorption on slit-pore activated carbon, the optimum pore width is 11.2 to 11.4 Å to create the maximum density for the adsorbed phase. Therefore, the pore width of AC_{opt} is close to the optimum pore width (13 Å), (Table 5). The activated carbon (without modification) under study presents the optimum parameters are estimated theoretically and present similar characteristics of many other materials. As it is expected, to the future, this material can be substantially improved, taking into account other important properties such as: density, compaction, chemical treatment and others. [1-3,9-11]

Table 5. Surface area of activated carbons and volume of monolayer N_2 at 77 K obtained from BET and DR Equation

Adsorbent	Surface área (m^2/g)	V_T (cm^3/g)	V_m (cm^3/g)	W_m (nm)	R_g (nm)	E_o (kJ/mol)
AC_{opt}	1540	0.63	0.494	1.3	0.6	19.27

Usually these materials have been studied with a view to its application in the automovilistic industry, but this is not the only interesting output, though financially it involves great benefits. For countries like ours is a very good alternative having this material, as it allows to investigate more in this field of applications. We have materials, raw materials resources and practices level scientist to make the necessary improvements to the introduction of this product in industrials applications.[2,6,7]

Table 6. Evaluation of the experimental

Exp.	ashes (%)	yield (%)	Iodine number (mg/g)	mechanical resist. (%)	molasses (%)
$AC_{optimum}$	6	64	1050	91.5	12

Methane adsorption

The methane adsorption is carried out to near the ambient temperature (298 K). To this temperature is already the fluid under supercritical conditions since the critical temperature of the methane it is 190 K and it is in gassy state, for then, the process of adsorption is recommended to make it to discharges pressures to achieve the gas adsorption into the micropores of the material. (Fig.4) shows the isotherm of methane. It also exhibits a behavior type I in fluids to supercritical conditions, like it happens to the methane, in which one gives the adsorption for monolayer formation or for two layers near the surface of the solid to discharges pressures. In the Toth model, t is usually less than 1, the more t deviates from 1, the more heterogeneous the system is.[7]This equations characterize the heterogeneity of the methane-granular activated carbon system. The isotherm parameters were adjusted for the model of Toth, the same the following results were obtained: factor storage (98.4 V/V), N_{max} (7.5 mmol/g), t (0.85), b (0.15 MPa^{-1}) and efficiency dynamic (0.68 %).These results are in correspondence with those obtained by other authors with similar materials.[1-3,6,7] Other results using activated carbons synthesized from lignocellulosic residues such as waste olive oil have storage capacities of 59 V/V. Other authors have reported storage capacities between 64-94 V/V using coconut shells. Capacities up to 95 V/V with activated carbon from coconut shell activated with phospho- ric acid have also been reported. Other values for activated carbon derived from waste tires have reached storage capacity of methane between 45 - 50 V/V. [8-11]

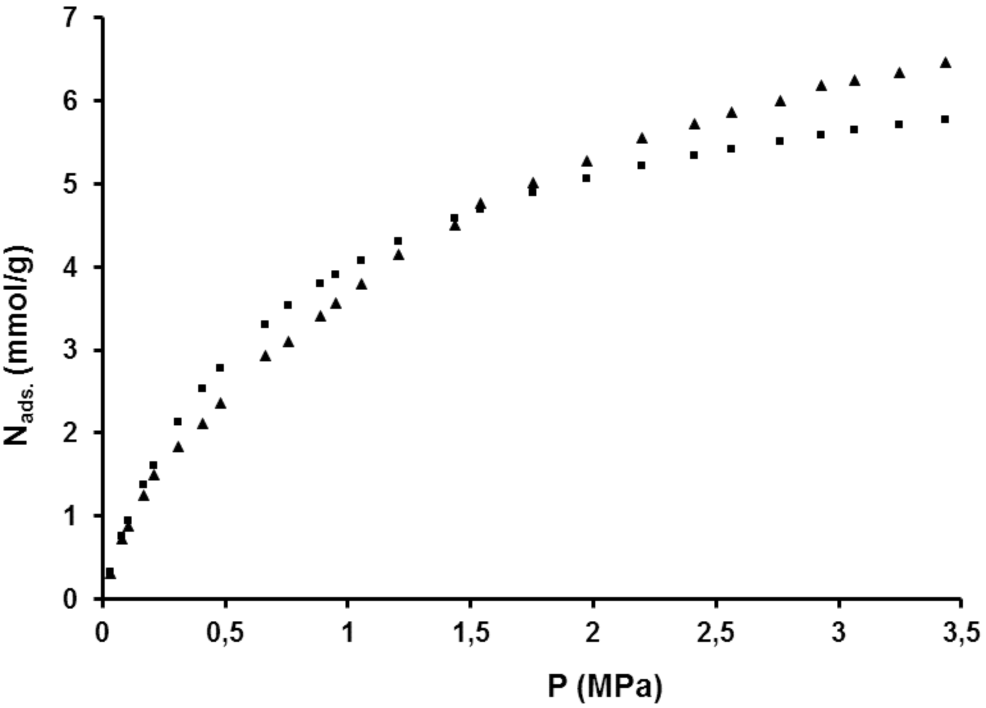

Fig. 4. Study of adsorption capacity of methane on $AC_{optimum}$:
Toth model (■) Experimental (♦)

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Toth model statistical analysis
It´s carried out a Kolmogorov - Smirnov test to compare the distributions of the two samples (experimental and calculated). Since the P-value (0.72) is greater than to 0.05, there is not a statistically significant difference between the two distributions at the 95 % confidence level. Of particular interest here are the standardized skewness and standardized kurtosis. Values of these statistics outside the range of -2 to +2 indicate significant departures from normality, which would tend to invalidate the tests. Standardized skewness values are within the range expected. Both standardized kurtosis values are within the range expected. F-test to compare standard deviations of the two samples. It also constructs confidence intervals or bounds for each. Since the interval (0.35 to 1.73) contains the value 1, there is not a statistically significant difference between the standard deviations of the two samples at the 95 % confidence level.

CONCLUSIONS
It was shown that the Cuban activated carbon (CA_{opt}) has natural qualities for adsorption of methane. These features allow considering this material as a candidate for use in methane storage. The baseline established under the experimental conditions, can be modified later with the introduction of improvements in the textural properties and density of this material. Toth model fits the experimental data well at the 95 % confidence level.
We believe that the results are still preliminary. It is likely that other characteristics influence the results obtained, and we believe that should be carried out other experiments with a considerably larger set of samples would be required to obtain a trend by statistics.

Acknowledgements

The authors thank to Programa de Estudantes-Convênio de Pós-Graduação (PEC/PG), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes), Brazil.

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