



## Studies of kinetics, balance and thermodynamics of diuron adsorption in aqueous solution using granulated Babassu coconout activated carbon

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**Resumo:** O carvão ativado granulado de babaçu (BAC) *in natura* foi utilizado como material adsorvente para investigar a eficiência do mesmo na remoção do herbicida diuron em solução aquosa. O balanço adsorptivo é representado pelas isotermas, parâmetros cinéticos e termodinâmicos de adsorção em duplicata, considerando o efeito da temperatura na adsorção em 298, 308 e 318 ± 2 K. O BAC apresentou área específica de 517,4 m<sup>2</sup> g<sup>-1</sup>, com estrutura predominantemente microporosa e superfície com tendência alcalina (pH de carga zero de 7,8). Os resultados indicaram que o balanço de adsorção foi atingido em 300 minutos, obtendo 34,40 mg g<sup>-1</sup> de adsorvido e eficiência de remoção de 62,3%. Os dados cinéticos foram melhor descritos conforme modelo de pseudo primeira ordem. As retenções de diuron foram favorecidas com o aumento da temperatura, indicando que este parâmetro tem grande importância na adsorção. Os dados do balanço ficaram ajustados ao modelo isotérmico de Langmuir, indicando que a superfície do BAC estava completamente coberta por uma monocamada de moléculas de diuron em 318 K (56,5 mg g<sup>-1</sup>). A adsorção de diuron no BAC resultou em um processo endotérmico espontâneo com aumento da desordem que ocorre no sistema que é regulado pelo efeito da fisissorção. Os resultados apresentam eficiência do BAC como adsorvente na remoção de diuron em solução aquosa.

Palavras-chave: Diuron, Solução aquosa, Adsorção, Carvão ativado de Babassu.

**Abstract:** The babassu coconut granular activated charcoal (BAC) was used as adsorbent material to investigate how efficient it was in the removal of the herbicide diuron in aqueous solution. The balance of data were represented by the isotherms, kinetic and thermodynamic parameters of adsorption in duplicate, considering the effect temperature on adsorption in 298, 308 and  $318 \pm 2$  K. The BAC submitted specific area of  $517.4 \text{ m}^2 \cdot \text{g}^{-1}$ , with predominantly microporous structure and surface with alkaline trend (pH of zero load of 7.8). The results indicated that the adsorption balance was reached in 300 minutes, getting  $34.401 \text{ mg} \cdot \text{g}^{-1}$  of amount adsorbed and removal efficiency of 62.3 %. Kinetic data were best described through the pseudo-first-order model. The retentions of diuron were favored with increasing temperature, indicating that this parameter has great importance in adsorption. The balance data were well adjusted to the isothermal model of Langmuir, indicating that the surface of the BAC was completely covered by a monolayer of molecules of diuron in 318 K ( $56.5 \text{ mg} \cdot \text{g}^{-1}$ ). The adsorption of diuron in BAC resulted in a spontaneous, endothermic process with an increase in the disorder of the system and regulated by physisorption. Results showed the efficiency of the BAC as an adsorbent in diuron removal from aqueous solution.

**Keywords:** Diuron, Aqueous solution, Adsorption, Activated babassu charcoal.

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## 1. Introduction

The environmental contamination by pesticides has raised many concerns worldwide about the preservation of the quality of water resources, such as (KONSTANTINOU, HELA, and ALBANIS, 2006 and GILLIOM, 2007). Emphasize, due to widespread use in agriculture worldwide and having different levels of toxicity, persistence, and mobility in the environment. From the herbicides used in agriculture, diuron (3-(3,4-diclorofenil)-1,1-dimethylurea) belongs to the family of the phenylurea replaced, used as pre- and post-emergent preferably in the growth control of a variety of broadleaf weeds, grass weeds and mosses, acting also with effectiveness in the treatment of non-agricultural areas, according to (BAHRI *et al.* 2012).

For being considered an emerging pollutant, responsible for the degradation of water quality, by (GIACOMAZZI, 2004). Was classified as dangerous to the environment in priority status of contamination by the European Community, according to (MALATO *et al.* 2002). Being the object of increasing environmental concern. Diuron has frequently been detected in several studies about rivers, surface water, groundwater, soil and sediment with concentrations above health regulations for drinking water in France ( $> 0.1 \mu\text{g}\cdot\text{L}^{-1}$ ), the United States ( $> 10 \mu\text{g}\cdot\text{L}^{-1}$ ) and Canada ( $> 150 \mu\text{g}\cdot\text{L}^{-1}$ ), according to literature. Some of its characteristics such as high environmental persistence (30 to 375 d), chemical stability, relatively high in soil and groundwater and high leaching potential of soil, according to (THURMAN; BASTIAN and MOLHAGEN, 2000), understand the fundamental factors in the contribution for increasing the pollution of aquatic environments.

Treatment of wastewater contaminated by pesticides has been one of the major efforts in recent decades. In general, the conventional treatment procedures are ineffective in recovering the wastewater contaminated by these agricultural residues. In recent years, the practice of adsorption with activated charcoal has been identified as the main way to remove with efficiency low concentrations of pesticides dissolved in aqueous solution, according to literature,(PIRBAZARI; BADRIYHA and MILTNER, 1991), (BHATNAGAR and SILLANPÄÄ, 2010) (LÓPEZ-RAMÓM *et al.* 2007), for being a versatile technique with simple operation and economic feasibility. Activated charcoal is a carbonaceous material with high surface area and enhanced porosity, which gives it high adsorbent capacity in water treatment. However, depending on the type of precursor used in its production and previous treatments, it can present some use limitations, such as high cost, loss of regeneration and short lifespan, according to (GUPTA and SUHAS, 2009) and (ZOLGHARNEIN; SHAHMORADI and GHASEMI, 2011).

The use of renewable agricultural by-products as a raw material in the usage of activated charcoal in adsorption has better advantages over other adsorbent materials, such as lower energy costs and viability, since they can be found in large quantity in Brazil, The

granular activated charcoal from the raw material of the babassu coconut, a palm tree native to Brazil from botany family *Arecaceae*, achieved efficient removals of different contaminants of solutions, such as drugs, dyes, metal, among others, as literature reports, (REGALBUTO and ROBLES, 2004) however, in the adsorption of diuron in aqueous solution using HPLC-UV, it has not yet been tested.

In this context, the aim of this study is to assess the efficiency of removal of the herbicide diuron in aqueous solution by adsorption process in babassu coconut granular activated charcoal by means of the isotherms, kinetic and thermodynamic parameters of adsorption.

## **2. Materials and Methods**

### **2.1 Preparation of the solutions of diuron and quantification**

The standard solution of diuron used in all tests of adsorption was prepared in a concentration of approximately  $25 \text{ mg}\cdot\text{L}^{-1}$  with ultrapure water Milli-Q and diuron, this one being used as received, without further purification (suspension concentrate, with 50% of active compound (m/v) and concentration of  $500 \text{ g}\cdot\text{L}^{-1}$ ). In tests of adsorption, the pH of the aqueous solution of diuron remained around 6.5 (without prior adjustment), since it reflects the same pH range that most wastewaters are normally found.

The calibration curve was prepared by the preparation of the solution stock  $1000 \text{ mg}\cdot\text{L}^{-1}$  from the analytical pattern of diuron, provided by Sigma Aldrich (purity 99.8 %) and methyl alcohol HPLC degree (purity 99.8 %). From that, different concentrations of diuron ( $20$  to  $0.0125 \text{ mg}\cdot\text{L}^{-1}$ ) by dilution in ultra-pure water Milli-Q were prepared.

The concentrations of diuron were determined for analysis by high-performance liquid chromatography (HPLC) (Gilson 307) equipped with a UV-vis spectrophotometer (model 151) ( $\lambda_{\text{máx}} = 247 \text{ nm}$ ) using column C18 Microsorb – MV maintained at  $35 \text{ }^\circ\text{C}$  and isocratic pump ( $4.6 \text{ mm} \times 250 \text{ mm}$ ,  $5 \text{ }\mu\text{m}$  and  $10 \text{ nm}$  ( $100 \text{ \AA}$ )). The mobile phase used for elution was a mixture of acetonitrile and ultra-pure water Milli-Q of 65:35 v/v (65:35 volume %), according to (TAN *et al.* 2012) a flow rate of  $0.75 \text{ mL}/\text{min}$ . The manual injection volume sample was of  $20 \text{ }\mu\text{L}$  and retention time of 8 min.

### **2.2 Characterization of adsorbent material**

The granular activated babassu coconut charcoal (BAC), with an average diameter of  $0.50 \text{ mm}$  (35 mesh).

The textural parameters of the adsorbent, which include micropores area, and micropores volume (t-plot method), total pore volume, micropores diameter (DA method), mesopores area, mesopores volume and mesopores diameter (BJH method) were assessed by N<sub>2</sub> adsorption and desorption isotherms in the equipment QuantaChrome model New 1000 Series, at 77 K with liquid N<sub>2</sub>. Before the experiments, the sample of BAC (≈50 mg) went through vacuum pre-treatment (10<sup>-2</sup> Pa) for 2 h at 105 °C. The specific surface area (S<sub>BET</sub>) was calculated by the BET equation (in the range 0.05 < P/P0 < 0.35).

The point of charge zero (pH<sub>PCZ</sub>) of the samples was estimated by the methodology described by (REGALBUTO and ROBLES, 2004) in which it evaluates the difference between the final and initial pH (ΔpH) in relation to the initial pH. For this, was assessed different pH conditions (1 to 12) with the exception of pH 7, in duplicate and under pH adjustment with solutions of HCl and NaOH at 0.1 mol·L<sup>-1</sup> and 1 mol·L<sup>-1</sup>. Samples were shaken to 200 rpm in a refrigerated incubator with orbital mechanical shaking, for 4 h at 25 ± 2 °C.

### 2.3 Adsorption kinetics of diuron in BAC

The kinetic study of adsorption was conducted in a refrigerated incubator to 25 ± 2.0 °C and under shaking 200 rpm. For this process, it was added 500 mL of an aqueous solution of diuron with an initial concentration of 25.72 mg·L<sup>-1</sup> kept at the neutral pH (around 6.5, without prior adjustment) in 2 g·L<sup>-1</sup> of BAC. When the shaking started, each sample was measured in duplicate at regular intervals of time of up to 360 min. After that, the samples were filtered in a 0.45 μm diameter and its concentrations were quantified HPLC-UV in 247 nm.

The maximum retentions of diuron in each sample before balance (q<sub>t</sub>) was calculated by Equation (1), whereas, the removal efficiency (% R) was calculated by Equation (2):

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad (1)$$

$$\% R = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where, q<sub>t</sub> is the amount of diuron adsorbed (mg·g<sup>-1</sup>) in each hour of time (h), m is the mass (g) of BAC, C<sub>0</sub> is the diuron initial concentration (mg·L<sup>-1</sup>), C<sub>t</sub> corresponds to the remaining concentration of diuron at equilibrium (mg·L<sup>-1</sup>) in each hour time (h), and V is the volume (L) of solution of diuron in contact with BAC.

The kinetic experimental data were adjusted to the pseudo-first order models and pseudo-second-order through Equations (3) and (4), according to (LAGERGREN, 1898) and (HO and MCKAY, 1999) respectively:

$$q_t = q_{eq} (1 - e^{-k_1 t}) \quad (3)$$

$$q_t = q_{eq} \frac{k_2 t}{1 + k_2 t} \quad (4)$$

where  $k_1$  is the constant rate of adsorption of the pseudo-first-order model ( $\text{h}^{-1}$ ),  $k_2$  is the constant rate of adsorption of pseudo-second order ( $\text{mg}/(\text{g}\cdot\text{min})$ ), and  $q_{eq}$  corresponds to the quantity adsorbed ( $\text{mg}\cdot\text{g}^{-1}$ ) of diuron in balance.

The model's parameters were estimated using the Statistic software for Windows®, version 7.0, nonlinear Simplex method, following the method of least squares with absolute error function. The graph was generated using the software Origin 9.0.

## 2.4 Adsorption balance of diuron in BAC

The balance data experimental adsorption were conducted in an incubator with thermostatically-controlled water bath considering the effect of temperature in adsorption in 298, 308 and  $318 \pm 2$  K, kept at neutral pH (around 6.5, without prior adjustment), shaking of 200 rpm, in duplicate. For this process, it was evaluated the influence of the mass of BAC, by adding 0.01 to 0.055 g, with intervals of 0.005 g of the mass of adsorbent in plastic bottles containing 25 mL of an aqueous solution of diuron with an initial concentration of  $23.77 \text{ mg}\cdot\text{L}^{-1}$ , for 10 h. After that, the samples were filtered and quantified by HPLC-UV in 247 nm.

The maximum retentions of diuron in each sample after balance ( $q_{eq}$ ) was calculated by Equation (1), replacing  $q_t$  by  $q_{eq}$ . Models Langmuir and Freundlich expressed in Equations (5) and (6), according to (LANGMUIR, 1918) and (FREUNDLICH, 1906), respectively, were used to investigate the adsorption balance of diuron in aqueous solution:

$$q_{eq} = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \quad (5)$$

$$q_{eq} = K_F C_{eq}^{1/n} \quad (6)$$

where  $q_{\max}$  is the constant that represents the maximum capacity adsorbed ( $\text{mg}\cdot\text{g}^{-1}$ ) in a monolayer under the adsorbent,  $C_{\text{eq}}$  corresponds to the concentration adsorbed of diuron in solution in balance ( $\text{mg}\cdot\text{L}^{-1}$ ),  $K_L$  is the equilibrium constant of Langmuir ( $\text{L}\cdot\text{mol}^{-1}$ ),  $K_F$  is the constant of Freundlich ( $(\text{mg}\cdot\text{g}^{-1})(\text{L}\cdot\text{mg}^{-1})^{1/n}$ ), and the exponent  $n$  expresses the intensity of the adsorption process.

Both the parameters of the models and the generated graph were obtained from the same programs used in the kinetic adsorption test, respectively.

## 2.5 Thermodynamics study of diuron adsorption in BAC

The thermodynamic quantities given by the heat of adsorption ( $\Delta H^\circ$ ), the entropy of the system ( $\Delta S^\circ$ ) and Gibbs free energy ( $\Delta G^\circ$ ) were determined considering the effect of the three temperatures evaluated in the adsorption isotherms. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated by Van't Hoff equation given by Equation (7):

$$\ln K_L = -\frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (7)$$

where  $T$  absolute temperature (K) and  $R$  the constant for ideal gases ( $8.314 \text{ J}/(\text{mol}\cdot\text{K})$ ).

Then, it was determined the variation of Gibbs energy by Equation (8):

$$\Delta G^\circ = \Delta H^\circ + \Delta S^\circ \quad (8)$$

## 3 Results and Discussion

### 3.1 Characterization of adsorbent material

According to Table 1, the total specific area of the BAC was  $517.4 \text{ m}^2\cdot\text{g}^{-1}$ , whose value is consistent with the limit recommended for commercial activated charcoal according to (DROSTE, 1997). Of this total, 74.41 % corresponds to the area of micropores and approximately 3.94 % to the area of mesopores, indicating the presence of a heterogeneous distribution of pores, with the predominantly microporous surface. The  $112.02 \text{ m}^2\cdot\text{g}^{-1}$  remaining correspond to the area of macropores. The result from the application of the t-plot method reveals that activated carbon showed a higher amount of micropore volume ( $V_{\text{micro}}$ ), it corresponds to 90.49 % of the total porous volume. In relation to the size of the pores, there was

predominance to primary micropores, presenting average diameter of 36.6 nm (3.66 Å), as well as a small contribution of mesopores with an average diameter of 341.2 nm (34.12 Å).

Table 1: Volume of pores of BAC

Sample	$S_{\text{BET}}$	$S_{\text{micro}}$	$V_{\text{total}}$	$V_{\text{micro}}$	$d_{\text{micro}}$	$S_{\text{meso}}$	$V_{\text{meso}}$	$d_{\text{meso}}$
BAC	517.4	385	0.305	0.27	3.66	20.38	0.03	34.12

$S_{\text{BET}}, S_{\text{micro}}, S_{\text{meso}} = \text{m}^2 \cdot \text{g}^{-1}$ ,  $V_{\text{total}}, V_{\text{micro}}, V_{\text{meso}} = \text{cm}^3 \cdot \text{g}^{-1}$ ,  $d_{\text{micro}}, d_{\text{meso}} = \text{Å}$  (0.1 nm)

As shown in this Figure 1, the linear sector of the chart (between 5 and 10) that crosses the x-axis determines the value of the  $\text{pH}_{\text{PCZ}}$  as being 7.88, indicating that the surface of the BAC was neutral and positively charged, revealed characteristics with the alkaline trend. According to (LÓPEZ-RAMÓM *et al.* 2007) on the surface of a granular activated carbon are generally found either phenolic hydroxyl groups or carboxylic groups. This same trend is also observed in the spectrum of the crude babassu coconut epicarp (170-80 mesh). Based on this, it is suggested that the surface of the adsorbent studied obtained a relatively higher amount of phenolic hydroxyl groups relative to the carboxylic groups.

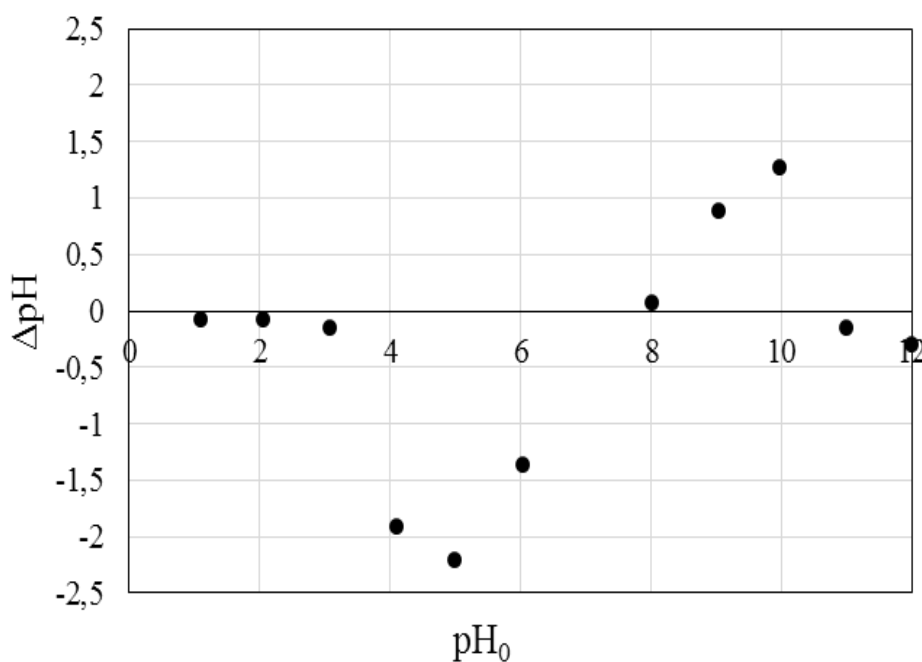


Figure 1: Determination of the zero load point of the BAC.

### 3.2 Adsorption kinetics

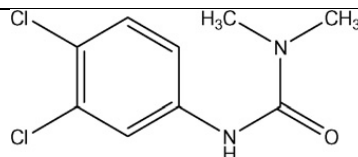
According to (FONTECHA-CÁMARA *et al.* 2007) diuron behaves as neutral in pH above 6.0, whereas below this pH, the species are positive. However, the pH of the aqueous solution of diuron after contact with the particles of the BAC has suffered a decline of 6.5 to

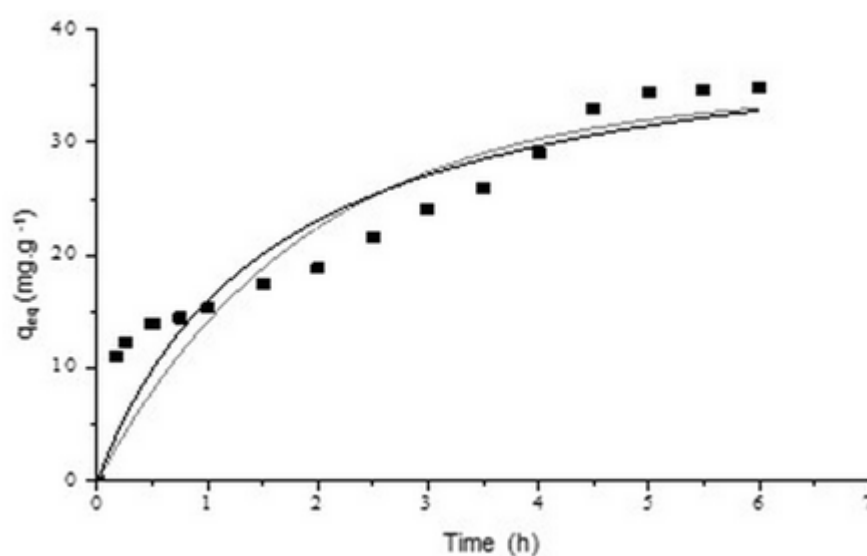


values around 4.5 - 5.5. Based on this information, under room temperature and  $pH_{PZC}$ , molecules of diuron positive were weakly adsorbed on the surface neutral and positively charged of the adsorbent, propelled by the repulsive forces of Van der Waals within the system diuron-BAC.

Since the solubility of diuron in water is relatively high, as shown in this Table 2, the hydrogen bonds formed between molecules of diuron and solvent are favored in low-temperature, however, due to the moderate hydrophobicity either of molecules of diuron or the surface of the BAC. They posed relative difficulty to form as planarity decreases and the dipolar moment of molecules of diuron, according to (SANTOS; O'MALLEY and ALMEIDA, 1998). Figure 2 presents the kinetic behavior of diuron at room temperature. As a result, the molecules of diuron became partially prevented from accessing the micropores of the BAC, showing the behavior of the sinusoidal experimental data (Figure 2).

**Table 2:** Structure and properties of diuron.

Properties	Diuron
Chemical Structure	
Solubility in water at 25 °C ( $mg \cdot L^{-1}$ )	42
log Kow	2.85
Moment dipolar (D)	7.55
Molecular Area ( $nm^2 \cdot molécula^{-1}$ )	0.75
Molecular size (nm)	1.29 x 0.77 x 0.74



**Figure 2:** Kinetic behavior of adsorption of diuron in BAC to 25 °C.

The system formed by diuron-water-adsorbent is quite complex, depending mainly on the physicochemical properties of the sorbent and adsorbate. Thus, relatively high molecular dimensions of diuron (area and size) (Table 1) and the presence of high amount of macropores, as well as a small contribution of mesopores in the surface of the adsorbent, according to (MORENO-CASTILLA, 2006) and (FONTECHA-CÁMARA *et al.* 2007), are factors that have also contributed in the reduced accessibility, and therefore, in the retention of absorption of molecules of diuron in the surface of the adsorbent studied, in virtue of the increase resistance to mass transfer. These results contradicted other studies involving diuron and granular activated charcoal such as (LÓPEZ-RAMÓN *et al.* 2007) (MORENO-CASTILLA, 2006) and (FONTECHA-CÁMARA *et al.* 2007), which reported the predominance of non-electrostatic interactions, due to surface and adsorbate both neutral at pH 7.

Thus, the balance of experimental adsorption of diuron in the BAC was only achieved in a longer time range, reaching a maximum experimental retention ( $q_t$ ) of 34.89 mg·g<sup>-1</sup>, removal efficiency (% R) of 63.23 % and final concentration balance ( $C_{eq}$ ) (in solution) equal to 9.46 mg·L<sup>-1</sup> in 360 min. This low quantity adsorbed is attributed to the nature of the adsorbent studied, according to (MORENO-CASTILLA, 2006), is a consequence of the relative amount of mesopores and the surface charge of the BAC, showing it as a not suitable sorbent to the removal of the herbicide diuron.

In Table 3, it is presented the parameters of the models of pseudo-first-order and pseudo-second-order for the kinetics of adsorption, which was calculated from the nonlinear regressions expressed in Equations (3) and (4). The pseudo-first-order model, compared with pseudo-second-order, obtained the best adjustment to experimental data because the  $q_{eq}$  (34.47 mg·g<sup>-1</sup>) remained closest to what was obtained experimentally (34.89 mg·g<sup>-1</sup>). However, the intermediate adjustment ( $R^2$ ) of 0.83 of this model indicated that the retention of the adsorbent studied (BAC) at room temperature wasn't effective in the proposed separation process, corroborating with low efficiency found for the contaminant in aqueous solution (62.23 %).

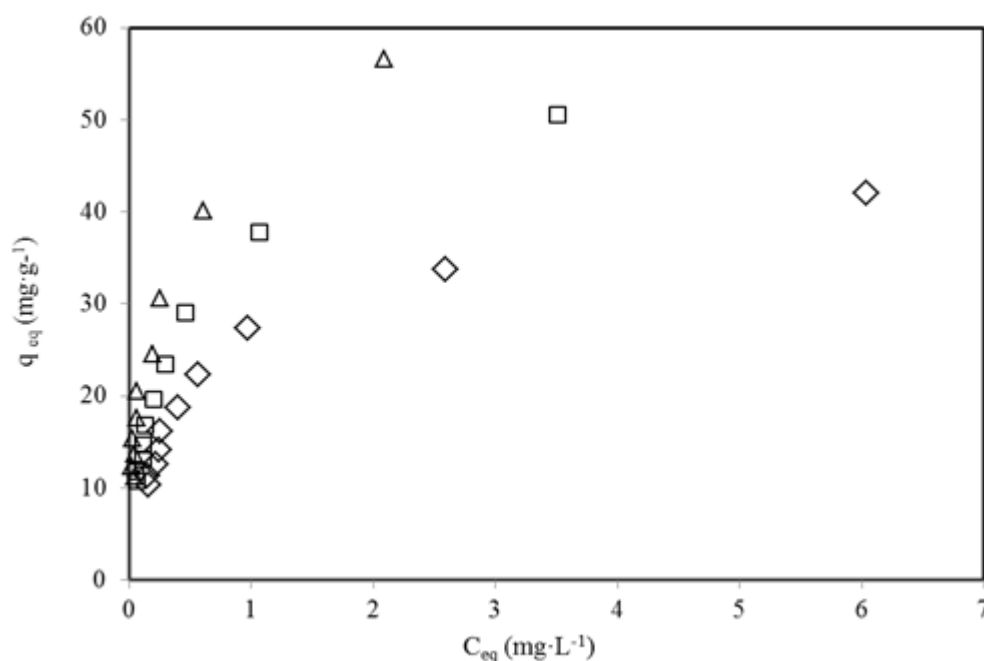
Table 3: Kinetics parameters of adsorption

Kinetic model	Parameters	pH 6
Pseudo-first order	$q_{eq}$ (mg·g <sup>-1</sup> )	34.48 ± 3.24
	$k_1$ (h <sup>-1</sup> )	0.53 ± 0.13
	$R^2$	0.83
Pseudo-second order	$q_{eq}$ (mg·g <sup>-1</sup> )	41.58 ± 4.55
	$K_2$ (h <sup>-1</sup> )	0.01 ± 0.01
	$R^2$	0.87

$k_1$  is the constant of pseudo-first-order,  $k_2$  is the constant of pseudo-second-order and  $q_{eq}$  is the amount adsorbed of the analyte.

### 3.3 Adsorption isotherms

The results behavior of diuron adsorption isotherms evaluated in the temperatures (298 K, 308 K, and 318 K) are displayed in Figure 3. Whereas in Table 4, are the values of the parameters of both models evaluated (Langmuir and Freundlich) in different temperatures, in pH slightly acid, calculated by Equations (5) and (6).



**Figure 3:** Adsorption experimental isotherms of diuron on BAC at 298 K ( $\diamond$ ), 308 K ( $\square$ ) and 318 K ( $\Delta$ ).

**Table 4:** Parameters of the adsorption isotherms of diuron in BAC.

Isotherms	Parameters	298 K	308 K	318 K
Langmuir	$q_{\max}$ ( $\text{mg}\cdot\text{g}^{-1}$ )	43.12	52.35	54.28
	$K_L$ ( $\text{L}\cdot\text{mol}^{-1}$ )	1.98	3.10	6.75
	$R^2$	0.99	0.98	0.95
Freundlich	$K_F$ ( $(\text{mg}\cdot\text{g}^{-1})(\text{L}\cdot\text{mg}^{-1})^{1/n}$ )	24.17	34.01	45.06
	$n$	3.02	2.86	2.95
	$R^2$	0.98	0.98	0.99

The maximum retentions of diuron in aqueous solution ( $q_i$ ) were of  $42.25 \text{ mg}\cdot\text{g}^{-1}$  at 298 K,  $50.55 \text{ mg}\cdot\text{g}^{-1}$  at 308 K and  $56.55 \text{ mg}\cdot\text{g}^{-1}$  at 318 K. It is observed (Figure 3) that, from the increasing quantity of mass of BAC for the entire range tested in concentration balance there was gradual increase in absorption of molecules of diuron with increasing temperature on

adsorption. This increase in adsorption capacity of diuron is attributed to the weakening of the interactions of hydrogen formed between molecules adsorbed and the solvent, as well as between the particles of the BAC and the solvent, in virtue of the decline in resistance to mass transfer as a result of the increase in the temperature, according to (FONTECHA-CÁMARA *et al.* 2006) and (TERZYK, 2004). This way, this behavior has allowed increasing the planarity and also of the dipolar moment of diuron molecules, so that the diffusion in pores and the dehydration of the diuron molecules were favored of the system.

It is possible to check (Table 4) that the maximum capacities adsorbed of diuron in Langmuir model remained closer to the values of  $q_t$  obtained experimentally for all temperatures than the Freundlich model, presenting very favorable adjustments ( $R^2$ ) (above 0.95). Thus, the Langmuir model best described the experimental data and this behavior suggest that the nature of the surface of the BAC is homogeneous and that the temperature was rising, molecules of diuron were best adsorbed adhering to the surface of the BAC in active sites defined and located with the same energy, according to Langmuir. In 318 K, there was greater removal of diuron in aqueous solution ( $56.55 \text{ mg}\cdot\text{g}^{-1}$ ) indicating the total surface of the BAC by a monolayer of the contaminant. Moreover, the rise in temperature increased the adsorption affinity (values  $K_L$ ) for molecules of diuron.

The Langmuir isothermal form was represented by the isotherm type L2, according to the classification of (GILES; SMITH and HUITSON, 1974). This type of isotherm characterizes propensity that does not increase with the concentration of diuron in solution, because of the decrease in the availability of the adsorption sites. Thus, in high temperatures, the affinity of diuron for BAC was more favorable when this hit the saturation level, indicating that there was no strong competition within the solvent by the active sites of adsorption. The same behavior was observed in studies of in buffered aqueous solution at pH 7 using chemically activated charcoal made of fiber and fabric, presenting adsorption with characteristics of a monolayer. On the other hand, (BAHRI *et al.* 2012). predicted the adsorption of diuron in chemically activated charcoal made of grapes seeds as adsorbent whose results were balanced isotherms of type L3 to S3 at low concentrations of diuron with an increase in temperature, with multiple layers of this herbicide under the adsorbent.

### 3.4 Thermodynamic study of adsorption

The adsorption isotherms measured at different temperatures were used for estimating the thermodynamic parameters of adsorption ( $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ ), is presented in Table 5. The values  $\Delta G^\circ$  for all temperatures were negative, reflecting the spontaneous nature of the adsorption process. The positive value of  $\Delta H^\circ$  indicates that adsorption is apparently endothermic, contrary to the usual behavior for gas adsorption. This endothermicity is due to the

dehydration of the molecules of diuron, allowing greater sequencing and accessibility of these molecules to the micropores and, consequently to the active sites of the BAC, as well as the strengthened interactions within the system diuron-BAC, according to literature.

**Table 5:** Thermodynamic parameters for the adsorption isotherms of diuron in BAC to 298, 308 and 318 K.

T (K)	$\Delta G^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta S^\circ$ (J/(K·mol))	$\Delta H^\circ$ (kJ·mol <sup>-1</sup> )	R <sup>2</sup>
298	-49.71	166.98	48.23	0.97
308	-51.38			
318	-53.05			

Despite the positive value of the enthalpy of the system, it is suggested that the overall adsorption of the present study was of physical nature, due to the decline of the interactions of hydrogen within the solvent-diuron system with temperature increase, occurring slowly (360 min). The positive value of  $\Delta S^\circ$  indicates that an increase in the degree of disorder in the liquid-solid interface was necessary, in relation to molecules of diuron adsorbed in aqueous solution, related with the best diffusion of these molecules to the interior of the micropores of the BAC, attracted by its superficial positive charge. As a result, the high value of  $\Delta S^\circ$  contributed significantly in a negative way for Gibbs energy, making the system energetically favorable for the given temperatures. All thermodynamic parameters were very satisfactory to the adsorption process of diuron since they showed great adjustment (R<sup>2</sup>) of 0.97.

#### 4. Conclusion

The potentialities of the activated charcoal from the babassu coconut were investigated in the evaluation of the efficiency of removal of the herbicide diuron in aqueous solution.

The results obtained in this study showed that, at room temperature, the BAC wasn't suitable in the removal of diuron in aqueous solution, achieving efficiency less than 65 % in 360 min, due to the predominance of repulsive interactions between diuron-solvent and the influence of the chemical characteristics within the diuron the adsorbent surface. The effect of temperature on adsorption was a determining factor in the capacity of adsorption of contaminants in solution. Thus, in 318 K, there was greater removal of diuron in aqueous solution reaching 56.55 mg·g<sup>-1</sup>, indicating that the surface of the BAC was completely covered by a monolayer of diuron. The pseudo-first-order equation and the Langmuir model were chosen to represent the experimental data, so that overall adsorption was done by biosorption. The adsorption process was spontaneous and endothermic with an increasing disorder of the system.

## 5. References

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