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DEVELOPMENT OF ACTIVATED CARBON FROM BAMBOO (*Bambusa vulgaris*) FOR PESTICIDE REMOVAL FROM AQUEOUS SOLUTIONS

ABSTRACT: Considering the water scarcity problems facing many countries, the need for water reuse can make activated carbon (AC) an essential product for modern society. In this context, to contribute with better activated carbons that could be used to serve in water treatment, this article discusses these materials production, using bamboo as raw material, and analyses their application effectiveness. The bamboo was collected, transformed into activated carbon, by simultaneous chemical and physical activations, and named H_3PO_4/H_2OAC. The obtained material was characterized by its yield, apparent density, ash content, thermogravimetric analysis, surface area, methylene blue and iodine indexes, pH and point of zero charge analysis, scanning electron microscopy and Boehm titration method. The AC was used as adsorbent for removing the metribuzin, 2,4-dichlorophenoxyacetic acid and furadan pesticides. The H_3PO_4/H_2OAC had a surface area of 1196.30 $m^2 \cdot g^{-1}$ and the obtained adsorption capacity was elevated for furadan (868.98 $mg \cdot g^{-1}$), metribuzin (756.47 $mg \cdot g^{-1}$) and 2,4-dichlorophenoxyacetic acid (274.70 $mg \cdot g^{-1}$).

DESENVOLVIMENTO DE CARVÃO ATIVADO A PARTIR DE BAMBU (*Bambusa vulgaris*) PARA REMOÇÃO DE PESTICIDAS DE SOLUÇÕES AQUOSAS

RESUMO: Considerando os problemas de escassez de água enfrentados por vários países, a necessidade de reuso das águas, pode fazer do carvão ativado (CA) um produto imprescindível à sociedade moderna. Neste contexto, para contribuir com a melhoria de carvões ativados que poderão servir ao tratamento de água, este artigo, discute a produção desses materiais, que teve o bambu, como matéria prima, e analisa a eficácia de sua aplicação. O bambu foi coletado, transformado em carvão ativado mediante ativação química e física simultânea e denominado CA H_3PO_4/H_2O. O material obtido foi caracterizado pelo rendimento, densidade aparente, teor de cinzas, análise termogravimétrica, área superficial, índices de azul de metileno e de iodo, análise do pH e ponto de carga zero, microscopia eletrônica de varredura e método titulométrico de Boehm. O CA foi usado como adsorvente para a remoção dos pesticidas metribuzin, 2,4-diclorofenoxiacético e furadan. O CA H_3PO_4/H_2O apresentou área superficial de 1196,30 $m^2 \cdot g^{-1}$ e a capacidade de adsorção obtida foi elevada para o furadan (868,98 $mg \cdot g^{-1}$), metribuzin (756,47 $mg \cdot g^{-1}$) e 2,4-diclorofenoxiacético (274,70 $mg \cdot g^{-1}$).

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INTRODUCTION

In recent years, there has been a rising expansion of the activated carbon (AC) global market. According to the Transparency Market Research (TMR), the product transactions reached, in 2012, 1.913 billion dollars and the predictions are that at the end of 2019 the numbers surpass the mark of 4.180 billion, presenting an annual increase rate of 11.9% in the 2013-2019 period. Moreover, if 42.14% of the world market volume in 2012 was directed for water treatment and for 35.21% air purification, there is a tendency for the activated carbon market to advance towards the food, pharmaceutical and medical industry (TMR, 2016).

AC is a highly porous carbonaceous material, with an elevated internal surface area and functional groups in its surface with an adsorption affinity for various contaminants. AC is obtained from controlled pyrolysis of a raw material, where temperatures vary from 400 to 1000 °C, and consequent physical and chemical activation (RIBEIRO, 2005; BRUM et al., 2008; AVELAR et al., 2010; COUTO et al., 2012; CARVAJAL-BERNAL et al., 2015; NOBRE et al., 2015; HÚMPOLA et al., 2016).

There are two ways of using activated carbon: liquid and gas. The most known applications are water treatment (remedying bodies of water, effluent treatment and sanitary landfill and water filters lixiviate); air purification (toxic gases and combustion gases removal); food and drink industrialization (sweetener purification, edible oils, glycerin, wine, organic and inorganic acids); pharmaceutical production (color and compounds removal from some drugs); medicinal use (toxic products elimination; tablets, curatives, odor control filters and masks productions), use in automotive vehicles (adsorbing combustible emissions or inside odors from them). It also is useful on oil refineries as a support for catalysts, gas storage, dehumidification (mold elimination and food conservation); in mining; and in the electronic industry (AVELAR et al., 2010; SALES et al., 2012; BAUTISTA-TOLEDO et al., 2014; SAUCIER et al., 2015; TMR, 2016).

In Brazil, there seems to be a limited number of researches and industries compromised with the development or production of first quality AC. In other words, AC that can be used in applications that demand, for example, specific pore distribution. For these reasons, the country is considered an emergent market in activated carbon production, with limited production and that has a median or low quality. Thus, to satisfy the national demand, there is an increasing rise in the product imports.

At the same time, there is a constant worry with rising water contamination, such as in the Guanabara Bay, in city, or the ones caused by sudden environmental disasters, such as the dam breakage of the Samarco Mining Company that affected the Doce River, which basin is the biggest of the southeast region of the country. Depollution projects of those water sources depend on much elaborated politics that revolves around population awareness and water treatment. New technologies that use AC are indispensable for removing pollutants that are causing increasing severe environmental damage (CARVAJAL-BERNAL et al., 2015; SAUCIER et al., 2015; HÚMPOLA et al., 2016; WERNERT; DENOYEL, 2016).

Bamboo use as a raw material for developing (production, characterization and application) of AC is relevant, for being a species with high presence of carbon and fibrovascular bundles, responsible for forming the activated carbon porous carbonaceous structure, among other characteristics such as fast grow, high productivity and small production circles.

In 2011, the Brazilian government sanctioned a law project that instituted the National Politic of Incentive to the Bamboo Sustainable Management and Cultivation, the "Bamboo Law" n.° 12484 (TIBURTINO et al., 2015). This act aims, among others, to stimulate the technological development and innovation of bamboo products.

In this context, to contribute with better activated carbons that could be used for water treatment, this article discusses these materials production, using bamboo as raw material, and analyses their application effectiveness.

MATERIAL AND METHODS

Raw material

Bamboo (*Bambusa vulgaris*) came from two-year-old plantations of the Celulose e Papel de Pernambuco S.A. (CEPASA) company, that belongs to *Grupo Industrial* João Santos, located at the municipality of Jaboatão dos Guararapes, Pernambuco state, Brazil. The material was cleaned with running water, dried in a shaded area, grinded and classified in 4; 8; 30; 40; 60 and 100 mesh sieves. The used fraction for producing AC was the one that passed on the 8 mesh sieve and was retained on the 30 mesh.

Variables of the process and activated carbon production

A total of five variables of the process were controlled: 1 activating agent / raw material ratio; 2 activation temperature; 3 heating rate; 4 residence time;

and 5 fluxes of steam and N_2 gas. Thus, the raw material was impregnated with a H_3PO_4 concentration solution at 2:1 (m:m), under agitation at 80 °C for 2 hours. Then, it was dried in a conventional oven at 103 ± 2 °C, for 24 hours. After that, the obtained material was activated in a rotating electric oven (CHINO), containing a tubular reactor, an electric boiler and an attached dewar container with N_2 (Figure 1).

The activation process occurred at a final temperature of 500 °C, with a 10 °C·min⁻¹ heating rate, 60 min residence time with a 100 mL·min⁻¹ steam water flux and 80 mL·min⁻¹ N_2 flux for all the activations. In the process, six repetitions were used. At the end of the process, the oven was turned off, the N_2 flux maintained until 300 °C and the AC taken off the oven after 150 °C.

The AC, named H_3PO_4/H_2OAC, was washed with distilled water, alternating hot and cold temperatures, until neutral pH. Finally, the mass of AC was dried in a kiln at 103 ± 2 °C, for 24 hours, and the AC yield (%) was determined according to Equation (1), where: m_f: final dried mass (g) of H_3PO_4/H_2OAC; m_0: initial dried mass (g) of the raw material.

$$Yield(\%) = \frac{m_f}{m_0} \cdot 100 \qquad [1]$$

Apparent density, ash content and thermogravimetic analysis

For apparent density (d), the AC was initially macerated, classified in a 40 mesh sieve and introduced in a previously weighted test tube, submitted to light lateral impacts until there were no variations in the compacted volume. The d was obtained by dividing the mass (g) AC by the volume (cm⁻³) occupied in the test tube.

For evaluating the ash content (AsC), about 1 g of H_3PO_4/H_2OAC was put in a crucible that was taken to a kiln at 103 ± 2 °C, where it stood for 1 hour and 30 minutes. The sample was transferred to a desiccator for cooling. The AsC was determined by the material combustion used at 750 °C, for 6h, in a muffle oven, according to Brazilian Regulatory Standard - NBR 8112, Brazilian Technical Norms Association - ABNT (1986). At the end of the process, the material was cooled on a desiccator for 20 minutes, when the AsC was calculated from the inorganic residue division by the dried mass of the H_3PO_4/H_2OAC, expressed in percentage.

The thermal decomposition behavior of the material was evaluated with a thermal balance (TGA-Q50 model, from TA Instruments). For such, a sample of about 10 mg of the activated carbon was placed into its platinum crucible and heated with a heating rate of 10 °C·min⁻¹, from 25 to 900 °C, under a 50 mL·min⁻¹ N_2 flux.

Surface areas, volume and pore diameter

A porosimeter (ASAP 2020 model from Micromeritics) was used to determine the BET surface area (S_{BET}) - based on N_2 at 77 K (SKAAR, 1988) - the microporous area (S_M), the Langmuir surface area ($S_{Langmuir}$), the external surface ($S_{external}$), the total pore (V_P), the micropore (V_{MP}) and mesopore (V_{MSP}) volumes and the average pore diameter (D) of the H_3PO_4/H_2OAC. The sample was degasified at 250 °C.

Estimated surface areas by the methylene blue and iodine indexes

The surface area formed by mesopores and some micropores (the methylene blue molecule has a minimum diameter of nearly 0.8 nm) was first estimated from the methylene blue (MB) adsorption and calculated according to the Equation 2, where: S_{MB}: estimated surface area by the methylene blue (m²·g⁻¹) index; $S°_{MB}$: surface area of the methylene blue ($S°_{MB}$ = 1.93 m²·g⁻¹); and q_m: maximum methylene blue adsorption capacity (mg·g⁻¹) by AC.

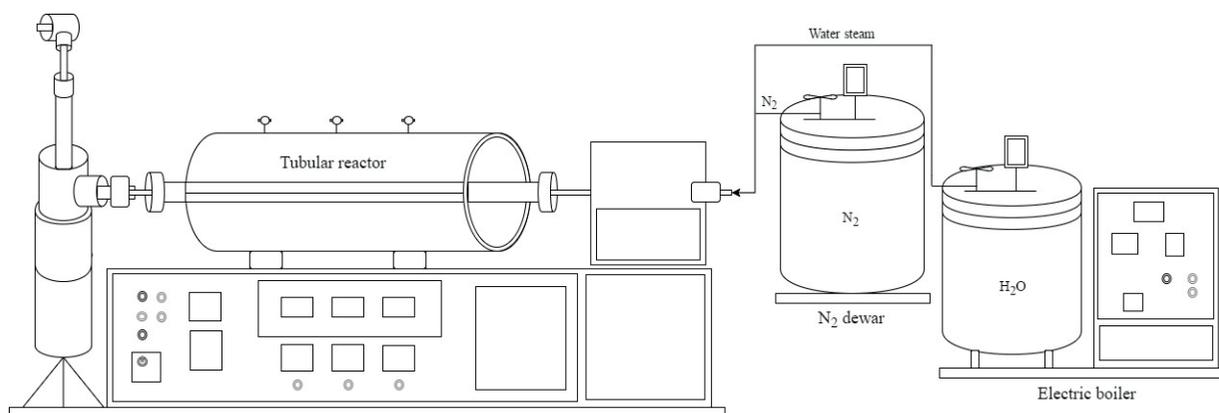$$S_{MB} = S°_{MB} \cdot q_m \qquad [2]$$

FIGURE 1 Rotating electric oven schematic representation used for the activation.

The iodine number (I) evaluates the AC micropores surface area (its molecule is rated as of small diameter, roughly 0.56 nm). For its determination, a 250 mL Erlenmeyer, previously dried, was used with a sample of 1.0 g of AC and 10 mL of HCl at 20%. The material was stirred and the formed suspension heated up to 150 °C and kept for 30 seconds in ebullition. Thus, a 100 mL of a standard iodine solution at 0.1 N was added. The solution was vigorously stirred for 30 seconds, and then, the sample was filtered in a glass funnel fitted with qualitative paper filter.

An aliquot of 50 mL of the filtered solution was transferred to a 250 mL Erlenmeyer. Then, it was titrated with a 0.1 N sodium thiosulfate and 2 mL of a 0.5% starch indicator solution. The analysis was made in duplicate and, in possession of the total volume of the sodium thiosulfate solution used in the titration, the iodine quantity (mg) adsorbed by each g of the activated carbon was calculated, according to the American Society for Testing and Materials - ASTM D 4607 (1994).

pH and point of zero charge determination

For the pH evaluation, a sample of about 1 g of the AC was transferred to a 250 mL Erlenmeyer and 100 mL of distilled water was added. The mixture was heated, kept in ebullition for 5 minutes and cooled to room temperature. Then, another 100 mL of distilled water was added and the pH of the solution was measured, using a digital pH meter, the DM-22 model from DIGIMED. The analysis was carried out in triplicate.

For pH point of zero charge (pH_{PZC}) determination, about 0.3 g of the produced material was transferred to a 100 mL container and then 50 mL of NaCl 0.01 mol·L^{-1} aqueous solution was added. The NaCl solution pH was adjusted to 2, 3, 4, 5, 7 and 9 values with HCl (0.01 mol·L^{-1} and 0.1 mol·L^{-1}) and NaOH (0.1 mol·L^{-1}) solutions, from a bench pH meter, a MPA 210 model from MS Tecnopon.

The container was sealed shut and agitated in a Shaker incubator (SL 221 model from SOLAB) with agitation control of 100 rpm and 25° C temperature during 24 hours. Later, the balance solution pH was measured and the chart was produced, disposing the final pH (Y-axis) versus the initial pH (X-axis). The point of zero charge is the pH where the curve crosses the line in which the initial pH is the same as the final. The analysis was carried out in triplicate.

Boehm method and scanning electron microscopy

The determination of the functional surface groups followed the Boehm titrimetric method (1994).

In 0.25 g of H_3PO_4/H_2OAC, 10 mL of NaOH, Na_2CO_3, $NaHCO_3$ (all at 0.05 mol·L^{-1}) were added and the material was maintained at agitation at 25 °C for 24 hours in a Shaker incubator (SL 221 model from SOLAB). After the agitation, the material was filtered with a filter paper (80 g·m^{-2} gramature, 205 μm thickness, 14 μm pores) and 5 mL rates were taken. In the NaOH and $NaHCO_3$ rates, 10 mL of HCl (0.05 mol·L^{-1}) and in Na_2CO_3 15 mL of HCl (0.05 mol·L^{-1}) were added. Next, they were titrated with NaOH (0.05 mol·L^{-1}) and the NaOH and HCL standardize. The acid group number was determined considering the sodium hydroxide, NaOH, neutralizes carboxylic acids, lactones and phenols; and the sodium carbonate, Na_2CO_3, acts in the carboxylic acids and lactones, while the sodium bicarbonate only neutralized carboxylic acids.

The superficial morphology of the material was obtained by scanning electron microscopy in a FEI Quanta 450, using 20 kv tension. For such, the samples were mounted in an aluminum platform using a double carbon strip with a thin gold layer deposited by Emitech K550X sputter.

Activated carbon application and adsorption kinetics evaluation

To evaluate the ability of the AC (H_3PO_4/H_2OAC) in the water treatment, adsorption experimental tests with three different pesticides were carried out (Table 1). In order to explore the adsorption kinetics, 10 mg of AC were mixed with 10 mL of distinct solutions based on the MTZ, 2,4-D and FRD having, each one, a concentration of 50 mg·L^{-1}. The containers were sealed shut and stirred in a shaker (SL 221, SOLAB) at 100 rpm and temperature of 25 °C.

TABLE 1 Employed pesticides characteristics.

Pesticides	Abbreviation	Nature	M (g·mol^{-1})	λ (nm)
Metribuzin	MTZ	Herbicide	214.29	294
2,4-dichlorophenoxyacetic	2,4-D	Herbicide	221.04	283
Furadan	FRD	Insecticide	221.25	276

At predetermined intervals of 1; 3; 6; 12 and 24 hours, samples of the solution having each about 3.5 mL were taken and its concentrations determined. The contaminant concentration was evaluateded using a spectrophotometer UV-VIS (UV-mini 1240, SHIMADZU).

Adsorption isotherms

The adsorption isotherms were obtained using 10 mg of AC and 10 mL of solutions having different concentration of MTZ, 2,4-D and FRD. The samples were stored in 20 mL recipients, kept under 100 rpm

rotation in a shaker (SL 221, SOLAB) for 24 hours, and at temperature of 25 °C. The equilibrium concentration was performed by an UV-VIS (UV-mini 1240, SHIMADZU) by employing appropriate wavelength (λ) for each contaminant in a punctual analysis of absorbance.

Calibration curves with concentrated solutions of 25; 50; 100; 250; 500 and 1000 mg·L^{-1} for each adsorbate (MTZ, 2,4-D and FRD) were prepared. The quantity of adsorbate adsorbed per gram, q_{eq}, was calculated according to Equation 3, where: C_0 and C_{eq}: represent, respectively, the initial and at balance concentrations (mg·L^{-1}); V: the adsorbate volume (L); and m: the adsorbent mass (g).

$$q_{eq} = \frac{(C_0 - C_{eq}) \cdot V}{m} \qquad [3]$$

Applied models for data fitting

The obtained data in the isotherms (q_{eq} and C_{eq}) were fitted to Langmuir and Freundlich models. Equation 4 describes the behavior of the Langmuir isotherm, while its linear form appears in Equation 5. On the other hand, Equation 6 represents the general form of the Freundlich model, which is conveniently linearized by the application of logarithms in two terms (Equation 7), where: q_{eq}: the adsorbed quantity (mg·g^{-1}) for a given adsorbate concentration (MTZ, 2,4-D and FRD); q_m: the maximum adsorption capacity (mg·g^{-1}); C_{eq}: adsorbate concentration after the equilibrium to be achieved (mg·L^{-1}); K_L: Langmuir constant; K_F: sorption coefficient and 1/n: sorption intensity measure - Freundlich constants.

$$q_{eq} = \frac{q_m \cdot K_L \cdot C_{eq}}{1 + K_L + C_{eq}} \qquad [4]$$

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m \cdot K_L} + \frac{1}{q_m} \cdot C_{eq} \qquad [5]$$

$$q_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}} \qquad [6]$$

$$\log(q_{eq}) = \log(K_F) + \frac{1}{n}\log(C_{eq}) \qquad [7]$$

RESULTS AND DISCUSSION

Yield, apparent density, ash content and thermogravimetrical analyses

The H$_3$PO$_4$/H$_2$OAC showed elevated yield values (39.00%) and apparent density (0.50 g·cm^{-3}) and low ash content (2.82%). The low ash content is a positive factor for the AC production, since the mineral matter, because of its hydrophilic characteristic, promotes the water adsorption competing with other compounds of interest (BRUM et al., 2008).

The thermogravimetrical analysis (TGA) registers a loss of mass of the material when submitted to a temperature program with time and temperature variation (SANTOS et al., 2012). By the TGA of the produced AC H$_3$PO$_4$/H$_2$O by its temperature, it can be observed that the first mass declivity happened next to 100 °C in an outcome of the moisture loss (RAMOS et al., 2009). Then, there was the decomposition of the material next to the final activation temperature (500 °C) and the residual percentage of the H$_3$PO$_4$/H$_2$OAC after the end of the analysis was around 62% (Figure 2).
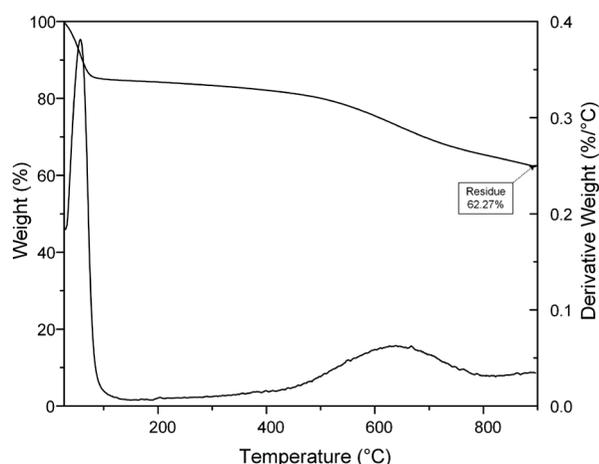

FIGURE 2 Thermogravimetrical analysis for the produced H$_3$PO$_4$/H$_2$OAC.

Surface areas and porosity

The H$_3$PO$_4$/H$_2$OAC got a 618.72 mg·g^{-1} S$_{MB}$ and 747.51 mg·g^{-1} I, with the methylene blue being adsorbed in the bigger mesopores and micropores region of the AC, while the iodine, with smaller dimensions, adsorbed in the microporous region. The obtained result for I was very satisfactory, since the Brazilian Specification - EB 2133, ABNT (1991) requires that the iodine index (I) be at least 600 mg·g^{-1} for the AC.

The adsorption and desorption isotherms of N$_2$ (Figure 3) indicated high adsorption at low N$_2$ pressures, evidencing the micropores formation (RAMOS et al., 2009). Furthermore, the produced AC has 1196.30 m^2·g^{-1} BET surface area - S$_{BET}$; 884.88 m^2·g^{-1} micropores; 1593.25 m^2·g^{-1} Langmuir; 311.42 m^2·g^{-1} external; 0.61 cm^3·g^{-1} total pore volume; 0.40 cm^3·g^{-1} total micropore volume; 0.15 cm^3·g^{-1} mesopores; and average diameter of 20.50 Å. The S$_{BET}$ was elevated
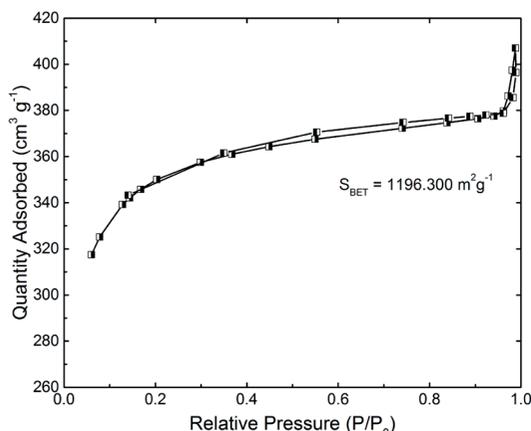
FIGURE 3 Adsorption/desorption isotherms of nitrogen (N_2) at 77 K for the produced AC.

and could have great influence in the adsorption, because generally great superficial areas could mean great adsorption capacity (BARBOSA et al., 2014).

Table 2 presents the surface area (S_{BET}) of our produced AC and of some well-known adsorbents for removal of pesticides. Even if the AC H_3PO_4/H_2OAC does not present higher BET surface area when compared to that of the others, it demonstrated to be more effective in removing FRD, MTZ and 2,4-D.

TABLE 2 Values of surface area (S_{BET}) and maximum adsorption capacity (q_m) for different adsorbents for removal of pesticides.

Adsorbent	S_{BET} ($m^2 \cdot g^{-1}$)	Pesticide	q_m ($mg \cdot g^{-1}$)	Reference
$H_3PO_4/$ H_2OAC	1196.30	*FRD	868.98	This study
		MTZ	756.47	This study
		2,4-D	274.70	This study
Rice straw AC	1304.80	FRD	312.50	Chang et al. 2014
SFHAC	1211.57	Bentazon	166.67	Njoku et al. 2014a
LEFBAC	1065.65	2,4-D	261.20	Njoku et al. 2015
DSAC	880.18	Bentazon	86.26	Salman et al. 2011
GAC F3000	731.48	2,4-D	181.82	Salman; Hameed, 2010
CFAC	483.00	FRD	198.40	Njoku et al. 2014b
Banana peels AC	-	MTZ	167.00	Ul Haq et al. 2015

* FRD = Furadan; MTZ = Metribuzin and 2,4-D = 2,4-dichlorophenoxyacetic.

pH, point of zero charge and Boehm method analysis

The AC from *Bambusa vulgaris* has an acid pH (2.90), which has origin in its agent of activation, i.e., the phosphoric acid. The pH is an important parameter, since it controls the electrostatic interactions between the adsorbate and the adsorbent, having great influence in the adsorption process (BAUTISTA-TOLEDO et al., 2005). The determined point of zero charge (pH_{PZC}) was 2.41, which indicates that the material tends to present negative charges in solutions with pH higher than 2.41. On the other hand, these charges become positive when the middle pH is lower than pH_{PZC}.

By the Boehm titration method, the H_3PO_4/H_2OAC showed functional acid groups in its surface, with a total acidity of 1.804 $mmol \cdot g^{-1}$. In terms of present higher quantities, the highlights were the carboxylic acids with 1.454 $mmol \cdot g^{-1}$ and the phenolic groups with 0.140 $mmol \cdot g^{-1}$.

Scanning electronic microscopy

The scanning electronic microscopy (SEM) analysis (Figure 4) showed the presence of an organized pore region in the fibrovascular bundle wall after the activation that permits the diffusion of the contaminants in a faster way to the inner regions of the produced H_3PO_4/H_2OAC (A). Besides, when the scale is increased, it is verified in the bundle wall the occurrence of region with protuberances that enhances the contact surface of the AC with the contaminants (B).
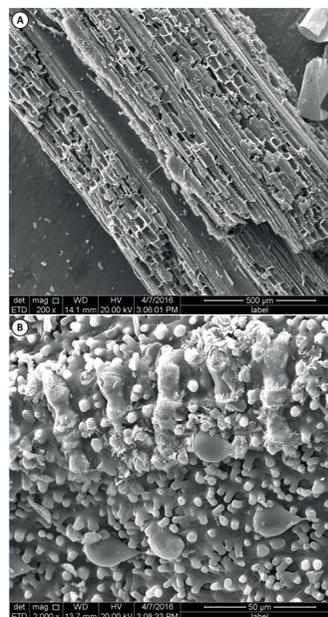

FIGURE 4 Surface morphology of H_3PO_4/H_2OAC obtained by scanning electronic microscopy for a 20 kv tension. Presence of an organized pore network (A) and regions with protuberances in the wall of the fibrovascular bundle of H_3PO_4/H_2OAC (B).

Activated carbon applications and adsorption kinetics

For the MTZ, the H_3PO_4/H_2OAC presented a removal percentage, in 1 hour, superior than 60%, with the filling of active sites of the produced AC happening at a fast rate. For the 2,4-D and FRD, there was a slower removal, requiring more time (Table 3).

The removed contaminant rate was increased with the pesticide/activated carbon contact time. The balance is reached at different times but, within 24 hours of reaction, it was verified that the systems were at balance for 2,4-D (96.69%), MTZ (92.90%) and FRD (92.27%).

TABLE 3 Kinetic adsorption for the MTZ, 2,4-D and FRD for the adsorbate/adsorbent contact time (10 mg of AC; 10 mL 50 mg·L^{-1} solution; 25 °C).

| Exposure time (Hours) | Adsorption kinetics for each pesticide | | | | | | | | |
| | MTZ | | | 2,4-D | | | FRD | | |
	*C_{eq}	q_{eq}	R (%)	C_{eq}	q_{eq}	R (%)	C_{eq}	q_{eq}	R (%)
1	18.03	31.97	63.93	22.31	27.69	55.37	25.57	24.43	48.86
3	15.85	34.15	68.31	12.26	37.74	75.48	14.77	35.23	70.45
6	5.19	44.81	89.62	7.16	42.84	85.67	6.82	43.18	86.36
12	3.83	46.18	92.35	3.58	46.42	92.84	5.11	44.89	89.77
24	3.55	46.45	92.90	1.65	48.35	96.69	3.86	46.14	92.27

* C_{eq} = balance concentration (mg L^{-1}); qeq = adsorbed contaminant mass, in mg, for each AC gram (mg g^{-1}); R (%) = contaminant removal (%); MTZ = Metribuzin; 2,4-D = 2,4-dichlorophenoxyacetic; and FRD = Furadan.

Adsorption isotherms and applied models

The Langmuir and Freundlich parameters are described in Table 4 and the adsorption isotherms for MTZ (A), 2,4-D (B) and (C) FRD are presented in Figure 5. The H$_3$PO$_4$/H$_2$OAC had elevated maximum adsorption capacity (q$_m$) for the FRD (868.98 mg·g^{-1}), MTZ (756.47 mg·g^{-1}) and 2,4-D (274.70 mg·g^{-1}). As well in the higher analyzed concentration (1000 mg·L^{-1}) it showed elevated values of q$_{eq}$ for the FRD (590.67 mg·g^{-1}), MTZ (519.31 mg·g^{-1}) and 2,4-D (280.11 mg·g^{-1}).

The adsorption isotherms are basic requirements for the understanding of the adsorption process. The isotherm indicates how the molecules are distributed between the liquid and the solid stage when the adsorption reaches the balance status (MEZOHEGYI et al., 2012). By the isotherms and R^2 values obtained, it can be noted that the MTZ and the FRD had a better adjustment to the Freundlich isotherm and the 2,4-D a better adjustment for Langmuir (Figure 5, Table 3).

The better adjustment for the Freundlich model shows that the adsorption happens in heterogenic and not specified sites of H$_3$PO$_4$/H$_2$OAC (BARBOSA et al., 2014). For the better Langmuir adjustment, however, it is proposed a monolayer of the 2,4-D pesticide in the H$_3$PO$_4$/H$_2$OAC surface, in which all the sites are identical and energetically equivalents.
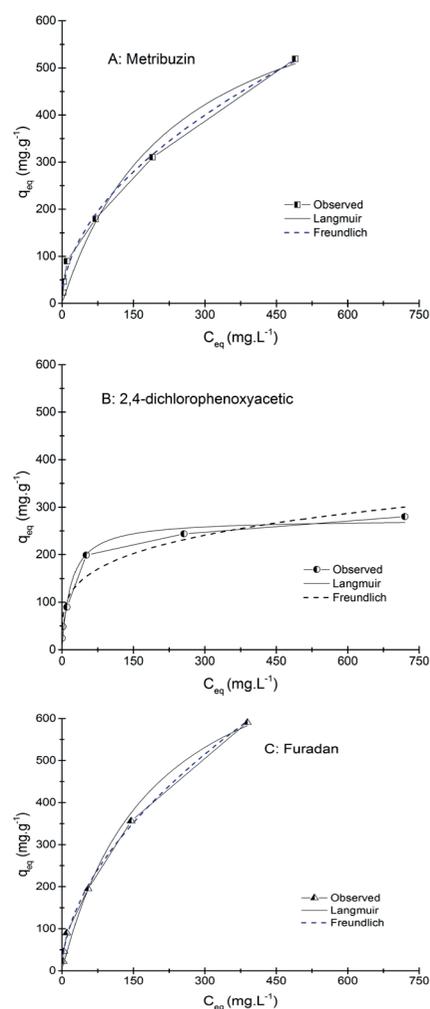
The most important activated carbon characteristics for the contaminant adsorption are the superficial area, pore distribution, surface chemistry and mineral component (DIAS et al., 2007). The observed results suggests the use of H$_3$PO$_4$/H$_2$OAC for a series of pesticide-contaminated effluents, in which the Health Ministry Ordinance N° 2914, of December 12th, 2011, dealing with the control and safety procedures of the water quality for human consumption and its potable standards, stablishes that the maximum limit for 2,4-D and FRD to be 30 μg·L^{-1} and 7 μg·L^{-1}, respectively (BRASIL, 2011).

TABLE 4 Physical-chemical parameters of adsorption obtained from the fitting to the Langmuir and Freundlich models for the three used pesticides.

| Pesticides | Adsorption parameters for the fitted models | | | | | |
| | Langmuir | | | Freundlich | | |
	*q$_m$ (mg·g^{-1})	K$_L$ (L·mg^{-1})	R^2	1/n	K$_F$ [(mg L^{-1})(L mg^{-1})$^{1/n}$]	R^2
MTZ	756.47	0.004	0.960	0.516	21.050	0.995
2,4-D	274.70	0.053	0.971	0.251	57.34	0.922
FRD	868.98	0.005	0.982	0.549	22.499	0.997

* q$_m$ = Maximum adsorption capacity (mg·g^{-1}); K$_L$ = Langmuir constant; R^2 = Correlation coefficient; 1/n = Freundlich parameter; K$_F$ = Freundlich constant; MTZ = Metribuzin; 2,4-D = 2,4-dichlorophenoxyacetic and FRD = Furadan.

FIGURE 5 Adsorption isotherms for the pesticides (A) metribuzin, (B) 2,4-dichlorophenoxyacetic and (C) furadan for the produced AC (10 mg of AC; 10 mL of different solution concentrations; 25 °C; q$_{eq}$ = adsorbed contaminant quantity; C$_{eq}$ = balance concentration).

For the MTZ, legislation about the allowed limit in Brazil was not found. However, the Environment Protection Agency (EPA) of the United States establishes as acceptable levels 200 $\mu g \cdot L^{-1}$ of MTZ, based on the concentration of this pesticide in potable water, where it is not expected to cause adverse effects to human health at the course of one life (EPA, 2003).

CONCLUSIONS

The H_3PO_4/H_2OAC had 39.00% yield, 1196.30 $m^2 \cdot g^{-1}$ S_{BET} and 0.61 $cm^3 \cdot g^{-1}$ V_P. By the obtained results for the S_M (884.88 $m^2 \cdot g^{-1}$) and I (747.51 $mg \cdot g^{-1}$) it can be observed that the produced AC is mainly microporous. Furthermore, it was efficient for removing the three analyzed pesticides, presenting high adsorption capacity for the FRD (868.98 $mg \cdot g^{-1}$), MTZ (756.47 $mg \cdot g^{-1}$) and 2,4-D (274.70 $mg \cdot g^{-1}$).

The results observed in this paper suggest the use of H_3PO_4/H_2OAC to a series of pesticide-contaminated water bodies, mainly in higher concentrations than established limits permitted by legislation. Lastly, complementary researches should be made to perfect, even more, the quality of the produced H_3PO_4/H_2OAC.

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