BIOCHAR PECAN NUTSHELL VIA PYROLYSIS FOR USE AS AN ADSORBENT: AN APPLIED STUDY FOR THE REMOVAL OF HEXAVALENT CHROMIUM

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***Abstract*– The pyrolysis process was used for the production of biochar and carried out a study for removal of Cr (VI) in aqueous solutions. The maximum removal reached was 94 % for a Cr (VI) solution at 50 mg L^{-1}. The Elovich model described very well the adsorption kinetics of Cr (VI) on the biochar and the adsorption equilibrium was described by Sips model. This suggests that adsorption of Cr (VI) onto biochar was probably controlled by chemisorption and the biochar was probably covered by the surface layer of the Cr (VI). The thermodynamic parameters showed that this adsorption process was spontaneous, favorable and exothermic. The results of this study show that this adsorbent material prepared by pyrolysis has a good response when applied to the removal of Cr (VI) in aqueous solutions.**

***Keywords*–pecan nutshell; pyrolysis; hexavalent chromium; biochar; adsorption.**

I. INTRODUCTION

The contamination by heavy metals in water is a serious problem related in nowadays then a series of studies has been carried out in an attempt to find alternatives to this environmental issue. Among these heavy metals is the Chromium, it is widely used in the industry and is released to the environment through wastewater.

The Chromium is present in its two forms, Cr (III) and Cr (VI). Trivalent chromium is not dangerous but the hexavalent chromium is toxic and causes various effects on human health. The European Commission and the US EPA recommend through their water guidelines total chromium concentration should not exceed 50 mg L^{-1} and 100 mg L^{-1}, respectively (Council Directive, 1998; US EPA, 2009). Removal of Cr (VI) from aqueous solutions can be accomplished using chemical precipitation, membrane filtration, ion exchange and reverse osmosis. However, most of these methods produce large volumes of waste, requiring high energy and high operating costs, limiting their use in practice, being the adsorption an interesting process for the removal of this metal.

According Crini (2006), the efforts of the scientific community have focused on the search for adsorbents having low price and high adsorption capacity. The cost depends on the degree of processing required and the pyrolysis process is a simple and low cost process. Besides this, local availability of the material based to manufacture the adsorbent to be very important. The low cost adsorbents generally are abundant in nature or are byproducts or waste materials from another industry (Rosales *et al*., 2015).

Many researchers have already been reported the use of biochar, as a cost effective sorbent for heavy metal removal from contaminated water. The majority of studies are focused on the metal cations, such as lead (Pb), copper (Cu), nickel (Ni) and cadmium (Cd) while limited research has been conducted on Cr (VI) removal by biochar (Inyang *et al.*, 2012; Liu and Zhang, 2009; Park *et al*., 2011; Uchimiya *et al*., 2010). The capacity adsorption of Cr (VI) has been previously reported and results have ranged from 123 mg g^{-1} for biochar from sugar beet tailings (Dong *et al*., 2011) and 23.1 mg g^{-1} for biochar from the residues of major food crops (Ma *et al*., 2014).

Although the application of alternative materials to the adsorption of metals in industrial effluents and research laboratories is scarce, some studies show that this strategy has potential. This justifies the research of new low cost materials such as *Carya illinoensis* fruit residues, which may become useful in the removal of metals in liquid effluents. The harvesting and processing of the pecan is relatively simple. After the harvesting of the nuts, which occurs with the opening of the epicarp and the fall of the fruit, they are placed in sacks and transported to the processing industry. In the industry, nuts are subjected to certain processing steps. The pecan peel is a byproduct of intense reddish color and difficult to break down. With the production of nuts on the rise, the discarding of their shells has become even greater. Considering about 45 % of the total mass of the nut and being usually deposited directly in the soil, taking time to decompose, and studies on the use of this residue are extremely important (Bansode *et al*., 2003).

This study has as objective to evaluate the application of biochar from pecan nutshell as an adsorbent to remove Cr (VI) from aqueous solutions. The adsorbent was prepared in previous study (Zazycki *et al.*, 2018). Then, the adsorption of Cr (VI) on the biochar will also be evaluated from the kinetic, equilibrium, and thermodynamic viewpoints.

II. METHODS

A. Materials

The precursor material for the adsorbent preparation was the pecan nutshell (*Carya Illinoinensis*) from a pecan-producing region in southern Brazil. The pecan nutshell were washed (deionized water), dried (60 ºC for 8 h), ground and sieved. The fraction lower a 710 µm was stored to be used in the adsorbent preparation. All chemicals, $K_2Cr_2O_7$, 1,5-diphenylcarbazide, H_2SO_4 and NaOH were analytical grade.

B. Biochar preparation and characterization

The adsorbent was prepared from pecan nutshell via pyrolysis process. The sample was prepared in a bench reactor which operates in batch system according Zazycki *et al*. (2018). To prepare the adsorbent a mass of approximately 50 g of pecan nutshell was used. A tubular reactor, a tubular furnace, nitrogen gas (N_2) at 0.25 L min^{-1} was used, then the reactor temperature was increased until 800 ° C (10 ° C min^{-1}) for 60 min and allowed to cool still under N_2 flow to room temperature. The samples (pecan nutshell and biochar) were characterized previously for Zazycki *et al.* (2018), using XRD, FTIR and surface area analysis techniques.

C. Adsorption experiments

For the adsorption study, a stock solution of $K_2Cr_2O_7$ (500 mg L^{-1}) was prepared. The assays were carried out in a stirred thermostatic bath (250 rpm). For the kinetic, equilibrium and thermodynamic studies, 0.1 g of biochar was added to 50 mL of solution at different initial concentrations (20, 30, 50 and 60 mg L^{-1}) and the pH was adjusted with 0.1 M H_2SO_4 and 0.1 M NaOH solution. In this study, pH effect was not evaluated. Recent studies proved that in the adsorption of Cr (VI) in bio-char has a strong interaction between the positively charged functional groups of biochar and the negatively charged chromate at lower pH (Zhang *et al*. 2013, Abdel-Fattah *et al*., 2015, Dong *et al.*, 2011). For this reason, together with the methodology where 1,5-diphenylcarbazide forms the complex one that results in the color being at low pH, 2.5, all solutions was adjusted to pH =2.5.Then, aliquots were taken at different times during the experiment. For the quantification of Cr (VI), the solid phase was separated by centrifugation and the concentration Cr (IV) in liquid phase was determined by spectrophotometry (λ_{max} = 540 nm) using a spectrophotometer (BEL photonics, SP 1105). The samples were analyzed after complexation with 1,5-diphenylcarbazide method according Cao and Zhang (2006).

D. Adsorption studies

For the adsorption study of Cr (VI) on the biochar of pecan nutshell, the expressions presented in Table 1 were used. To evaluate the adjustments of these equations, we used nonlinear regression analysis using the software package STATISTICA 9.0 (Statsoft, USA). To all models, the Quasi-Newton estimation method was used and the quality of fit assessed was by using the correlation coefficient (R^2). Accordingly, the correlations of the above mentioned models with the experimental data were further validated by Chi-square (X^2) test.

III. RESULTS AND DISCUSSION

A. Materials characterization

The properties of pecan nutshell and biochar are presented by Zazycki *et al*. (2018) and in this studies they concluded that the biochar sample have amorphous structure. Besides that, the material produced have micropores and mesopores with dimensions below 25 Å, BET surface area (93 m^2 g^{-1}), high total pore volume (0.055 cm^3 g^{-1}) and an average pore size of 12 Å. In addition to the characterization carried out by Zazycki *et al*. (2018), FTIR analysis was performed before and after the Cr (VI) adsorption on the biochar with the objective of verifying if Cr (VI) and adsorbent binding occurred. These results are shown in Fig. 1 and will be discussed later.

B. Adsorption kinetic study

The effect of contact time on Cr (VI) adsorption was shown in Fig. 2 (a) . The percentage removal shows that the Cr (VI) adsorption increases with increases sorbate concentration. Moreover, the results show that the metal ion removal by the sorbent increased quickly at the initial 30 min and then increased slightly with the rise in contact time and reaches the equilibrium where it showed the maximum removal at 120 min. The best % removal among all assays was 94 %.

For evaluating the removal efficiency of the contaminants by biochar, the identification of the underlying mechanisms of the adsorption process is needed. To better understand the kinetic profile, pseudo-first order, pseudo-second order and Elovich models were fitted with the experimental data, this data are showed in Fig 2 (b). The kinetic parameters for the Chromium adsorption onto biochar were listed in Table 2.

Elovich kinetic model gave a better fit and provided the best correlation to the data compared to pseudo-first order and pseudo-second order ($R^2 > 0.99$), then the Elovich model was the more suitable to represent the adsorption kinetics. This suggests that adsorption of hexavalent chromium onto biochar was probably controlled by chemisorption, and the biochar was probably covered by the surface layer of the Cr (VI). Similar behavior was obtained by Zhang *et al*. (2010) in adsorption studies of hexavalent chromium on sulfonated lignite and Han *et al*. (2016) studies about adsorption kinetic of magnetic biochar derived from peanut hull on removal Cr (VI) from aqueous solution.

Since the Elovich model was established to describe variation in chemisorption, chemical bonds must have formed when Cr (VI) was adsorbed to biochar. This can be observed in Fig. 1, where shows changes in the function groups of pecan nutshell biochar were visible after Cr sorption.

The peaks located at 3400, 1620 cm^{-1} remain unchanged and one peak appeared at 1445 cm^{-1}, which represented C = C stretching of aromatic rings (Dong *et al*., 2011). These results showed that the aromatic rings are the main functional groups for sorption of heavy metals.

Table 1. Equations used in adsorption study.

Parameter	Equation	Unit	Equation	Literature
	Removal percentage and adsorption capacity			
removal percentage	$\%Removal = \frac{(C_0 - C_t)}{C_0} \times 100$	%	(1)	-
qt, adsorption capacity at any time *t*	$q_t = \frac{V \times (C_0 - C_t)}{m}$	mg g^{-1}	(2)	-
qe equilibrium adsorption capacity	$q_e = \frac{V \times (C_0 - C_e)}{m}$	mg g^{-1}	(3)	-
	Adsorption kinetic study			
pseudo–first order	$q_t = q_1 \times (1 - \exp(-k_1 \times t))$	mg g^{-1}	(4)	Lagergren (1898)
pseudo–second order	$q_t = \frac{t}{\frac{1}{k_2 \times {q_2}^2} + \left(\frac{t}{q_2}\right)}$	mg g^{-1}	(5)	Ho and McKay (1998)
Elovich	$q_t = \frac{1}{a} \times \ln(1 + a \times b \times t)$	mg g^{-1}	(6)	Qiu *et al* (2009)
	Equilibrium isotherms			
Freundlich	$q_{e=K_F \times {C_e}^{1/n}}$	mg g^{-1}	(7)	Freundlich (1906)
Langmuir	$q_{e=} \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e}$	mg g^{-1}	(8)	Langmuir (1918)
Redlich-Peterson	$q_e = \frac{K_{RP}\, C_e}{1 + \alpha_{RP}\, {C_e}^{\beta RP}}$	mg g^{-1}	(9)	Zarei *et al.* (2018)
Sips	$q_e = \frac{q_{ms} \times K_S \times {C_e}^{1/ms}}{1 + K_s\, {C_e}^{1/ms}}$	mg g^{-1}	(10)	Zarei *et al.* (2018)
Khan	$q_e = \frac{q_s \times b_k \times C_e}{(1 + b_k \times C_e)^{ak}}$	mg g^{-1}	(11)	Zarei *et al.* (2018)
	Thermodynamic study			
Kc is the equilibrium constant	$Kc = \frac{C_{ads}}{Ce}$		(12)	Chao *et al*. (2017), Brito *et al.* (2010)
	$\ln(Kc) = -\frac{\Delta H°}{R \times T} + \frac{\Delta S°}{R}$		(13)	Chao *et al*. (2017), Brito *et al.* (2010)
Standard Gibb's free energy change	$\Delta G° = \Delta H° - T \times \Delta S°$	kJ mol^{-1}	(14)	Chao *et al*. (2017), Brito *et al.* (2010)

Table 2. Kinetic parameters for the adsorption of Cr (VI) on the biochar.

Kinetic model	Initial dye concentration (mg L^{-1})			
	20	30	50	60
Pseudo-first order				
q_1 (mg g^{-1})	4.19	10.87	20.95	30.29
k_1 (min^{-1})	1.04	2.25	3.86	5.13
R^2	0.78	0.87	0.91	0.98
Pseudo-second order				
q_2 (mg g^{-1})	17.22	20.88	20.96	30.30
k_2 (g mg^{-1} min^{-1})	$3.30 \cdot 10^{-4}$	$7.89 \cdot 10^{-4}$	3.10	4.93
R^2	0.99	0.99	0.91	0.98
Elovich				
a (mg g^{-1} min^{-1})	0.11	0.15	0.11	0.18
b (g mg^{-1})	0.09	0.40	0.13	20.65
R^2	0.99	0.99	0.99	0.99

Additionally it can be stated that, under strongly acidic condition, the negatively charged Cr (VI) species were migrated to the positively charged surfaces of biochar (protonated carboxylic, alcohol and hydroxyl groups), as showed in Fig. 1.

From these observations associated with fitting Elovich model it can be concluded that the Elovich model is able to represent well the adsorption kinetics of chromium onto biochar studied.

C. Equilibrium isotherms

The simulation of equilibrium isotherms of Cr (VI) on the biochar was based on the Langmuir, Freundlich, Redlich-Peterson, Sips and Khan models. The adsorption isotherms were obtained at 298 K. The fitting results are presented in Table 3.

The Table 3 shows that all the used models correlated well with the experimental data ($R^2 > 0.99$) in the following order: Sips > Langmuir = Khan > Freundlich > Redlich-Peterson . Based in the high values of R^2 and low value of X^2, it is clear that Sips model was the more adequate to represent the isotherm curve. Sips model is a combination of the isotherm of Langmuir and Freundlich. At low concentration of adsorbate, this model assumes Freundlich form and at high concentration the model as-

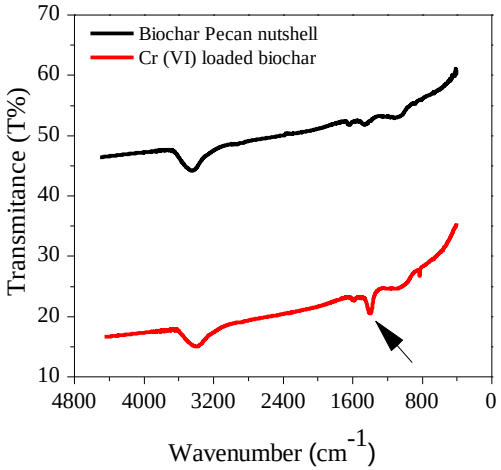

Figure 1. FTIR spectra of biochar and Cr (VI) loaded biochar.

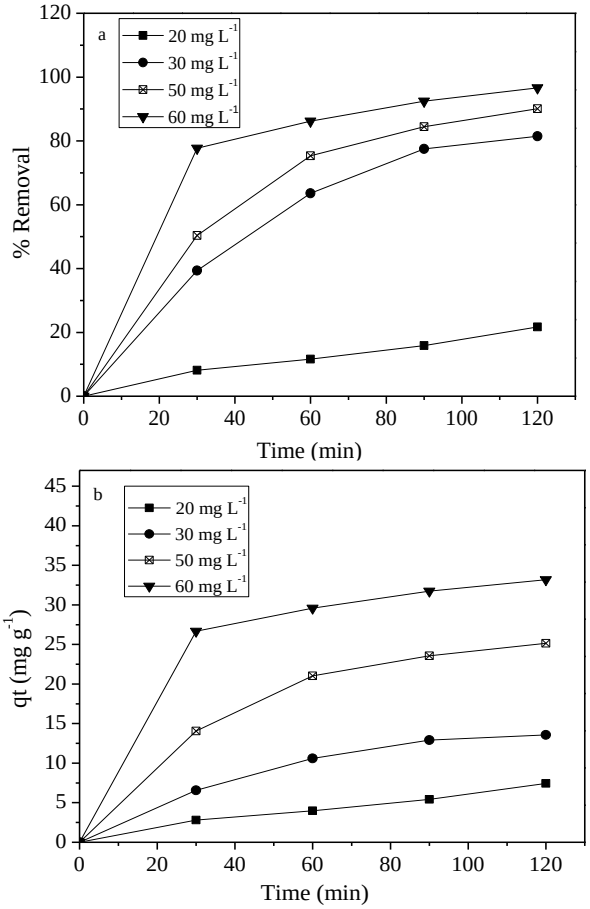

Figure 2. (a)The % removal Cr (VI) by biochar pecan nutshell and (b) adsorption kinetics.

sumes Langmuir form. In the Fig. 3 it is verified the experimental behavior in relation to the sips model. This result corroborates with the study by Mohan *et al*. (2011), where it was evaluated of chromium remediation from water using low cost biochar (Oak wood and oak bark chars). In this study the sips model was the better, they affirmed adsorption is diffusion controlled at low chromium concentrations while monomolecular adsorption with a saturation value takes place at high chromium concentrations.

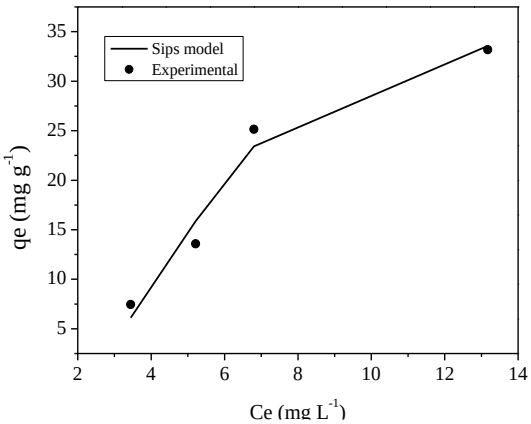

Figure 3. Comparison between experimental and sips model.

Table 3. Isotherm parameters.

Parameters	Values
Langmuir	
q_m (mg g^{-1})	144.648
K_L (L mg^{-1})	0.024
R^2	0.943
X^2	2.754
Freundlich	
K_F (mg g^{-1})	3.663
n (g L^{-1})	1.148
R^2	0.937
X^2	2.959
Redlich-Peterson	
K_{RP} (L mg^{-1})	0.088
α_{RP} (L $mg^{-1})^{\beta RP}$	-0.976
β_{RP}	-0.0038
R^2	0.936
X^2	2.967
Sips	
m_s	3.365
q_{mS} (mg g^{-1})	35.424
K_s (L mg^{-1}) ^{ms}	0.0031
R^2	0.987
X^2	0.887
Khan	
q_s (mg g^{-1})	992.523
b_k (L mg^{-1})	0.0034
a_k (L g^{-1})	6.191
R^2	0.943
X^2	2.734

D. Thermodynamic study

The adsorption thermodynamics was evaluated according to the values of standard Gibb's free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0). The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of Van't Hoff plot (*ln Kc vs. 1/T*). These values are shown in Table 4.

The negative ΔG^0 values indicated that the hexavalent chromium adsorption onto the biochar was a spontaneous and favorable process. The negative ΔH^0 corroborated the Cr (VI) adsorption onto biochar was exothermic in nature. Similar results were found by Shahverdi *et al.* (2016) in the study on Cr (VI) removal from aqueous solution. From the magnitude of ΔH^0 is possible to infer about the adsorbent/adsorbate interactions. Bonding forces lower than 40 kJ mol^{-1} refer to physisorption while

Table 4. Thermodynamic properties of adsorption of Cr (VI) on the biochar.

C (mg L^{-1})	T(°C)	Kc	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1})	R^2	ΔG^0 (kJ mol^{-1})	% R
	25	9.148	-90.87	-0.27	0.989	-5.75	89.07
30	40	5.733				-4.37	82.56
	45	2.995				-2.99	66.61
	25	29.675	-75.16	-0.22	0.998	-8.37	96.63
60	40	6.566				-5.01	84.77
	45	4.512				-3.89	77.84

forces higher than 40 kJ mol^{-1} refer to chemisorption (Zazycki *et al*., 2018). Then, the chemisorption occurred in the Cr (VI) adsorption onto the biochar. It was also possible to observe that with the increase in temperature there was a decrease in the % removal of Cr (VI). The negative ΔS^0 values indicated that the disorder in solid/liquid interface decreased after the adsorption process.

IV. CONCLUSIONS

This study carried out an investigation about biochar from pecan nutshell produced by pyrolysis process as alternative adsorbent to remove hexavalent chromium from aqueous solutions and it was concluded that:

1. The maximum adsorption capacity was around 35.4 mg g^{-1}, indicating that the adsorption performance of the material prepared in this work was similar and superior to other adsorbents reported in earlier studies.
2. Findings suggest that pyrolysis has potential to create effective, adsorbents relevant to environmental application.
3. The adsorption of Cr (VI) onto the biochar was a spontaneous, favorable and exothermic process, being that chemical bonds occurred between the ions and the adsorbent.
4. The results indicated that the biochar is an effective adsorbent for the removal of Cr (VI) ions from aqueous solutions, and it could be useful in treatment of Cr (VI) polluted wastewaters.
5. Concerning the Cr (VI) loaded biochar, the metal can be desorbed. So, both, the metal and the biochar can be reused. Furthermore, if desorption is not possible, the Cr (VI) loaded biochar can be disposed in landfills.

NOMENCLATURE

a is the Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorption (g mg^{-1}).

a_k parameter from Khan model.

b the adsorption rate of the Elovich equation initial (mg g^{-1} min^{-1}).

b_k parameter from Khan model (L mg^{-1})

C_{ads} is the concentration of Cr (VI) adsorbed (mg L^{-1})

C_e is the equilibrium of Cr (VI) concentration in liquid phase (mg L^{-1})

C_t is the Cr (VI) concentration in liquid phase at any time (mg L^{-1})

C_0 is the initial Cr (VI) concentration in liquid phase (mg L^{-1})

k_F is the Freundlich constant related to the relative adsorption capacity (mg g^{-1})

k_L is the Langmuir constant related to the free energy of adsorption (L mg^{-1})

Kc is the equilibrium constant

K_s is Sips model isotherm constant (L mg^{-1})

K_{RP} is the Redlich-Peterson isotherm constant (L mg^{-1})

k_1 is the rate constant of pseudo–first order model (min^{-1})

k_2 is the rate constant pseudo–second order model (g mg^{-1} min^{-1})

m is the amount of adsorbent (g)

ms is the isotherm exponent by Sips model

n is the heterogeneity factor (g L^{-1})

q_e is the equilibrium adsorption capacity (mg g^{-1})

$q_{e,exp}$ is the experimental capacity data

$q_{e,calc}$ is the model equilibrium capacity data

q_m is the maximum adsorption capacity Langmuir model (mg g^{-1})

q_{ms} is the maximum adsorption capacity from Sips model (mg g^{-1})

q_s is the maximum adsorption capacity from Khan model (mg g^{-1})

q_t is the adsorption capacity at any time t (mg g^{-1})

q_1 is the theoretical value for the adsorption capacity (mg g^{-1})

q_2 is the theoretical value for the adsorption capacity (mg g^{-1})

R is the universal gas constant (8.314 J mol^{-1} K^{-1})

R^2 is the correlation coefficient

t is the time (min)

T is the temperature (K)

V is the volume of solution (L)

X^2 is the Chi-square

α_{RP} is the Redlich-Peterson isotherm constant (L $mg^{-1})^{\beta RP}$

β_{RP} is the isotherm exponent by Redlich-Peterson model

$\Delta G°$ is the Gibb's free energy change (kJ mol^{-1})

$\Delta H°$ is the enthalpy change (kJ mol^{-1})

$\Delta S°$ is the entropy change (kJ $mol^{-1}K^{-1}$)

% Removal is the removal percentage (%)

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