Conjecturas

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The influence of biochar pyrolysis temperatures on the efficiency of soil amendment for Imazapic sorption

A influência das temperaturas de pirólise do biocarvão na eficiência da correção do solo para sorção de Imazapic

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ABSTRACT

Weeds are responsible for losses in sugarcane productivity, often requiring the application of herbicides to control their infestation in crops. One of the herbicides commonly used in sugarcane cultivation is Imazapic. However, this chemical can be leached into environmental compartments when applied to soil, contaminating it. Scientific research has shown that the soil amended with biochar can reduce the leaching of herbicides, avoiding environmental pollution. Therefore, the present work aimed to evaluate the adsorption efficiency of Imazapic in a dystrophic Yellow Ultisol amended with biochar cultivated with sugarcane. Biochars were produced with sugarcane bagasse by pyrolysis at temperatures of 300, 500, and 700ºC to evaluate the adsorption capacity of Imazapic by the soil amended with biochar. The experiments revealed an increase in Imazapic adsorption with soil amended with biochar and that the adsorptive potential is more significant for pyrolyzed biochars at higher temperatures. In this way, the biochars produced can reduce the risks of groundwater contamination by increasing the residence time of Imazapic in the surface layer of the soil, being subject to the action of microbial degradation and other forms of degradation.

Keywords: Pesticides; Isotherms; Pyrolysis; Pollution

RESUMO

As plantas daninhas são responsáveis por perdas na produtividade da cana-de-açúcar, muitas vezes exigindo a aplicação de herbicidas para controlar sua infestação nas lavouras, é o caso do Imazapic (IMZ). No entanto, o IMZ pode ser lixiviado em compartimentos ambientais quando aplicado ao solo, contaminando-o. Pesquisas científicas mostraram que o solo corrigido com biocarvão pode reduzir a lixiviação de herbicidas, evitando a poluição ambiental. Portanto, o trabalho teve como objetivo avaliar a eficiência de adsorção do IMZ em um Argissolo Amarelo distrófico modificado com biocarvão na cultura de cana-de-açúcar. Biocarvões foram produzidos com bagaço de cana por pirólise nas temperaturas de 300, 500 e 700ºC para avaliar a capacidade de adsorção do IMZ pelo solo corrigido com biocarvão. Um aumento na adsorção de IMZ com solo corrigido com biocarvão foi observado e que o potencial adsortivo é mais significativo para biocarvão pirolisado em temperaturas mais altas. Desta forma, os biocarvões produzidos podem reduzir os riscos de contaminação das águas subterrâneas aumentando o tempo de residência do IMZ na camada superficial do solo, ficando sujeito à ação da degradação microbiana e outras formas de degradação.

Keywords: Pesticida; Isotermas; Pirólise; Poluição

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INTRODUCTION

Sugarcane cultivation in the Northeast region of Brazil has been carried out since the colonial period, with the predominance of cultivated areas in the coastal and wild regions of the states of Alagoas, Pernambuco, and Paraíba (OLIVEIRA *et al.*, 2016). According to CONAB (2022), this region produces more than 58 t ha^{-1} and, together with the country's northern region, accounts for 6% of the national sugarcane harvest.

Sugarcane cultivation can be harmed by pests, diseases, and weeds, causing significant losses in productivity when not adequately controlled. Herbicides are commonly employed to control weed infestation and minimize their effects on crops. However, these chemicals can be harmful not only to weeds but also to the cultivation of sugarcane. This feature is due to their ability to move in the environment, being able to be transported together with the percolation water (leaching), as well as by surface runoff, thus reaching the water reservoirs (surface and subsurface water) (LOPES; ALBUQUERQUE, 2018).

One of the herbicides commonly used in sugarcane cultivation is Imazapic, which can control the purple nutsedge (*Cyperus rotundus L.*), one of the leading invasive plants in areas cultivated with sugarcane (ASSIS *et al.*, 2021). The study developed by Assis et al. (2021) points out that the use of Imazapic in the cultivation of sugarcane in the state of Pernambuco demands attention regarding the application of the product.

The high rainfall in the southern and northern forests of the state (> 1500 mm per year), associated with the irrigation system, raises concerns about the concentration of this product used as a pre-emergent herbicide. In this way, the herbicide can be leached to other environmental compartments, becoming a contaminant.

On the other hand, the presence of organic matter in the soil can increase the adsorption of contaminants, consequently reducing their leaching to deeper layers. Some researchers, such as Abdelhafez, Abbas, & Li (2017); de Figueredo, da Costa, Melo, Siebeneichlerd, & Tronto (2017); Hai Nguyen Tran et al. (2020); Petter et al. (2019) point to the application of biochar on the soil as a way to reduce the leaching of organic contaminants, such as Imazapic, which can reduce the risks of soil and water contamination. Therefore, it becomes relevant to study the addition of biochar to the soil as a retention agent for Imazapic.

In this context, the present work aimed to evaluate the efficiency of adding pyrolyzed biochar to the soil at different temperatures, obtained from sugarcane bagasse, in the adsorption of the herbicide Imazapic in a Yellow Ultisol with sugarcane cultivation.

MATERIAL AND METHODS

Study area and soil sampling

The study area is characterized by the predominance of dystrophic Yellow Ultisol (YUd) of medium texture with sugarcane cultivation on a half slope (7°47'59.02"S and 35°0'18.45"W). According to Vale *et al.* (2019), the soil has a total porosity of 36.74%, a pH of 6.7, and a potential Cation Exchange Capacity (CEC) of 4.83 $cmol_c$ dm^{-3}.

The sampling of the soils was carried out in soil with the herbicide Imazapic during the dry period (February 2016). Twenty simple samples were randomly collected to form a composite sample from the 0-20 cm layer of soil.

To obtain Air Dry Soil (ADS), the soil samples were crushed, air-dried, and passed through a 2.00 mm sieve for further physical and chemical analysis using the EMBRAPA method (TEIXEIRA, P. C. *et al.*, 2017).

The physical properties of soil determined were granulometry, dry bulk density, particle density, and total porosity. The chemical parameters were active soil acidity (pH), soil organic matter, available phosphorus (P), potassium (K^+), sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), exchangeable acidity (Al^{3+}), and Potential acidity (H + Al). After obtaining these physicochemical parameters, the sum of bases (SB), potential and effective cation exchange capacities (CEC and ECEC), base saturation (V), and Aluminum saturation (m) values were calculated. All analyses were performed based on EMBRAPA analytical methods (TEIXEIRA, P. C. *et al.*, 2017).

Production and analysis of biochar

Biochar was produced from sugarcane bagasse collected in the same sugarcane mill where the soil was collected. The bagasse was washed and placed to dry in an oven at 105ºC for 72h. The material was crushed in an industrial blender with titanium blades, sieved in a 1 mm mesh sieve, stored in bags, and sealed until the beginning of the biochar production process.

Biochar was produced by the slow pyrolysis of sugarcane bagasse in a Muffle furnace JUNG Model LF2312O, with Nitrogen (N_2) being the carrier gas used in the pyrolysis to eliminate oxygen (O_2) from the system. Table 1 presents the pre-established operating conditions for the pyrolysis process.

Table 1 - Operating conditions of sugarcane bagasse pyrolysis

Description	Values used
Initial reactor heating rate	10°C min^{-1}
N_2 flow	1,8 L min^{-1}
Residence time	30 min
Size of the pyrolyzed particles	≤ 1 mm
Reactor power	4 kW, 220 V
Temperature range	300, 500 e 700ºC

After production, the biochars were placed in a desiccator later used in kinetics and adsorption isotherms assays and submitted to physicochemical characterization analyses. Biochars were produced at temperatures of 300, 500, and 700°C.

To calculate the yield of biochar (Y), the mass of bagasse verified before pyrolysis and the mass obtained after pyrolysis were considered. The pH, electrical conductivity (EC), and Apparent Density (Dap) of the biochars were analyzed by adapting the methodologies proposed by EMBRAPA (TEIXEIRA, P. C. *et al.*, 2017).

The total carbon (C), nitrogen (N), and hydrogen (H) contents of the biochars were determined in an Elemental Analyzer (Vario Macro Cube, Langenselbold, Germany). The surface morphology of the biochar was obtained by employing Scanning Electron Microscopy (SEM). High-resolution images were obtained using a TESCAN microscope, model VEGA3 LMU, performed at the Research Support Center at UFRPE (CENPESQ).

Assessment of the interaction of Imazapic with the soil

The adsorption of the herbicide Imazapic in unamended (control) and biochar-amended soil samples was assessed through kinetic and adsorption isotherm assays. In the analytical curves prepared for reading Imazapic in the High-Performance Liquid Chromatography (HPLC) device, the Imazapic molecule with 99.5% purity (CAS nº 104098-48-8, PESTANAL®, analytical standard) was used, obtaining a coefficient of determination (r^2) above 0.99.

The mobile phase used for the HPLC readings consisted of a mixture of Acetonitrile: water (60:40, v/v), acidified to pH 3.0 with phosphoric acid (1:1, v/v), and a flow rate of about 1.0 mL min^{-1}. The maximum wavelength for detection was 212 nm.

The kinetics experiment for soil unamended with biochar consisted of mixing 10 mL of solute (V_1) of known concentration of Imazapic 0.5 g L^{-1} (C_o) and a mass of soil (m_s) of 5 g. For the soil amended with biochar, the total mass consisted of the addition of 4.95 g of soil and 0.05 g of biochar. This procedure was used for the three pyrolysis temperatures.

After reading in HPLC, the data were fitted to two kinetic models, one of pseudo-first-order and the other of pseudo-second-order, using the methodology of Yaneva; Koumanova (2006). The Nash-Sutcliffe methodology has been employed to evaluate the modeling efficiency (NASH; SUTCLIFFE, 1970).

The study of adsorption isotherms was carried out for unamended and biochar-amended soil samples. The commercial product Plateau® (BASF, composed of 70% of the Imazapic molecule and 30% of inert material) was used. As observed in the kinetic assays, a time interval of 24 hours of agitation at room temperature was considered for the Imazapic to reach equilibrium with the soil.

In the batch equilibrium tests, a volume of 10 mL of Plateau herbicide (Imazapic) and a proportion of 4.95 g of soil + 0.05 g of biochar was mixed in a reaction tube (falcon) to maintain the percentage of 1% of biochar in the soil, which according to Rezende *et al.*, (2011) is within the optimal range for soil conditioning. The concentrations of the herbicide Imazapic (mg L^{-1}) used in the assays in three replicates were 20, 50, 125, 255, 510, 1020, 1590, and 2040 mg L^{-1}. These values were adopted because they include the herbicide concentrations applied in the field in the study area. The pH of the solution containing Imazapic was adjusted to the soil one. The extracts were analyzed by HPLC, which allowed estimating the equilibrium concentration (C_{eq}).

The concentration of Imazapic, adsorbed to the soil, was the difference between its value before contact with the soil (C_0) and after reaching equilibrium (C_{eq}).

The calculation for the assessing of the adsorbed Imazapic concentration was performed according to equation 1 (LAVORENTI; PRATA; REGITANO, 2003):

$$S = \frac{\left(C_0 - C_{eq}\right)V_l}{m_s} \quad (1)$$

where, S is the adsorption capacity (g kg^{-1}); C_0 is the initial solute concentration (mg L^{-1}); C_{eq} is the solute concentration after equilibrium (mg L^{-1}); V_l is the volume of the solution (mL); m_s is the sum of soil and biochar masses (g).

For the statistical analysis of the data, calculations of the means and standard deviation of the three repetitions were performed. With the help of Solver from Excel (Microsoft Office 365), the best fit of the experimental data was estimated using the Freundlich and Langmuir isotherm models (Table 2) in their direct or even linearized forms (models of Freundlich and Langmuir).

The parameters of Freundlich and Langmuir models in linearized forms were determined in data analysis by Regression using the Excel application (Microsoft Office 365). The linear model was determined directly from Excel.

Table 2 - Nonlinear and linearized Freundlich and Langmuir Isotherm models using Excel Solver (Microsoft Office 365) for direct model adjustments.

Model	**Freundlich**	**Langmuir**	
Nonlinear	$S = K_F C_{eq}^{\ n}$	$S = \frac{S_M K_L C_{eq}}{1 + K_L C_{eq}}$	
		Model 1	**Model 2**
Linearized	$\ln S = \ln K_F + n \ln C_{eq}$	$\frac{1}{S} = \frac{1}{S_M} + \frac{1}{K_L S_M C_{eq}}$	$\frac{C_{eq}}{S} = \frac{1}{K_L S_M} + \frac{C_{eq}}{S_M}$

S - Amount of adsorption in equilibrium (g kg^{-1}); K_F - Freundlich constant related to adsorption capacity (g kg^{-1}) (L g^{-1}); C_{eq} - Equilibrium fluid concentrations (g L^{-1}); n - Constant related to the adsorption intensity; S_M - Amount of adsorption corresponding to the monolayer coverage (g kg^{-1}); K_L - Langmuir's constant (L g^{-1}).

RESULTS AND DISCUSSION

Characterization of biochar

The biochars produced at different temperatures (300, 500, and 700°C) differed in several physical and chemical aspects. It is worth noticing that the temperature used in the pyrolysis of biomass influences the various properties of biochar, as attested by

Figueredo *et al.* (2017). Table 3 shows the characterization of the biochars produced at different pyrolysis temperatures.

Table 3 - Physicochemical characterization of biochars produced for different temperatures.

Parameters	300ºC	500ºC	700ºC
Yield (%)	41	21.7	15.7
pH	5.3	6.7	7.9
EC (µS cm^{-1})	167	328	268
D_{ap} (g cm^{-3})	0.10	0.09	0.08
AS (m^2 g^{-1})	10.95	215.28	442.67
AM (m^2 g^{-1})	2.01	141.61	277.82
AEX (m^2 g^{-1})	8.94	73.67	164.85
ASAP (m^2 g^{-1})	3.83	36.56	102.74
ASDP (m^2 g^{-1})	1.72	18.26	87.36

pH - Hydrogen potential; CE – Electric conductivity; D_{ap}: Apparently density; AS - Surface area; AM - Micropores area; AEX- External surface area; ASAP - Cumulative surface area of pore adsorption; ASDP: Cumulative surface area of pore desorption.

Table 3 shows that with the increase in the pyrolysis temperature, there was a reduction in the yields of the biochars produced. For Rodrigues *et al.* (2013), this is due to the loss of thermolabile structures, which characterizes the beginning of the pyrolytic process. Ding *et al.* (2014) e Pires *et al.* (2018) also found a similar mass reduction in their experiments, concluding that the yield is greater between milder temperatures.

The pH values obtained in the biochar analyzes (Table 3) were similar to the values found by Figueredo *et al.* (2017), Song *et al.* (2014), and Ding *et al.* (2014). It can be observed that these values grew with the increase in the temperature used in the pyrolysis. Colen *et al.* (2020) stated that the higher the pyrolysis temperature, the higher the pH of the biochar produced. The accumulation of alkaline salts can explain this increase in pH value during pyrolysis. In the biochar produced at 700°C, the alkaline pH was observed. For Ahmad *et al.* (2014) e Abdelhafez; Abbas; Li (2017), biochars with these pH values have the utility of inducing the liming effect for acidic soils.

Still, considering Table 3, each biochar's electrical conductivity (EC) varied with the increase in the pyrolysis temperature, increasing its values between 300°C and 500°C and a slight reduction in the temperature of 700°C. These results corroborate those of Abdelhafez; Abbas; Li (2017), who state that in biochars of plant origin, the increase in

temperature is capable of causing an increase in EC. The temperature rise caused a reduction in the apparent density of the biochar.

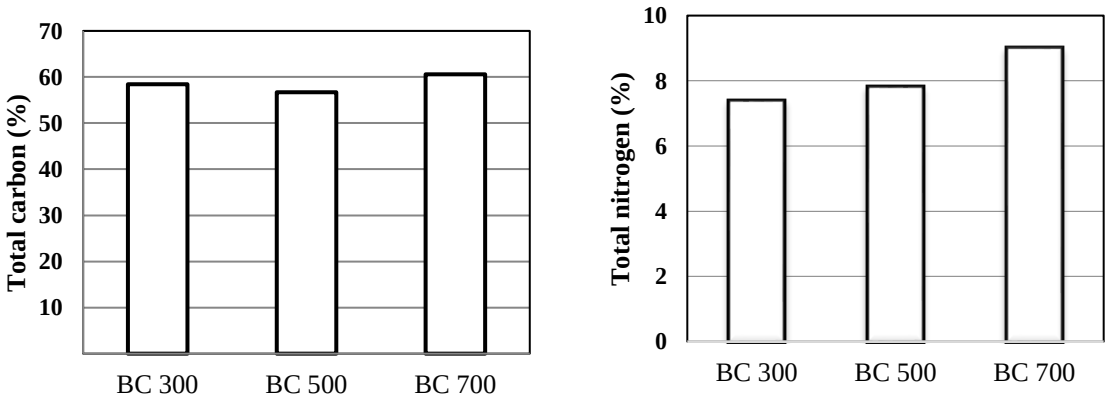
It is worth mentioning that the introduction of biochar to the dystrophic Yellow Ultisol probably increases its porosity, which, consequently, contributes to water retention and aeration since the apparent density of the biochars is significantly lower than the dry bulk density of the studied soil and, the lower the density, the greater the pore volume. In this sense, when there is a reduction in the apparent density, there is an increase in the specific surface area (SSA). In practical terms, this implies that biochars produced with high pyrolysis temperatures present higher SSA and, consequently, greater capacity to retain contaminants by adsorption (AHMAD *et al.*, 2014; SAFAEI KHORRAM *et al.*, 2016).

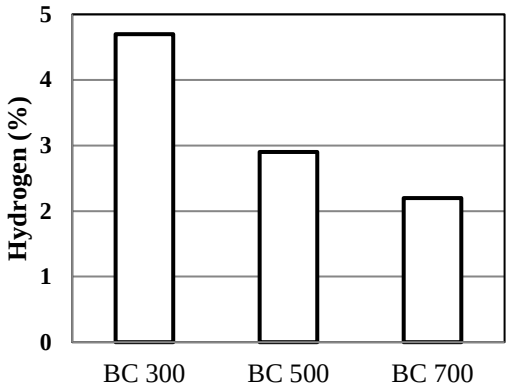
Another parameter capable of affecting the adsorbent potential of biochar is microporosity, expressed in terms of Micropore Area (MA). It was observed that the parameter was considerably higher for the 500°C and 700°C biochars. These results follow Maia (2011), who showed that the increase in temperature in the pyrolysis process leads to an increase in micropores in the material.

The external surface area (ESA) increased with the rise of pyrolysis temperature and the cumulative surface area of adsorption and pore desorption. The thermal addition to the biomass can explain this phenomenon since the burning and decomposition of the substance unclogs the pores.

The elemental composition analysis made it possible to know the percentage by mass of the elements N, C, and H and their relationships (Figure 1).

Figure 1- Elementary composition of biochars produced under different temperatures (BC300, BC500, and BC700).





All the analyzed elements showed some variation with the change in pyrolysis temperature. For Figueredo *et al.* (2017), the type of biomass and pyrolysis temperature influence the elemental composition of biochars.

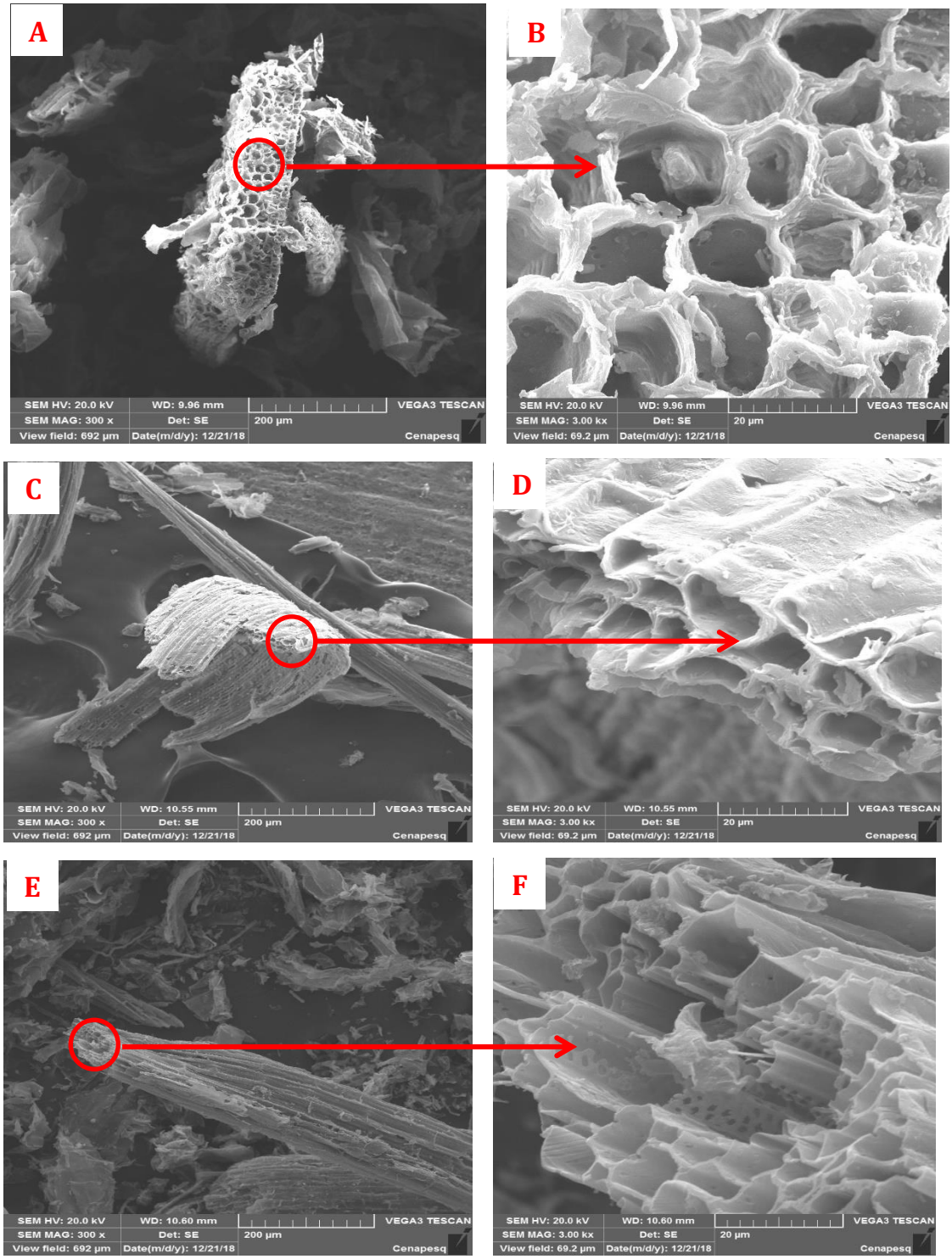
Figure 1 attests to the fact that biochar is a material rich in carbon (PETTER; FERREIRA; SINHORIN; LIMA; *et al.*, 2019; SANCHEZ-REINOSO; ÁVILA-PEDRAZA; RESTREPO, 2020). The percentage values of this element were greater than 50%, as foreseen by Mangrich; Maia; Novotny (2011), with the highest total carbon content obtained for the BC700. The increase in carbon concentrations in the biochars from the increase in pyrolysis temperature was also observed by Figueredo *et al.* (2017), Montero *et al.* (2018) e Song; Guo (2012).

The values of N were low when compared to the values of C. This fact can be associated with the great volatilization of the N of the matter in the initial temperatures. N values for biochars from agricultural residues are usually low because most of the nitrogen in the feedstock starts to be volatile at temperatures above 200°C (ABDELHAFEZ; ABBAS; LI, 2017). The N contents found in this research were higher than those obtained by Abdelhafez; Abbas; Li (2016) and increased with the thermal increment of pyrolysis. There was an increase of approximately 1.6% in the contents between temperatures of 300°C and 700°C. According to Figueredo *et al.* (2017), this may indicate the presence of nitrogenous compounds with structures not easily decomposed.

The H contents reduced 2.5% from the temperature of 300°C to 700°C. This gradual hydrogen reduction behavior with increasing pyrolysis temperature was also observed by Pergoraro (2015).

Figure 2 shows the morphology of the biochars produced by sugarcane bagasse by microscopic analysis.

Figure 2 – Scanning Electron Microscopy of biochars produced under different temperatures (300, 500, and 700°C).



(A) BC300 – magnification 30X (B) BC300 – magnification 3000X (C) BC500 – magnification 30X (D) BC500 – magnification 3000X (E) BC700 – magnification 30X (F) BC700 – magnification 3000X.

Source: Personal archive, 2018.

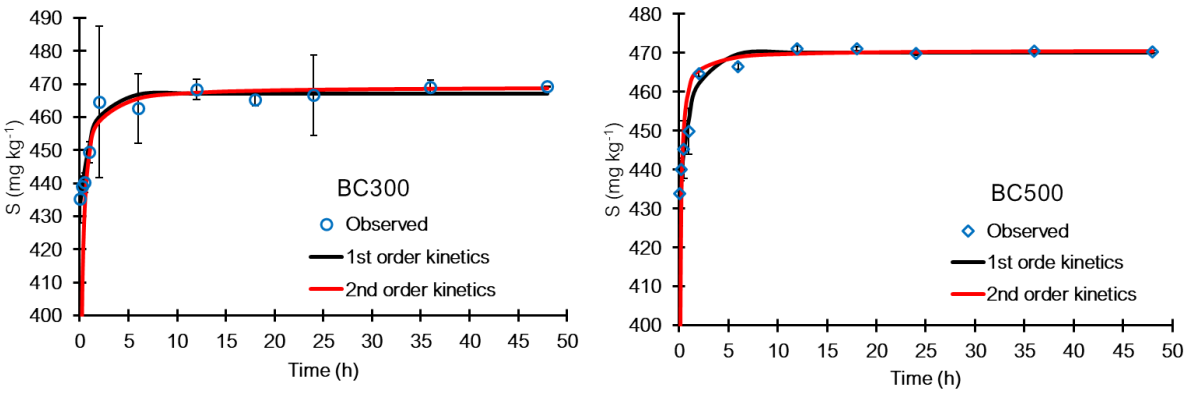
The three types of biochar presented porous surfaces, which can be attributed to the loss of gaseous and volatile compounds (SONG; GUO, 2012). It is possible to observe the presence of transverse channels, similar to the shape of a rod, and smoother and elongated surfaces in the BC500 and BC700 biochars.

BC300 showed a more significant amount of macropores, while BC700 showed the appearance of micropores in its morphological structure. BC700 presented a distinct characteristic, which refers to the presence of sub-pores on the internal walls of the pores, which can offer greater adsorptive capacity for this material. According to Pereira *et al.* (2020), the high porosity of biochars reveals the adsorbent potential to contaminants and toxic substances in the soil.

Soil adsorption kinetics

The kinetics assay allowed us to determine the time interval for the adsorption of Imazapic to become approximately constant in the soil, that is, to reach equilibrium. This data is relevant since the observed equilibrium time was used as the sample agitation time in the isotherm assays. The curves presented in Figure 3 represent the behavior of the herbicide when in contact with the soil, with higher amounts of Imazapic adsorbed in the initial phase of the assay.

Figure 3 - Adsorption kinetics curves for dystrophic Yellow Ultisol amended with biochar at temperatures of 300, 500, and 700ºC



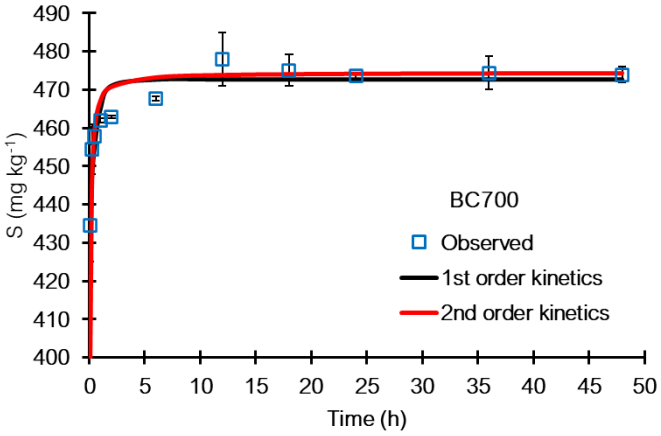


Table 4 shows the kinetic parameters associated with the pseudo-first-order and pseudo-second-order models.

Table 4 - Parameters of pseudo-first-order and pseudo-second-order kinetic models.

		BC300	BC500	BC700
Pseudo-first-order kinetics	S_1	467,22	470,14	472,60
	k_1	0,804	0,775	1,559
	r^2	0,963	0,986	0,864
	RMSE	0,541	0,353	0,963
	EM	0,963	0,986	0,864
Pseudo-second-order kinetics	S_2	469,16	470,74	474,43
	k_2	0,046	0,094	0,133
	r^2	0,938	0,858	0,733
	RMSE	0,867	0,960	0,936
	EM	0,826	0,845	0,700

S_1 and S_2 – First and second-order equilibrium sorption capacities, respectively; k_1 and k_2 – constant rates of first and second-order sorption, respectively; r^2 – coefficient of determination; RMSE – root mean square error; EM - Modeling Efficiency.

From the kinetic curves shown in Figure 3, it can be seen that the sorption of Imazapic occurred more quickly in the first 12 hours and then showed slower growth of adsorbed concentrations, with a smaller increase in sorption until reaching the stabilization. It can be noted that 24 hours after the beginning of the assay, Imazapic came into equilibrium with the soil, with a slight variation of adsorption over time. Similar

behavior to this was observed by Petter *et al.* (2019), Saleh; Hedia (2018) and Silva (2016).

The form of kinetics observed in Figure 3 for each type of biochar was similar, suggesting the involvement of similar mechanisms in the adsorption process. However, it was observed that the amount (S) and the adsorption rate (k) of adsorbed Imazapic were slightly higher for BC700.

The pseudo-first-order kinetic model presented Modeling Efficiency (EM) values closer to unity (1) and higher than those obtained by the pseudo-second-order kinetic model. Therefore, the model that best represented the observed data was the pseudo-first-order kinetic model.

Adsorption isotherms

Figure 4 shows the adsorptive behavior of the soil unamended and amended with biochars produced at temperatures of 300, 500, and 700°C. The isotherms were plotted as a function of the concentration of Imazapic adsorbed to the soil (mg kg^{-1}) and the substance concentration in the solution after reaching equilibrium (mg L^{-1}).

Figure 4 - Adsorption isotherms for the dystrophic Yellow Ultisol unamended and amended with biochar at 300, 500, and 700ºC.

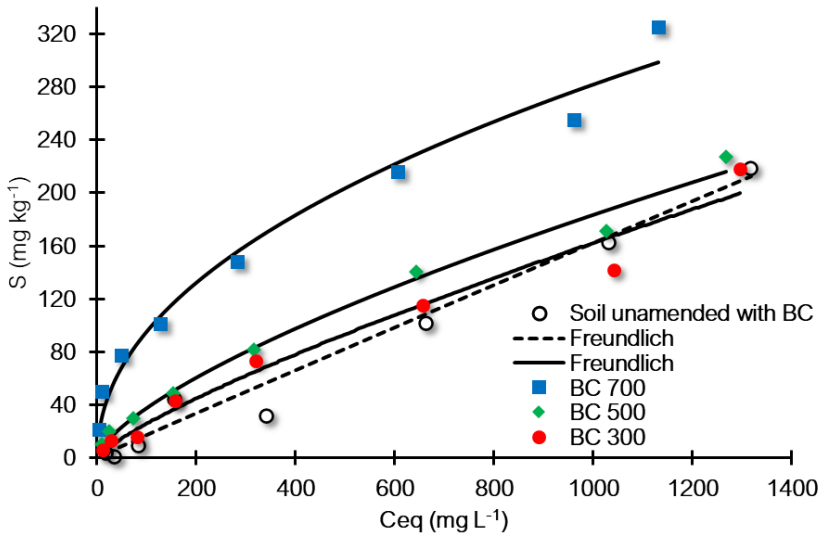


Figure 5 - Adsorption isotherms with the Freundlich and Langmuir model for the dystrophic Yellow Ultisol amended with biochars.

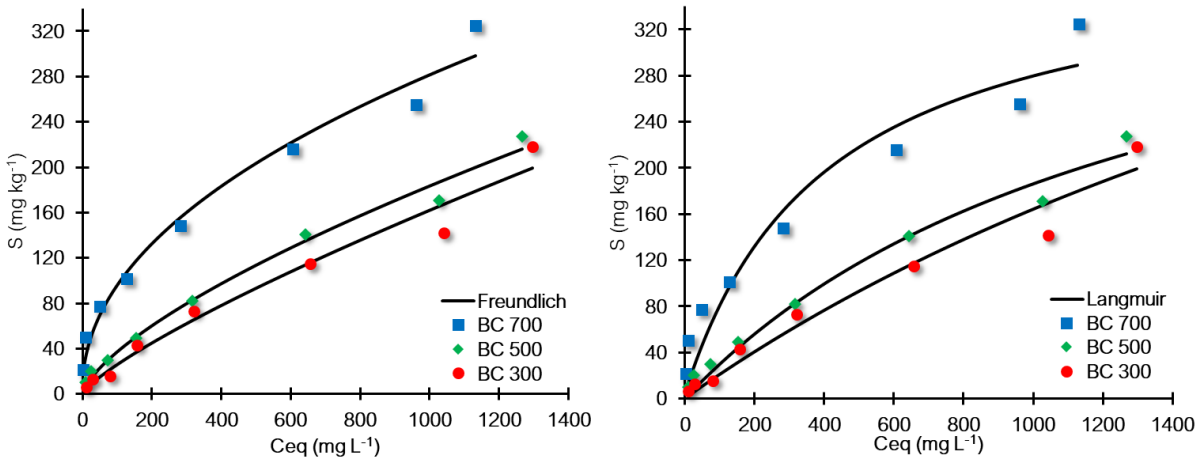


Table 5 - Data on the parameters of the adsorption isotherms for the dystrophic Yellow Ultisol (YUd) unamended and amended with biochar at different temperatures.

Soil amended with biochar						
Freundlich						
	Linear fit			**Non linear fit**		
Rep	K_F	N	R^2	K_F	n	R^2
	mg kg^{-1} (L mg^{-1})^n	---	---	mg kg^{-1} (L mg^{-1})^n	---	---
BC 300	0.98	0.73	0.973	0.65	0.80	0.966
BC 500	2.47	0.62	0.991	1.56	0.69	0.988
BC 700	15.36	0.41	0.978	11.06	0.47	0.975
Langmuir						
	Linear Model 1			**Linear Model 2**		
Rep	K_L	S_M	R^2	K_L	S_M	R^2
	L kg^{-1}	mg kg^{-1}	---	L kg^{-1}	mg kg^{-1}	---
BC 300	0.008	74.31	0.928	0.001	321.08	0.596
BC 500	0.013	94.66	0.953	0.002	280.20	0.818
BC 700	0.049	161.62	0.963	0.006	323.56	0.906
	Non linear fit					
Rep	K_L		S_M		R^2	
	L kg^{-1}		mg kg^{-1}		---	
BC 300	0.0003		714.00		0.958	
BC 500	0.0007		458.14		0.978	
BC 700	0.0025		390.04		0.919	
Soil unamended with biochar						
	Linear fit					
	K_D	R^2				
	0.1596	0.988				

When observing the graphs presented in Figure 5, it was verified that the curvature of the Langmuir and Freundlich isotherms was more remarkable as the pyrolysis temperature increased, approaching the linear format at the temperature of 300°C.

In the Freundlich isotherm model, the values of the coefficient *n* did not approach unity (Table 5). Therefore, it can be considered that the adsorption is not linear because the binding energies are not identical for all adsorption sites (NASCIMENTO *et al.*, 2014).

Based on the values of the adsorption coefficients K_F (Freundlich) and K_L (Langmuir), as well as the values of the coefficients of determination (R^2) observed in Table 5, the best adjustments were made using the Freundlich model. The isotherms here presented are similar to type I, which are associated with adsorption to micropores, according to Silva (2016).

The biochar showed good adsorption capacity of Imazapic, which differed considerably in the temperature at which the biochar was produced. According to the constructed isotherms, the higher the biochar's temperature, the more significant the increase in the adsorptive potential. The premise that more significant adsorption of organic substances is obtained with the application of biochar produced under high temperatures and being reaffirmed in this research is defended by Abdelhafez; Abbas; Li (2017). For the authors, pyrolyzed biochars at high temperatures exert greater adsorption of organic contaminants, while those at lower temperatures have an essential role in retaining heavy metals.

The value of K_D (direct adjustment) for YUd unamended with biochar was 0.1596, being lower than those obtained with the same soil amended with biochar (Silva, 2016), which obtained a higher K_F (11.06) when BC700 was used (Table 5). Thus, it is considered that the addition of biochar to YUd increased the adsorption capacity of Imazapic.

In the nonlinear fit of the Langmuir isotherms, the K_L constant increased with the pyrolysis temperature, with the highest value observed for BC700 (0.0025). Increasing these values means the binding energy between the soil and the herbicide is higher for biochars produced at high temperatures.

The biochars' distribution coefficients (K_D) varied from 0.149 to 0.233 L kg^{-1}, registering an increase in the values with the addition of the pyrolysis temperature of the biochars. This variable demonstrates the tendency of Imazapic to become adsorbed to the

soil or sediment. Thus, there was a higher K_D value for BC700, demonstrating greater adsorption potential attributed to this biochar.

Barbosa *et al.* (2013) obtained results in studies in which biochars promoted the most significant adsorption with higher pH. As in this research, the higher pH biochars were pyrolyzed at higher temperatures (Table 2). For the authors, the increase in pH may have favored the deprotonation of the functional groups of the biochar, resulting in more significant adsorption of cations. However, in the adsorption of Imazapic, possibly the pH was not the decisive factor in the increase of the adsorption. Thus, other characteristics attributed to biochars produced under high temperatures may have been responsible for the increase in adsorption, such as specific surface area (SSA), porosity, fixed carbon content, and mineral fraction. It is worth mentioning that BC700 presented SSA 40 times greater than BC300 and twice that of BC500 (Table 2) and presented in its porous structure, the presence of sub-pores, which may have contributed to the increase of its adsorptive potential.

As confirmed in the data obtained, biochar is an effective adsorbent in immobilizing organic pollutants. The high adsorbent capacity of this material can be translated into the reduction of Imazapic leaching and the risks of groundwater contamination. In addition, if the greater immobilization of Imazapic resulted in a slow release to the soil solution, it could reflect greater crop use. If proven, it would avoid the doses applied to the soil being lost to the water table and decrease the productive potential of the soils, thus reducing the risks of environmental pollution. The benevolent effect of applying biochar to the soil is also justified because Imazapic can persist in the soil for up to 410 days.

Considering that Assis *et al.* (2021) report that Imazapic has a high Groundwater Vulnerability Index (GUS), the YUd amended with sugarcane bagasse biochar may cause its immobilization in the more superficial layers of the soil (0-20 cm), decreasing its movement to other environmental compartments. Therefore, adopting this technique can reduce the risks of water contamination by Imazapic.

It is worth mentioning that the greater adsorption capacity conferred on the soil can be obtained through the application of BC700, which, according to the results of this research, caused more significant adsorption between the herbicide and the solid adsorbent material.

BC500 can offer intermediate adsorption greater than BC300, but not as expressive as that observed with the addition of BC700. In this way, the application of BC500 can be helpful to prevent a "trapping" of Imazapic, preventing it from being so retained on the surface that it cannot be used to control weeds; being necessary to carry out desorption studies to confirm this hypothesis. Applying this biochar can considerably reduce leaching rates and allow the release of the adsorbed Imazapic to the soil solution, increasing its availability to weed seeds.

In general, the biochar produced from sugarcane bagasse can reduce the risks of contamination of groundwater since it makes Imazapic stay longer in the surface layer, being subject to the action of microbial degradation and other forms of degradation.

CONCLUSIONS

This research showed that changes in pyrolysis temperatures influence the properties of the produced biochar, such as morphological structure, specific surface area, and amount and area of micropores present. Using the Freundlich isotherm model, our experimental data pointed out that the higher the biochar pyrolysis temperature, the higher the augmentation in the dystrophic Yellow Ultisol's adsorptive potential. Overall, the present work indicates that incorporating sugarcane bagasse biochar in the soil can increase the adsorption of herbicide Imazapic in the dystrophic Yellow Ultisol (YUd), reducing leaching risks and contamination of the groundwater.

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AUTHORS' CONTRIBUTION

Daniele Aparecida wrote the master's thesis that gave rise to this article, being responsible for biochar production and participating in laboratory assays. André Maciel designed and supervised this research work, contributing to the discussion and revision of this manuscript. João Paulo actively participated in the laboratory's experimental assays and the construction of the graphs of the results. José Victor Chaves performed experimental procedures for isotherm assays. Ademir Amaral participated in discussing and reviewing the text and its translation into English.

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