

## INFLUENCE OF PYROLYTIC TEMPERATURE ON URANIUM ADSORPTION CAPABILITY BY BIOCHAR DERIVED FROM MACAUBA COCONUT RESIDUE

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### ABSTRACT

Biochar (BC) is a carbon-rich product obtained when biomass is thermally decomposed at relatively low temperatures (under 700°C) and limited supply of oxygen in a process called pyrolysis. The conversion of biomass into BC can not only result in renewable energy source of synthetic gas and bio-oil, but also decrease the content of CO<sub>2</sub> in the atmosphere, as well as improving soil fertility. Because of its porous structure, charged surface and surface functional groups, BC exhibits a great potential as an adsorbent. Brazilian agro energy chain involves tons of biomass waste, providing a wide range of biomasses with different chemical and physical properties. BC characteristics strongly depend on the feedstock and the pyrolysis conditions, in which the temperature is the key parameter. The aim of this study was to evaluate the adsorption potential for the removal of uranium, U(VI), from aqueous solutions using BC obtained through the pyrolysis of the macauba (*Acrocomia aculeata*) coconut endocarp as a function of the final pyrolytic temperature. BCs produced at higher temperatures are likely to present lower H/C and O/C ratios, indicating the loss of easily degradable carbon compounds such as volatile matter. In contrast, low-temperature pyrolysis produces not only a higher BC yield, but also richer in surface functional groups which will likely enable interactions with the U(VI) ions. The endocarp was subjected to six different pyrolytic temperatures, ranging from 250 °C to 750 °C. The influence of parameters such as pH, sorbent dose and initial concentration on the adsorption of U(VI) was investigated. The maximum adsorption capacity (q) was achieved for the BC obtained at 250°C (BC250), which presented a removal percentage of approx. 86%, demonstrating the potential of the BC from macauba endocarp for treatment of wastewaters. Thus, submitting the endocarp to temperatures higher than 250°C becomes unnecessary, saving time and reducing operating costs.

## 1. INTRODUCTION

Radioactive uranium aqueous wastes emerge as a result of many distinct nuclear activities such as mining, research, fuel cycle and nuclear medicine. Environmental issues have become increasingly important in the last few decades especially due to the large number of uranium production facilities which have been taken out of operation recently. Decommissioning and rehabilitation have become a concern, since the remediation of formerly utilized sites involves a broad investigation of the environment and the extent to which it has been affected, before applying the necessary administrative and technical actions to restore it under the auspicious control of regulatory agencies [1]

Monitoring of the water from uranium mills is required to ensure that all constituents are within regulatory compliance. Treatment of contaminated wastewater is essential before its discharge into the environment. Combined techniques and operations such as chemical precipitation, reverse osmosis, solvent extraction, micellar ultrafiltration and adsorption are normally required for the treatment of uranium contaminated wastewaters and liquid radioactive wastes [2, 3]. Among the possible techniques, adsorption stands out for its efficiency and specificity, requiring a simple design and low investment [4].

Agricultural by-products have been studied as a sustainable solution for wastewater treatment [5], providing a wide range of renewable sources for the production of biochar, a porous stable material. Several studies have demonstrated that biochar can be applied for wastewater treatment because it effectively removes heavy metals from aqueous solutions [6, 7].

Biochar may be produced using pyrolysis technique, in which the biomass is heated to relatively low temperatures ( $< 700^{\circ}\text{C}$ ) in the absence of oxygen [8]. Heating rate, residence time and temperature have a direct impact in the distribution and yield of each of the biochar [9, 10]. Of these parameters, the maximum temperature to which the biomass is subjected in the pyrolysis reactor, called highest treatment temperature (HTT) has the greatest overall influence on the biochar properties [11, 12, 13].

Macauba (*Acrocomia aculeata*) is a palm tree prevalent in the Brazilian savannah, which coconut is used to produce oil. As a residue of the nut-oil extraction, the endocarp has a potential to be used as feedstock for biochar production, because of its elevated lignin content [14].

In this study, the endocarp has been subjected to six different pyrolytic temperatures: 250, 350, 450, 550, 650 e  $750^{\circ}\text{C}$ . The effect of the pyrolytic highest treatment temperature (HTT) on the biochars produced at each different temperature was evaluated by performing adsorption tests using batch technique. The influence of parameters such as pH, adsorbent dose and initial concentration on the adsorption of U(VI) was investigated.

## 2. MATERIALS AND METHODS

### 2.1. Materials

The endocarp from macauba coconut was supplied by Acrotech (Viçosa, Minas Gerais). Separation of the parts of the fruit comprised the depulping, in which the pulp is removed. The chestnut, constituted by the endocarp and almond, was broken using a jaw crusher, allowing the separation of the endocarp.

A standard solution of 1000 mg L<sup>-1</sup> of uranium was prepared through the dissolution of a U<sub>3</sub>O<sub>8</sub> certified material supplied by New Brunswick Laboratory (NBL CRM 129-A). This solution was used to prepare both adsorption and calibration solutions. All solutions were prepared with ultrapure water (18.2 MΩ cm resistivity) and analytical grade nitric acid (HNO<sub>3</sub> 65%, Merck, Darmstadt, Germany).

### 2.2. Sample preparation

After sampling for removal of dirt and unbroken coconuts, the shells were ground in a cutting mill passing over a 3/8 Mesh screen and subsequently dried at 100 °C for 3 hours.

### 2.3. Biochar production

Pyrolysis of the endocarp was conducted in a Lindberg Blue M horizontal tubular steel reactor heated by an electric furnace at the Laboratory of Recycling, Waste Treatment and Extraction (LAREX, University of Sao Paulo) under inert argon atmosphere, ranging from 250°C to 750°C. The carbonized samples were denominated as “BCT”, in which “T” corresponds to the HTT; for instance: BC250 when the HTT is 250°C. The dried endocarp was subjected to six different HTTs, as shown in Table 1.

For each HTT, approximately 30 g of endocarp was processed applying an argon (Ar) gas flow of 40 mL min<sup>-1</sup>. The sample was kept at each HTT for 1 h (residence time). By the end of the process, the furnace was switched off and the reactor was allowed to cool.

**Table 1: Pyrolysis heating steps at a heating rate of 5°C min<sup>-1</sup>**

Steps	250°C	350°C	450°C	550°C	650°C	750°C
1	50 min	-	-	-	-	-
2		70 min	-	-	-	-
3			90min	-	-	-
4				1h50	-	-
5					2h10	-
6						2h30

The argon flow proceeded during the cooling process in order to purge the reactor of any remaining pyrolysis gases and to prevent any oxygen exposure of the biochar while still above ignition temperature.

After that, the alumina crucible containing the biochar was removed from the furnace and allowed to cool at room temperature in a desiccator. Finally, the biochar was ground in a cutting mill passing over a 120 Mesh screen.



**Figure 1: (1) macauba endocarp pre-pyrolysis; (2) pyrolysis reactor; (3) biochar; (4) cutting mill; (5) ground biochar.**

## 2.4. Adsorption experiments

Equilibrium adsorption experiments were conducted using batch technique and the experiments were performed in a rotary shaker using 100 mL glass Beckers, 120 rpm stirring rate at room temperature (25°C) during 24 hours. The adsorbent was separated by filtration using a 0.45 micron Teflon membrane filter (DigiFILTER, SCP Science, Quebec, Canada).

The U(VI) concentration in the remniscent filtrate solution was subjected to a determination using inductively coupled plasma optical emission spectrometry (Spectro ARCOS, Spectro Analytical Instruments, Kleve, Germany). The adsorption of U(VI) was evaluated as a function of pH, adsorbent dose, initial concentration and contact time. The initial pH was adjusted using 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> and 0.1 mol L<sup>-1</sup> NaOH solutions.

The adsorption capacity (mg g<sup>-1</sup>) of the adsorbent was calculated using the Eq. (1):

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

where  $q_t$  is the adsorbed amount of adsorbate per gram of adsorbent at any time  $t$ ,  $C_0$  and  $C_t$  the concentrations of the adsorbate in the initial solution and at any time  $t$ , respectively (mg L<sup>-1</sup>);  $V$  the volume of the adsorbate solution added (L) and  $M$  the amount of the adsorbent used (g).

The extraction efficiency was determined through the following equation:

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

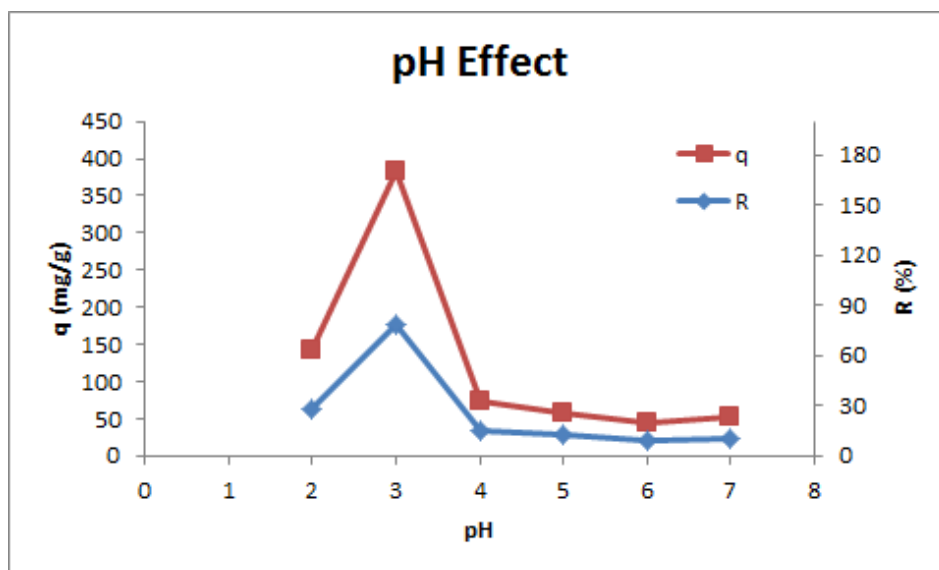
where R is the efficiency of extraction or retention percentage,  $C_o$  ( $\text{mg L}^{-1}$ ) is the initial concentration of each adsorbate and  $C_t$  ( $\text{mg L}^{-1}$ ) represents the concentration of the adsorbate at time t.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of pH

The pH of the aqueous solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of the solute. The pH values were evaluated in a range between 2.0 and 7.0, while the other parameters (dosage of  $10 \text{ g L}^{-1}$  and  $5 \text{ mg L}^{-1}$  U initial concentration) were held constant.

BC350 was selected for the preliminary experiments based on the relationship between the gravimetric yield and fixed carbon (GY x FC) [15]. The influence of pH on the removal of U(VI) ions onto macauba biochar is presented in Fig. 2.

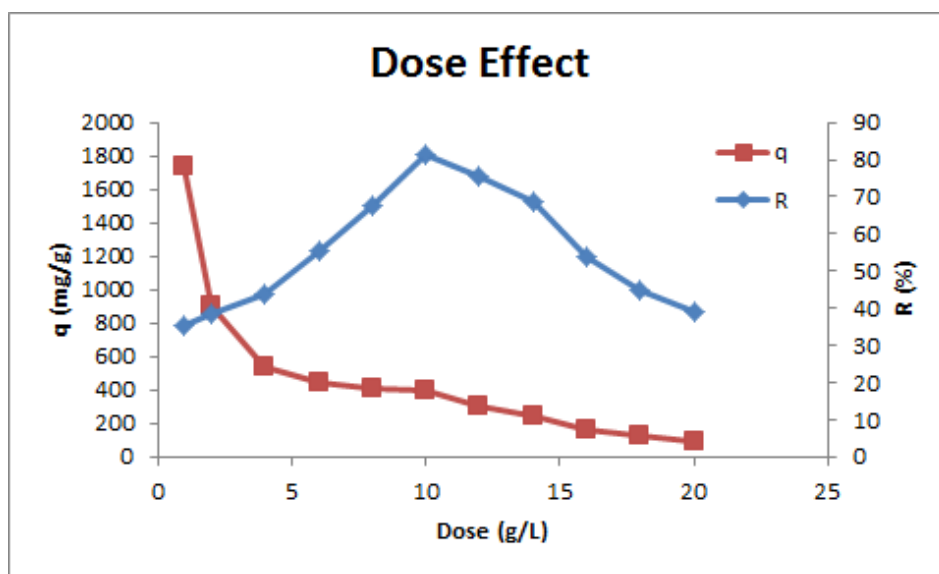


**Figure 2: Effect of initial pH on the adsorption capacity of U(VI) onto BC350;  $C_o(\text{U}) = 5 \text{ mg L}^{-1}$ , adsorbent dosage =  $10 \text{ mg L}^{-1}$ , contact time = 24 h;  $T = 25 \pm 2^\circ\text{C}$ .**

As can be seen in Fig. 2, the adsorption ability for uranium onto BC350 strongly depends on the pH value. The uptake amount of U(VI) reached the maximum adsorption capacity at pH 3.0. The observed behavior can be explained by the presence of different mononuclear and polynuclear uranium (VI) hydrolysis products in the form of  $[(\text{UO}_2)_p(\text{OH})_q]^{(2p-q)+}$  at different pH values in the solution [16]. At lower pH values ( $\text{pH} < 5$ ), the predominant species is  $\text{UO}_2^{2+}$ .

### 3.2 Effect of adsorbent dosage

The adsorbent dosage is an important parameter because it is associated to the determination of the adsorption capacity of an adsorbent for a given concentration of adsorbate. The adsorption studies of U(VI) onto biochar materials were conducted by varying the adsorbent dosage from 1 to 20 g L<sup>-1</sup>. The influence of adsorbent dosage on adsorption of U(VI) ion is shown in Fig. 3.



**Figure 3: Effect of the adsorbent dose on the adsorption of U(VI) onto BC350;**  
 $C_0(\text{U}) = 5 \text{ mg L}^{-1}$ ,  $\text{pH} = 3$ ,  $\text{contact time} = 24 \text{ h}$ ;  $T = 25 \pm 2^\circ\text{C}$ .

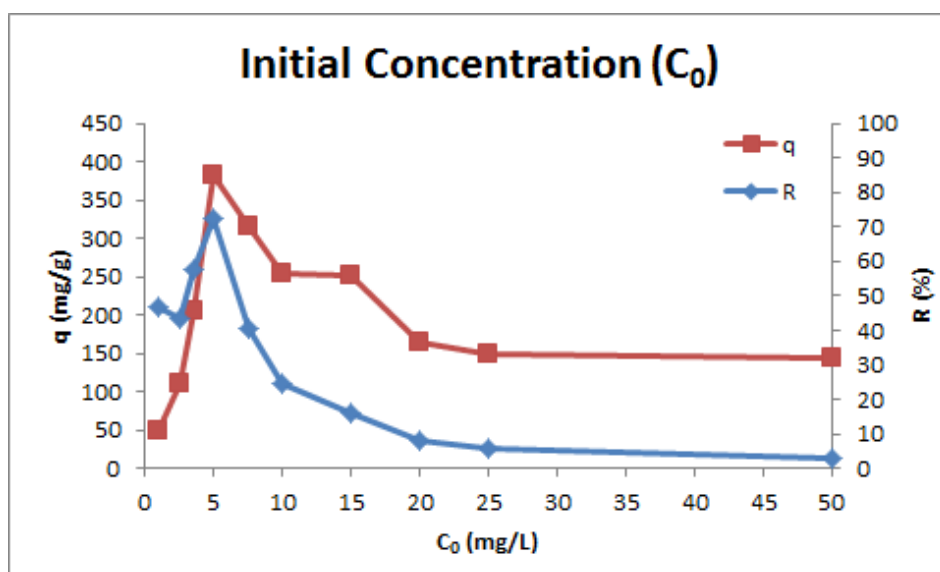
As seen in Fig. 3, increasing the adsorbent dose up to 20 g L<sup>-1</sup> substantially decreases the adsorption capacity (the amount adsorbed per unit mass of adsorbent) for U(VI), which is mainly due to the sites remaining unsaturated during the adsorption process and can be mathematically explained [17]. Another reason may be attributed to the particle interactions, such as aggregation, caused by high adsorbent concentration [18]. Such aggregation would lead to a decrease in the total surface area of the adsorbent [19]. Thus, further increase of adsorbent dosage does not afford exhaustive adsorption of U(VI). However, in terms of removal, the maximum effect is observed when a dose of 10 g L<sup>-1</sup> is used. Therefore, this dose was adopted for adsorption experiments.

### 3.3. Effect of initial concentration

The initial concentration ( $C_0$ ) of the U(VI) aqueous solution was evaluated for a range of concentrations from 1 to 50 mg L<sup>-1</sup>. The experiments were performed using a dose of sorbent of 10 g L<sup>-1</sup> and adjusting the solutions to pH 3.

The influence of initial concentration ( $C_0$ ) on adsorption of U(VI) ion is shown in Fig. 4. An increase of the adsorption capacity ( $q_t$ ) is observed when  $C_0$  was increased from 1 to 5 mg L<sup>-1</sup>, reaching the maximum  $q_t$  at 5 mg L<sup>-1</sup>. As the concentration was increased to higher

concentrations, a steady decrease of  $q_t$  was observed until  $25 \text{ mg L}^{-1}$  after which it appears to assume a constant behavior.



**Figure 4: Effect of the initial concentration on the adsorption of U(VI) onto BC350;  $pH = 3$ ; adsorbent dose =  $10 \text{ g L}^{-1}$ ; contact time = 24 h;  $T = 25 \pm 2^\circ\text{C}$ .**

This is in accordance to the selected dose, which was optimized for the given initial concentration ( $C_0 = 5 \text{ mg L}^{-1}$ ). In the event of working with more concentrated solutions, new correlations to other doses should be evaluated.

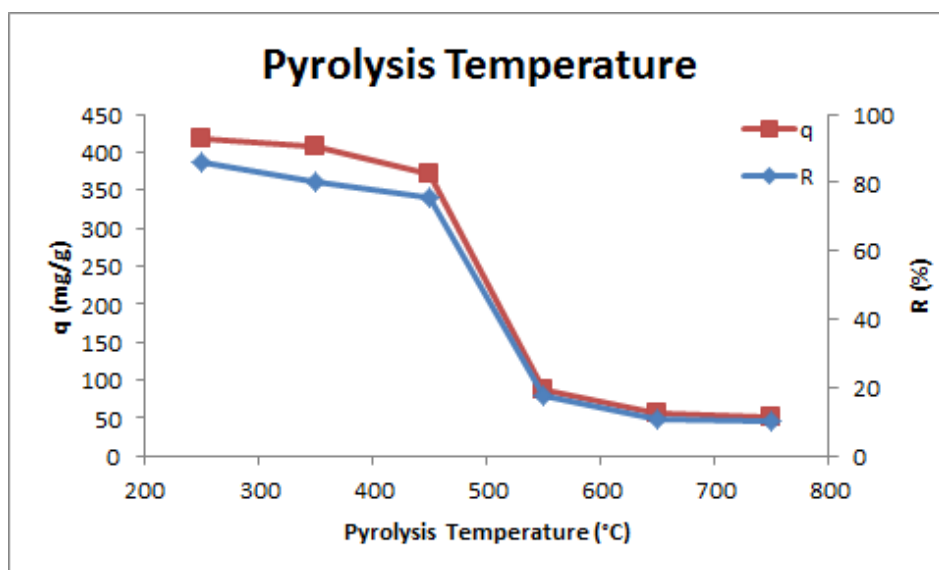
### 3.4. Adsorption on different BCs

The adsorption capacities of the BCs obtained in different pyrolytic temperatures were evaluated under the optimal conditions and the results are given in Table 2.

**Table 2: Influence of pyrolytic temperature on the removal of U ions**

BC	$q_t$ ( $\text{mg g}^{-1}$ )	R (%)
250	417	85.9
350	408	80.1
450	372	75.8
550	88	17.7
650	56	10.9
750	52	10.4

Fig. 5 illustrates the relationship between the pyrolytic temperature at which each BC was obtained with the adsorption capacity. Removal above 75% was achieved for temperatures under  $450^\circ\text{C}$ , and the highest  $q_t$  was obtained at  $250^\circ\text{C}$ . A drastic decrease of the  $q_t$  was observed when the endocarp was subjected to temperatures higher than  $450^\circ\text{C}$ .



**Figure 5: Effect of the pyrolytic temperature on the adsorption of U(VI) onto BCs produced at different temperatures;  $pH = 3$ ; adsorbent dose =  $10 \text{ g L}^{-1}$ ; initial concentration =  $5 \text{ mg L}^{-1}$ ; contact time = 24 h;  $T = 25 \pm 2^\circ\text{C}$ .**

This way, BC250 was preferably selected for treatment of uranium from aqueous solutions, because of its high adsorption capacity. In addition, the production of BC250 entails less overall costs (energy, time, labor-time), making it a potential value-added material for uranium containing wastewater treatment.

#### 4. CONCLUSION

Batch experiments were employed to evaluate the adsorption capacity of the biochar derived from macauba coconut residue for removing uranium ions from aqueous solutions aiming its application for the treatment of liquid wastes and contaminated wastewaters. The pyrolysis of the macauba endocarp was carried out at six independent temperatures under inert argon atmosphere. The results revealed that the optimal conditions were achieved at  $pH=3$ , adsorbent amount of  $10 \text{ g L}^{-1}$  and U (VI) initial concentration of  $5 \text{ mg L}^{-1}$ . The highest uranium removal efficiency (86%) was achieved for the biochar produced at  $250^\circ\text{C}$  using a heating rate of  $5^\circ\text{C min}^{-1}$  and a residence time of 1 h. Thus, submitting the endocarp to temperatures higher than  $250^\circ\text{C}$  becomes unnecessary, saving time and reducing operating costs. The results demonstrated the potential of the macauba biochar as a value-added material for uranium removal from aqueous wastes.

#### ACKNOWLEDGEMENTS

We thank Acrotech (Viçosa, Minas Gerais) for supplying the macauba endocarp.



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