KINETIC STUDY OF URANIUM REMOVAL FROM AQUEOUS SOLUTIONS BY MACAUBA BIOCHAR

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ABSTRACT: Macauba (*Acronomia aculeata*) is a palm tree native of the Brazilian "cerrado" and a valuable renewable source of vegetable oil for human consumption and biodiesel production. Residue from the extraction of the coconut oil, the shell, or endocarp, can be used as a raw material for the production of biochar (BC) aiming the removal of uranium from aqueous solutions. Biochars are obtained by thermal decomposition of the biomass under inert atmosphere (pyrolysis) and, because of their surface properties and porous structure, they exhibit great potential as adsorbents. Adsorption of U(VI) was studied by a batch technique using a biochar produced through slow pyrolysis at 350°C of the macauba endocarp. The effect of contact time was investigated and a kinetic study was conducted to determine the mathematical model that best describes the adsorption process. The adsorption capacity (q_{max}) obtained for BC350 was 405 mg g^{-1}.

KEYWORDS: biochar, macauba, uranium, adsorption.

1. INTRODUCTION

Various activities in the nuclear area (mining, research, fuel cycle, nuclear medicine) generate aqueous wastes containing radioactive uranium. Recently, many uranium mining and production plants have been taken out of operation. Therefore, proper decommissioning and environmental rehabilitation are required according to the international radiation protection guidelines and standards and to national regulations (NEA/OECD, 1999).

Treatment of contaminated wastewater and aqueous radioactive wastes is essential for environmental management and the restoration of the affected ecosystem's natural conditions. To do so, a combination of techniques and operations has been used over the years, such as: precipitation, reverse osmosis, solvent extraction, ultrafiltration and adsorption (Sakr *et al.*, 2003; Ozdemir & Usanmaz, 2009). Among these techniques, adsorption stands out for its efficiency and specificity, allowing a simple application with low investment (AIEA, 2003).

Agriculture by-products are being studied as a sustainable solution for wastewater treatment (De Gisi *et al.*, 2016), providing a wide range of renewable sources for the production of biochar, a porous, carbon-rich material. Many studies have shown that biochar can be applied for wastewater treatment because it effectively removes heavy metals from aqueous solutions (Inyang *et a.l*, 2016; Patra *et al.*, 2017).

Biochars can be produced using the pyrolysis technique, in which the biomass is carbonized at temperatures below 700°C in the absence of oxygen (Lehmann, 2009). The parameters that have a direct impact on the yield and properties of the biochar are the heating rate, residence time and final pyrolysis temperature (Bridgwater & Peacoke, 2000; Lu *et al.*, 2009), from which the maximum temperature at which the biomass is submitted to the pyrolysis furnace, called the highest treatment temperature (HTT), has the greatest influence (Antal & Gronli, 2003;

Lua *et al.*, 2004; Özçimen & Ersoy-Meriçboyu, 2008).

Macauba (*Acronomia aculeata*) is a palm tree native to the Brazilian "cerrado" and a valuable renewable source of vegetable oil for human consumption and biodiesel production (Ratter, 2003). After extraction of the oil from the fruit's nut, the shell, technically referred to as the endocarp, remains as residue. This residue can be used as a raw material for the production of biochar (BC) applied for the removal of uranium from aqueous solutions (Guilhen, 2017a).

The process of adsorption is influenced by some factors such as pH, initial concentration, adsorbent dose and contact time. The first three parameters were examined in a previous study (Guilhen, 2017b). Contact time represents the physical time allowed for the contact of the phases. The time to reach adsorption equilibrium corresponds to the sufficient contact time to allow diffusion process and attachment of the adsorbate molecules onto the adsorbent. Adsorption isotherms and kinetic parameters have been estimated from the experimental results.

2. MATERIALS AND METHODS

2.1. Materials

Pyrolysis of the macauba endocarp was carried out at the Waste and Metallurgy Recycling Laboratory (LAREX, Poli / USP-SP). The endocarp was supplied by Acrotech (Viçosa, Minas Gerais).

Knife mills from Rone (FA300) and Marconi (MA340) were used in grinding the endocarp and biochar, respectively. A horizontal tubular furnace from Linderg (Blue M) with central temperature control was used for the pyrolysis of the endocarp.

For the determination of uranium in the adsorbate solutions, an inductively coupled plasma optical emission spectrometer (ICP OES) from Spectro (Spectro ARCOS) was used.

2.2. Preparation of solutions and standards

All solutions were prepared using ultrapure water (18.2 MΩ resistivity) and analytical grade nitric acid (HNO_3 65%, Merck, Darmstadt, Germany). A stock solution of 1,000 mg L^{-1} uranium was prepared using NBL Certified Reference Material (U_3O_8, CRM 129-A).

2.3 Endocarp Characterization

The macauba endocarp was initially characterized according to the following parameters: moisture, density, elemental and molecular composition.

2.4. Sample preparation

The endocarp was previously ground in a knife mill using an ASTM 3/8 inch stainless steel sieve allowing homogenization of the sample and thereby greater uniformity in carbonization. The milled material was oven-dried at 100°C for 3 h and stored in a desiccator.

2.5. Pyrolysis

An approximate fraction of 30 g of endocarp was processed each time in an alumina crucible (13x4cm) under a continuous argon flow of 40 mL min^{-1}. Before starting the heating, a 20 min purge with argon was performed. Heating was initiated with a heating rate of 5 °C min^{-1} until reaching the highest treatment temperature (HTT) of 350 °C, at which it remained for a residence time of 1 h.

At the end of the pyrolysis, the furnace was switched off and the sample was slowly cooled to approximately 100°C under inert atmosphere, then removed from the furnace to prevent condensation of vapors and stored in a desiccator until room temperature was reached.

The grinding was carried out in a knife mill using Mesh 10 mesh sieve. The ground material was packed in polypropylene tubes and identified as BC350.

2.6. Contact time effect

The effect of contact time on uranium adsorption by macauba biochar was evaluated by varying the stirring time of the solution in contact with the adsorbent. To that end, 11 independent

solutions with an initial concentration of 5 mg L^{-1} of U were prepared at pH 3 and brought into contact with a dose of 10 g L^{-1} of the adsorbent, BC350, being subjected to shaking at 130 rpm and withdrawn at predetermined time intervals to a total of 5 h (300 min).

2.7. Adsorption kinetic study

Isotherms were used to mathematically describe the adsorption process. They demonstrate the amount of mass of the adsorbed compound (adsorbate) by the solid (adsorbent) as a function of the concentration of the compound in the equilibrium solution.

3. RESULTS AND DISCUSSION

3.1. Feedstock characterization

Table 1 presents the main characteristics of the macauba endocarp used as feedstock for biochar production.

Table 1. Properties and composition of the macauba endocarp.

Parameter	Endocarp
Moisture (%)	9.95
Density (g cm^{-3})	1.34
C (%)	50.6
H (%)	6.4
N (%)	1.0
S (%)	0.3
O (%)	47.4
Cellulose (%)	37.91
Hemicellulose (%)	17.97
Lignin (%)	34.66

3.2. Effect of contact time on U adsorption

The effect of contact time on the removal of U (VI) by BC350 is shown in Fig. 1. It is noted that a minimum of 3 h of contact is required to reach the adsorption equilibrium. Therefore, it is not necessary to subject the system to longer periods of contact.

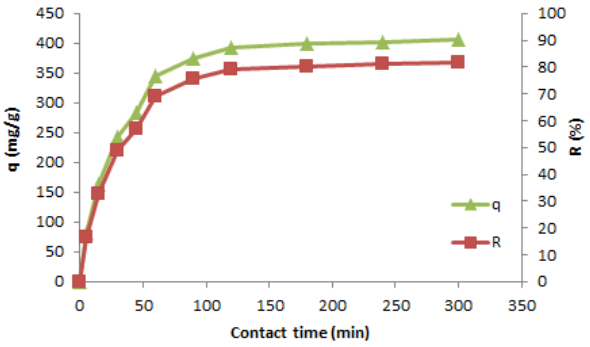

Figure 1. Effect of contact time on U adsorption by BC350

3.3. Kinetic modeling

Four models were used to evaluate the adsorption kinetics of U (VI) by BC350: the kinetic models of pseudo-first order (PFO) (Lagergren, 1898), pseudo-second order (PSO) (Ho and McKay, 1999), intraparticle diffusion (IPD) (Weber and Morris, 1962) and Elovich (Elovich and Zhabrova, 1939).

Table 2. Kinetic equations for each model.

Model	Equation
PFO	$log(q_e - q_t) = log\, q_e - k_1 t$
PSO	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
IPD	$k_{di} = \frac{q_t}{t^{½}} + C$
ELOVICH	$q_t = \frac{1}{\beta}(ln\alpha\beta) + \frac{1}{\beta}(lnt)$

Table 3. Kinetic parameters values for U (VI) onto BC350.

Pseudo-first order				
K_1 (min^{-1})	q_e calc (mg g^{-1})	q_e exp (mg g^{-1})		R_1
32,7 x 10^{-3}	411	400		0,998
Pseudo-second order				
K_2 (g mg min^{-1})	h (mg g min^{-1})	q_e calc (mg g^{-1})	q_e exp (mg g^{-1})	R_2
0,110	19,3	439	400	0,999
Intraparticle diffusion				
C (mg g^{-1})	K_{dif} (mg g $min^{0,5}$)			Ri
123	20,1			0,745
Elovich				
α (mg g^{-1} min^{-1})	β (g mg^{-1})			R_E
147	11,6 x 10^{-3}			0,973

The parameters of each model were derived from their respective linear graphs and are presented in Table 3. A comparison between the calculated and measured results are shown in Fig. 2.

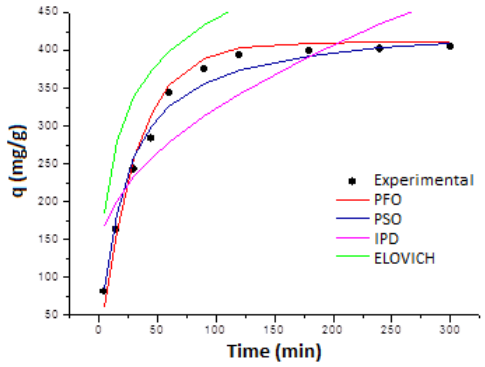

Figure 2. Comparison between the measured and modeled time profiles for adsorption of U (VI) by BC350

The values of q_e calculated (q_e calc) for both PFO and PSO are close to the experimentally observed values (q_e exp).

However, although the R^2 value of the pseudo-second order model (0.999) is closer to 1.0 than the R^2 value of the pseudo-first order model (0.998), this difference is not statistically significant. Therefore, the best fit of the experimental data is attributed to the pseudo-first order model, since the calculated q_e is the one closest to the experimentally observed value (q_{exp}).

The lack of adjustment to the IPD and Elovich models suggests that the adsorption is not taking place inside of the pores.

From these results, adsorption of U (VI) by BC350 can be best described by the kinetic model of pseudo-first order, indicating that the adsorption of U (VI) by BC350 is limited to the monolayer.

Moreover, the pseudo-first order model is equivalent to the linear driving force equation proposed by Glueckauf (1955) for chromatographic processes. By applying such

model, the mass transfer coefficient K_1 could be related to the effective diffusivity of U(VI) if biochar particles are assumed to be spherical. In this case, assuming that the diameters of the biochar particles vary between 500µm and 1000µm, it is possible to conclude that the diffusivity of U(VI) may range from $2{,}27.10^{-12}$ m^2 s^{-1} to $9{,}08.10^{-12}$ m^2 s^{-1}. Typical diffusivities for dilute solutions of ionic compounds in water are around 10^{-9} m^2 s^{-1}, but, in theory, could be reduced to $10^{-11}m^2$ s^{-1}, depending on the medium conditions (Samson *et al*., 2003).

The q_{max} is also an important parameter in the evaluation of the adsorption capacity of the adsorbents.

Table 4. Comparison of the adsorption capacity, qmax in mg g^{-1}, of the U (VI) in adsorbents of different origins.

Adsorbent	**q_{max}**	**References**
Chemically and thermally modified bentonite	29	Tsuruta, 2002
Conventional activated carbon	45	Morsy & Hussein, 2011
E. canadensis	89	Yi *et al*, 2016
Thermally treated carbono microspheres	92	Zhang *et al*., 2013

The value of q_{max} for removal of U (VI) by BC350 in the present study was 405 mg g^{-1}. Compared to other organic, inorganic and biological adsorbents, reported in the literature (Table 4), the BC350 presents a better performance in the adsorption of U (VI).

4. CONCLUSION

The effect of contact time on the U(VI) adsorption by the BC350 was evaluated and the results showed that the adsorption has reached the equilibrium after 3 hours of contact time. According to the kinetic study, the best fit for the experimental data was achieved when the pseudo-first order model was applied. The U(VI) adsorption capacity (q_{max})achieved for the BC350 was 405 mg g^{-1}, which, compared to other adsorbents in the literature, is significant higher. Thus, the BC350, obtained from the pyrolysis of the macauba endocarp at 350°C, has a great potential to be applied for the removal of U(VI) from aqueous solutions.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

Thanks to Dr. Jorge Tenório from the Waste and Metallurgy Recycling Laboratory (LAREX, Poli / USP-SP) and Felipe Morbi from Acrotech (Viçosa, MG).